STUDIES ON POLYMER BLENDS FOR MEDICAL APPLICATIONS

A Thesis Presented

By

S. N. PAL

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CERTIFICATE

I, S. N. Pal hereby certify that I had personally carried out the work depicted in the thesis entitled *"Studies on Polymer Blends for Medical Applications"*, except where external help was sought and has been duly acknowledged.

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The Thesis
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(S. N. Pal)

NOMENCLATURE

ABS	Acrylonitrile-butadiene-styrene
a_T	Shift factor
CAPD	Chronic ambulatory peritoneal dialysis
D_E	Extrudate diameter
DEHP	Di(2-ethyl hexyl) phthalate
ΔG_m	Gibbs free energy of mixing
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
DMA	Dynamic mechanical analysis
D_R	Die swell ratio
E	Activation energy
η	Viscosity
EVA	Ethylene-vinyl acetate
E^*	Complex modulus
E'	Storage modulus
E''	Loss modulus
FTIR	Fourier transform infra-red
$\dot{\gamma}$	Corrected shear rate
G	Shear modulus
I.V.	Intra-veinous
MBS	Methacrylate-butadiene-styrene
MFI	Melt flow index
NBR	Nitrile-butadiene rubber
n'	Flow behaviour index
P	Gas permeability constant
PE	Polyester
PTFE	Poly(tetra fluoro ethylene)

PVC	Poly(vinyl chloride)
Q	Volumetric flow rate
R.H.	Relative humidity
ρ	Density
RI	Refractive index
rpm	Revolutions per minute
SBS	Styrene-butadiene-styrene
SEM	Scanning electron microscope
S_R	Recoverable strain
Subscript "a"	Apparent
$\tan\delta$	Loss tangent
TEB	Tensile energy to break
T_g	Glass transition temperature
THF	Tetrahydrofuran
TPU	Thermoplastic polyurethane
$\tau_{11} - \tau_{22}$	Normal stress difference
τ_{12}	Shear stress
UE	Ultimate elongation
UTS	Ultimate tensile stress
U.V.	Ultra violet
WA	Water absorption

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ABSTRACT

CHAPTER - I

ABSTRACT

Polymers are the most important class of material used in medicine today. Poly(vinyl chloride) is one polymer that is used most in disposable medical applications. Plasticized PVC suffers from a number of disadvantages, the most important among them is the loss of plasticizer, when in contact with a biological medium and the resultant *"non permanence"* due to change in properties. Review of literature indicates that various approaches have been adopted to overcome the shortcomings of plasticized PVC. The benefit of these attempts could not be exploited in medical applications for one reason or the other. *'Polymer blend' approach appears to be the most attractive of all.* However, there are hardly any reports of studies done on PVC based polyblends for medical applications. With these aspects in mind, the *scope and objectives* of the present investigation have been formulated.

The subject matter of this thesis is presented in *five chapters.* The current chapter is an *abstract* of the thesis and outlines the contents. The *introductory chapter* II traces the importance and relevance of the problem, reviews the state of current knowledge and defines the scope and objective of the present investigation. The details of *materials used and experimental techniques adopted* are given in chapter III.

The results and discussions of the present investigation are embodied in chapter IV, which has ***seven sections.*** Rheological and processing studies, given in section 1, include blend compositions and studies on blending techniques, MFI, Plasticorder torque and extrusion. Analysis of the data has been carried out with respect to viscosity and die swell ratio. The mechanical properties are presented in section 2 and discussions are made in terms of stress-strain behaviour, ultimate tensile stress, elongation at break, modulus, tensile energy to break, hardness and the generalised model proposed for mechanical properties of blends. DMA and brittleness temperature studies and discussions for the observed behaviour of the samples are given in the next section. Morphology and interactions studied by SEM and FTIR techniques are the content of section 4. The important aspects of migration and permanence are dealt in section 5 and very interesting conclusions are drawn from the results of these studies. In section 6, discussions are made for the results of water vapour, O_2, CO_2 and N_2 permeability. Clarity and haemolytic potential of the blends studied are the subjects for discussions in section 7.

Summary and conclusions of the present study are recorded in chapter V. This chapter also contains suggestions for future investigations in related area.

INTRODUCTION

CHAPTER - II

INTRODUCTION

Polymers find widespread applications in medicine. Poly(vinyl chloride) is one polymer that is used most in disposable medical applications. Plasticized PVC suffers from a number of disadvantages, the notable among them being loss of plasticizer and resultant change in mechanical properties. Review of literature indicates that various approaches have been adopted to overcome the shortcomings of plasticized PVC. 'Polymer blend' approach appears to be the most attractive of all. However, there are hardly any reports of studies done on PVC based polyblends for medical applications.

With the above aspects in mind, the scope and objectives of the present investigation have been designed. The main objective of the study has been to investigate the possibility of using PVC based polyblends in medical applications with more permanence imparted to the properties.

In this chapter, literature survey of medical applications of polymers, shortcomings of currently used polymers in medicine, attempts to overcome the problems of PVC, polymer blends and their significance, and characterization of polyblends have been presented. The scope and objectives of the present investigation are also discussed at the end of the chapter.

2.1 MEDICAL APPLICATIONS OF POLYMERS

2.1.1 Overview

Use of polymers in medical applications has revolutionised the patient care. The preventive, diagnostic and treatment of many health related problems today are tackled routinely with the help of polymers and polymer based devices. There are thousands of possible applications of synthetic polymers in clinical medicine (Ratner, 1989). Use of polymers in medicine has helped millions of people all over the world to have a productive and happy life who would otherwise be condemned to a curtailed activity level, or death. The importance of polymers in medicine can also be recognised from the fact that polymers for medical applications constitute about 6 % by dollar sales of total processed polymers in USA (Rosato, 1982).

The success of polymers as biomedical material is due to their attractive properties like light weight, apparent inertness, low cost, ease of fabrication, possibility of wide range of modification and versatility in design. The use of polymers in medicine include both thermoplastics and thermosets and they are used in the categories of solid, liquid and water soluble polymer systems (Hoffman, 1984).

2.1.3 *Categories of Medical Products*

Practically all known polymers are used in medical applications in one or more *market categories* of intracorporeal, paracorporeal and hospital products and rest homes. The major polymers used in medicine are LDPE (22%), PVC (20%), polystyrene (20%), HDPE (12%), polypropylene (10%), thermoset polyesters (4%), polyurethanes (2%), acrylics (2%), nylon (2%) and epoxies and others like acetals, cellulosics, thermoplastic polyesters, polycarbonates, polysulfones, silicones etc. (5%) (Rosato, 1983).

The medical devices from polymers are diverse and can be divided into different *categories corresponding to the different requirements of applications* (Plast. and Rubb. Res. Inst., TNO). These are:

i) products intended for long term implantation within the body tissue e.g., artery grafts, hip prosthesis, hydrochephalus shunt etc.

ii) products intended for long term contact with mucosal surface or conjunctiva e.g., dentures, contact lenses etc.

iii) products intended for short term use within the body or in contact with mucosal surface e.g., endotracheal tubes, urological catheters etc.

iv) products intended to be used in long term contact with skin e.g., prosthetic legs.

v) products used to contain or administer substances, including blood and blood products for introducing parentally, but they themselves may not make contact with recipients body tissue e.g., syringes, haemodialysis equipments, blood bags, pump tubing, administration sets etc.

2.1.4 Requirements of Polymers for use in Medical Applications

Polymers for biomedical applications differ from those used in other applications (Plast. and Rubb. Res. Inst., TNO). In biomedical applications one should not only consider the requisite mechanical and physical properties, but also their influence on their biological environment and conversely, the influence of the biological environment on the materials themselves. Requirements for each particular application are different and have to be considered for material selection (Kalliyanakrishnan, 1984). Some of the *basic requirements* are:

a) *Intrinsic properties of the materials:* These include i) functional performance e.g., gas permeability in case of oxygenator membranes, ii) structural performance e.g., non leakage in case of dialysis membranes, iii) adaptability to shape i.e., ease of fabrication by conventional technique, iv) durability e.g., heart valve prosthesis is expected to last for 10-25 years, v) sterilizability i.e., sterilizable without causing attack, deformation etc.

b) *Influence of biological environment:* The polymers should be able to resist biodegradation, especially enzymetic hydrolysis, chemical degradation by water, salt, oxidants etc., and physical degradation as a result of stress, especially environmental stress.

c) *Influence on biological environment:* The polymers should not contain leachable toxic substances, should not cause allergic reactions, inflammation, blood clotting, denaturation of body proteins, should not be carcinogenic and should not interfere with normal cell structure. If the material is biodegradable, degradable products should not cause cell damage or interfere with normal metabolism.

2.1.5 Shortcomings of Polymers Currently used in Medicine

Polymers have, no doubt, contributed to the tremendous improvement in patient care over the years. But the polymers that we synthesise have little homogeneity and functionality compared to polymeric materials from living systems. Synthetic polymers suffer from a distribution of molecular weights and from chain compositions controlled by stochastic factors and natural biopolymers exhibit perfect molecular homogeneity (Ratner, 1989). In many of the applications, the polymers that we use today are far from ideal, though, there does not seem to be any better alternative.

Silicone rubber, one of the most biocompatible materials is used in heart valve prosthesis and hydrocephalus shunt. Lipid absorption, swelling and embrittlement in use impairs the functions for which these materials are employed (Frisch, 1984; Swanson, 1974). The undesirable local tissue reaction due to the wear of polymers used in joint replacement prosthesis is another example of non-ideality of polymers (Wright, 1976). In total artificial heart implantation, significant problems have been attributed to biomaterials related infection and thromboembolic complications (DeVries, 1988).

Regenerated cellulose is the most commonly used membrane for dialysis for last four decades. Yet, this has not been perfected enough to have performance comparable to natural kidney. Muir et al. describe the ways in which dialysis membranes need improvement particularly in terms of
a) increased permeability and/or better selectivity,
b) improved blood compatibility, c) increased strength and
d) better fabrication properties (Muir, 1973). Polytetrafluoroethylene and silicone rubber membranes are used in blood oxygenators. Though of both these materials have reasonably good blood compatibility, CO_2 retention and fabrication difficulty for PTFE and poor mechanical property of unfilled silicone are the drawbacks (Galletti, 1971).

PVC is the polymer used most in disposable category. Since virgin PVC cannot be used and compounded PVC normally has additives with low molecular weight, PVC formulations lack permanence. Extracted additives that may enter patients body may be risky for the patient. Detailed discussions of these problems have also been done in the section 2.2.3.

2.2 PVC IN MEDICAL APPLICATIONS

2.2.1 Importance of Disposables

The challenges and requirements of polymers used in implantables are much more stringent than in disposables. However, it is the disposables made from cheap commodity polymers which have made more significant contribution in improving the patient care. Implantable devices are utilised only in specialised centres and involve lot of expense. Disposables are utilised in all places from patient's home to specialised medical centres. Much more number of patients benefit from disposables than implantables. Rosato (1983) estimated that in 1983 disposables accounted for 80% in an overall market of $3.1 billion for medical polymers. In another study it has been estimated that market for medical disposables is expected to grow at 8% per year and by 1992 world market will reach $8.3 billion sales level (Plast. and Rubb. Intl., 1988).

Disposable devices greatly reduce the risk of infection and saves time and the labour spent in cleaning and sterilization of re-usable devices. Of late, disposables have also become important in patient care delivery system because of the fear of possible contamination due to AIDS.

2.2.2 Applications and Importance of PVC

The applications of PVC have been outlined in section 2.1.2. Flexible PVC finds application in a whole range of medical products which include open heart surgery equipment, haemodialysis apparatus, blood taking and giving sets, endotracheal tubes, catheters, suction and drainage tubing, enema packs and a host of other hospital products.

For a great number of applications, particularly those which are short term, PVC is often the material of choice. This stems from its versatility and the wide range of properties that can be imparted depending on the nature and the amount of additive. By selecting proper formulation it can be made hard or soft, crystal clear, radio-opaque or conductive and surface properties can be enhanced (Vincent, 1981). It does not melt but softens over a range of temperature resulting in a material which is readily formed or shaped when heated. It can be readily bonded with solvent and can be sterilized by a number of methods.

PVC accounts for 20% of all polymers used in medicine and among disposables plasticized PVC definitely occupies the leading position because of its economic and design advantages (Biggs, 1979).

2.2.3 Shortcomings of PVC

Virgin PVC is a hard and horny material. This is thermally unstable and is very difficult to process. To make it into a processible and useful material a number of additives like plasticizers, stabilizers, lubricants, antioxidants etc., are added. In medical applications, it is almost invariably this plasticized and stabilized PVC that are utilised. Geertz et al. (1974) conducted a detailed analysis of the commercially available medical devices made from PVC and identified the various additives used in medical grade PVC. A number of studies have shown that low molecular constituents of compounded PVC leach out during use (Daun, 1977; Jager, 1972; Wiethy, 1976; Cromton, 1979; Srivasthava, 1985). The amount of leaching depends on chemical nature of the ingredients used in compounded PVC, nature of the media in contact and storage conditions (Srivasthava, 1985; Miripol, 1977; Kevy, 1981).

Di(2-ethyl hexyl) phthalate (DEHP) is most frequently used plasticizer in medical compounds (Prins, 1979). DEHP is normally added in quantities upto 60% of the resin in flexible grades of PVC for medical application. Generally a plasticizer is not chemically bonded onto PVC backbone and it can migrate from PVC into the media in contact with it. In case of medical applications, oily substances such as contents of the digestive system and blood are capable of extracting monomeric plasticizers from PVC (Biggs, 1979; Kevy, 1981). There are *two consequences* of this:

1. changes in properties of the PVC due to loss of plasticizer.

2. possible toxic and biological effect arising from the transfer of plasticizer to a patient.

For devices with very short contact time none of above effects may cause visible and apparent problems. In applications like stomach feeding tube and wound drainage tube, the PVC may be kept in position for long durations. Hayhurst and Wyman (1975) reported that loss of plasticizer and non-permanence of the flexibility of PVC tubes in these cases result in hardened device. They also experienced that removal of these are traumatic for the patient and surgery or special equipment could become necessary.

Use of flexible PVC in applications like blood storage containers and haemodialysis equipment poses possible toxic and biological effects to a patient. Patients receiving multiple blood transfusions could receive extracted plasticizer repeatedly. Patients undergoing regular dialysis could similarly receive regular doses of plasticizer in still higher quantities. Donors of blood protein fractions who receive back the reconstituted blood fractions are also at risk of receiving plasticizer.

Presence of phthalates in blood and milk, stored in PVC bags, has been detected (Sherwin, 1982; Wildbrett, 1973; Miripol, 1977). Jager and Rubin (1972) also reported for the first time the detection of DEHP in tissues of patients who received blood transfusion from PVC blood bags. Studies have shown that DEHP is hepatotoxic, mutagenic, and carcinogenic (Albro, 1982; Tomita, 1982). The hazard to which a patient is exposed for the use of flexible PVC devices has generated lot of interest and a number of publications have appeared regarding this (Jager, 1972; Geertz, 1974; Jager, 1970; Turner, 1974; Rubin, 1976; Baker, 1978; Kevy, 1981). Much of the work is inconclusive in terms of effect on human beings. However, Prins and Scheepatra (1979) noted that solubility of DEHP in aqueous media and its toxicity are low. Biggs and Baldwin (1979) argue that acute toxicity of DEHP is very low and there is no evidence of chronic effects and metabolism of DEHP by the human body is rapid and does not appear to generate unacceptable by-products. They conclude that the benefits of using flexible PVC outweigh the risk. However, it is not desirable that patients with less than perfect health condition should be dosed with plasticizers and be risked with the possible long term effect, however minimal the possibility may be.

One more deficiency of PVC is its tendency to discolour or 'yellow' when sterilized by gamma-irradiation technique. However this problem is being addressed to and a solution is in sight (Mod. Plast. Intl., 1988; Saxena, 1987).

2.2.4 Attempts to Overcome Shortcomings of PVC

The shortcomings of PVC have been discussed in the previous section. The approaches to overcome these problems generally have been through one of the following routes.

1. *Replacement of PVC*
2. *Copolymerization of vinyl chloride*
3. *Use of alternative additives*
4. *Surface modification of PVC*
5. *Blending PVC with other polymer(s)*

2.2.4.1 Replacement of PVC

Some materials have been considered as possible replacements for PVC. Vincent (1981) has reviewed the available materials and their merits and demerits. Ethylene vinyl acetate copolymer appears to have some potential as a clear to translucent rubbery material available in a range of hardness and flexibility. But poor kink resistance and low softening temperature which restricts steam sterilization are the main disadvantages. It is also more difficult to bond and thermoform than PVC.

Styrene-butadiene-styrene (SBS) block copolymers are available in wide range of hardness and is translucent in absence of additives. It has good resilience but poor permanent set. Transition on softening is very sharp and is difficult to thermoform. There are difficulties in bonding with solvents. The properties of SBS do not commend it as a material to be used as replacement for PVC.

Thermoplastic polyurethane is available in limited hardness range. On processing and exposure to U.V. the colour darkens from initial light straw. Kink resistance is very poor and heat welding and solvent bonding are good. In processing, it sticks to itself and there are difficulties in take off and reeling. TPUs cost much more than plasticized PVC and these also cannot be thought to be materials of replacement for PVC.

2.2.4.2 Copolymerization of Vinyl Chloride

The development of such copolymers arose from the desire to increase the thermoplastic flow of poly(vinyl chloride) under processing conditions, to improve the solubility characteristics of vinyl chloride polymers, to improve impact resistance and heat distortion temperature while retaining some of the other generally good physical properties of poly(vinyl chloride). Introduction of comonomers for plasticization of poly(vinyl chloride) is referred as 'internal plasticization'.

Kline and Skiest (1976) have reviewed the comonomers that have been tried with vinylchloride. These include vinyl acetate, acrylic esters, acrylo nitrile, vinylidene chloride, esters of unsaturated dicarboxylic acid, olefins, vinyl-ethers and a host of other monomers (Kline, 1976; Walsh, 1984 a; Walsh, 1984 b). They also describe a number of attempts that have been made for block and graft polymerization with PVC as the base polymer. The most interesting among them is the development of graft polymer of vinyl chloride to poly(ethylene-vinyl acetate) substrate (Plast. Technol., 1967).

2.2.4.3 Use of Alternative Additives

In order to overcome the concern for phthalate leaching and the possible toxic effects attempts have been made to use alternative plasticizers. Biggs and Baldwin (1979) evaluated alternative plasticizer to DEHP which included monomeric, polymeric and copolymers. Monomeric plasticizers included di-(2-ethyl hexyl) adipate, acetyl tributyl citrate and straight chain trimellitate. Polymeric adipate, phthalate, polyurethane were the polymeric plasticizers evaluated by them. Copolymers studied were ethylene/vinyl acetate, ethylene/vinyl acetate/PVC and propylene/vinyl chloride. They discarded all the above materials excluding polymeric adipates due to low plasticizing efficiency.

Kevy, Jacobson and Harmon (1981) evaluated a new plasticizer, Hatcol-200, which is an ester of a branched oxo-alcohol and 1,3-dihydro-1,3-dioxo-5-isobenzo-furan carboxylic acid. Rate of leaching of this plasticizer in serum was claimed to be one hundredth that of DEHP. They concluded that Hatcol-200 is an ideal replacement of DEHP.

In another recent study Blass (1990) evaluated invitro and exvivo compatibility of PVC plasticized with plasticizers other than DEHP and compared the performance to DEHP.

2.2.4.4 Surface Modification

Modification of the exposed surface of PVC has been thought to be one way of getting over the problem of plasticizer migration and non-permanence. There have been two approaches to this. In one approach a very thin layer with a thickness of 500 A° or less has been added or modified by glow discharge or grafting technique (Inside R & D, 1985). Ludwig (1989) has recently advocated plasma polymerization technology for production of barrier layers to prevent diffusion of gases and liquids. This may have useful applications in PVC based medical devices.

In another approach a thicker layer of another polymer has been added to the exposed surface. Bev-a-line^R is such a range of product which has PVC outer layer and undisclosed inner layer (Bev-a-line). This ensures the good physical properties of PVC with a surface which is best suited for contact with physiological fluids, food, beverage, drugs and chemicals.

2.2.4.5 PVC based Polymer Blends

The problem of diffusion and loss of plasticizer from flexible plasticized PVC can be solved in principle by use of a soft, high molecular weight polymer that is molecularly compatible with the rigid PVC (Hammer, 1978). This principle has been applied for the development of a number of blend systems. Recently Katsaros et al. (1990) reported about a new technology of making blends to derive the strength and chemical resistance of plastics and the flexibility and low temperature toughness of rubber. PVC homopolymer is a stiff and brittle plastic with a T_g of about 80°C. Blending with elastomer systems improves toughness. Methacrylate-butadiene-styrene (MBS), ABS, NBR have been used for this purpose (Petrich, 1972; Matsuo, 1968). Bauer and Guillod (1977) studied transparent acrylic/PVC systems for possible outdoor applications. Milner and Duval (IPI, 1990) and Schwarz and Bley (1988) have recently reported the characteristics of NBR that make it suitable for blending with PVC. Varughese et al. (1988; 1989) studied PVC-Epoxidized natural rubber blend system and reported single phase behaviour in the entire range of composition. Menzel (1979), Matsuo (1968) and Terselius et al. (1981) have studied blends of PVC with EVA. Addition of EVA was found to improve impact strength, ageing resistance and weathering performance.

B.F Goodrich has recently launched several new vinyl alloys and alloying agents (Plast. Technol., 1989). These include heat resistant PVC compound, gamma sterilizable rigid vinyl medical compounds, static dissipating alloys and a line of antistatic alloying agents.

There is hardly any literature that is available regarding use of PVC based polymer blends for medical applications. Biggs and Baldwin (1979) considered few polymeric products as plasticizer for PVC. Their intention was to look for alternative plasticizer to DEHP. Systems studied by them are given in section 2.2.4.3. They considered plasticizer efficiency as the main criteria and discarded all the above excepting polymeric adipates, which this purpose (Petrich, 1972; Matsuo, 1968). Bauer and Guillod (1977) studied transparent acrylic/PVC systems for possible outdoor applications. Milner and Duval (IPI, 1990) and Schwarz and Bley (1988) have recently reported the characteristics of NBR that make it suitable for blending with PVC. Varughese et al. (1988; 1989) studied PVC-Epoxidized natural rubber blend system and reported single phase behaviour in the entire range of composition. Menzel (1979), Matsuo (1968) and Terselius et al. (1981) have studied blends of PVC with EVA. Addition of EVA was found to improve impact strength, ageing resistance and weathering performance.

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Of all the approaches that have been adopted to overcome the shortcomings of PVC, *polymer blend approach is advantageous* for a number of reasons. The important advantages are (i) changes in existing process technology are not required and (ii) possibility of very high product cost by other approaches is avoided.

2.3 POLYMER BLENDS

2.3.1 Introduction

To improve performance of the existing polymers, polymer industry has rarely changed to a new and probably more expensive polymer. The improvement is more easily achieved by shifting from homopolymers to copolymers or polyblends by mixing different polymers either during polymerisation or as polymers during a processing stage. *Polymer blends* are intimate mixtures of more than one kind of polymer with no covalent bonds between them. The components in polyblends adhere together only through van der Waals forces, dipole interactions or hydrogen bonding. Some level of thermodynamic compatibility is necessary between the components to prevent phase separation during processing and use. The other types of mixing polymer pairs are graft copolymers, block copolymers and inter-penetrating networks. Polymer blends are the most attractive of the 'mixed polymers' in view of the ease of designing and producing the blends compared to other 'mixed polymer' types.

Polymer alloys are the synergistic polymer combinations with real property advantage derived from high level of thermodynamic compatibility and greater inter molecular attractive forces between the constituents. Alloys form practically a single phase system with unique glass transition temperature.

Polymer combination for a blend/alloy is normally selected so as to complement each other in cost, processibility, mechanical properties, thermal performance, warpage resistance, chemical resistance etc. Kienzle (1988) has segmented polymers into four families of commodity, transitional, engineering and performance. By combining polymers from two different families the property profile of more costly polymer can be exploited with reduction in overall cost. A second method of combining polymers is the choice of one crystalline and one amorphous polymer. Such a combination usually results in good dimensional stability, ease of processing, chemical resistance, and mechanical properties that can be tailored for a specific application. Combination of plastics with elastomers is another way of getting useful polyblend. Generally, the plastic provides the strength and stiffness and the elastomer provides impact modification.

Very often when two polymers are mixed, a high interfacial tension and poor adhesion between the two results. High interfacial tension and high viscosity lead to poor mixing and poor adhesion, which ultimately lead to poor mechanical properties of the blends. Presence of certain species, usually block or graft polymers suitably chosen can reduce these problems due to their ability to alter the interfacial situation. Paul (1978 b) has made a very exhaustive review of such species, also referred to as "compatibilizers".

2.3.2 *Commercial Significance of Polymer Blends*

The combination of two or more commercially available polymers through alloying or blending represents an inexpensive route to product differentiation and that is why the use of blends has increased by leaps and bounds during last 10-15 years. In 1986, engineering polymer blends and alloys, for example represented 300 million pounds of commercial sales in the USA (Technomic, 1988). It is estimated that by 1995, US consumption of engineering alloys and blends will reach approximately 700 million pounds. Blend and alloy *demand growth* will outstrip that for engineering base polymers by nearly two to one and will average at least 9% annually. Sivaram, (1990) in a recent article, estimates that 25% of the current world wide consumption of high performance polymer is composed of blends/alloys which could grow as high as 50% by 1995.

Scientific and commercial interest in blends and alloys as a class of material is testified by the fact that on an average about 4 patents everyday and 1000 publications every year appear on blends (Sivaram, 1990). The commercial significance and technical feasibility is apparent from the list of products already commercially available. Such lists are given in a number of books and publications (Sivaram, 1990; Kienzle, 1988).

2.3.3 Polymer Blends in Medical Applications

Publications on use of polymer blends in medicine are very limited. In a recent report it is stated that polymer blends and alloys are having a growing role in medical applications (Mod. Plast. Intl., 1988). In many areas blends are broadening the cost/performance choices for designers of medical products.

Cardionostics Inc., USA has introduced Monsanto's Triax 1120, a nylon/ABS alloy, for Hotlter cardiac monitor that weighs only 250 gm, including cassette tape and batteries. The new Hi-Tech model is worn on the hip like a portable cassette player and is subject to rough handling. Nylon was considered too brittle and the alloy's tough and rubbery character were considered appropriate for the application.

Amoco's Mindel S-1000, a blend of polysulfone/thermoplastic polyester, is used for storage and disinfection of soft contact lenses. The material has to withstand high temperature and salt water environment. Compared to the earlier choice, polysulfone, the blend has the advantages of cost and better moulding.

Blends of PPE has been used in housing panel of blood analyzer, laboratory equipment and disposable surgical equipments.

2.3.4 *Blending Methods*

Blending of polymers are carried out by variety of means including melt blending, solution blending and latex or dispersion blending (Angove, 1967; Shundo, 1966). In *melt blending* two or more polymers and other additives like fillers, reinforcements etc., are mixed at elevated temperature in the presence of mechanical shearing forces. In *solution blending,* solution of the polymers are normally made in a common solvent and the solvents are then removed by suitable means. *Latex or dispersion blending* uses coagulant to give an intimate alloy or blend mixture.

Melt blending has several *advantages* over solution and latex blending. A solvent or dispersing agent is eliminated in melt blending. This gives rise to saving in cost associated to solvent removal, recovery and loss. Chances of contamination are also minimal in melt blending method. The ability to use inplace equipment by sharing of processing facilities like extruders across product lines and reduced capital investment required to introduce a new product line are the other advantages of melt blending. Melt blending, however, has the possibility of undesired cross linking, grafting, polymer degradation and colouration.

2.4 CHARACTERIZATION OF POLYMER BLENDS

2.4.1 Thermodynamics and Miscibility

2.4.1.1 Thermodynamics

The structure and stability of polymer blends depend primarily on the miscibility of polymers used in making the blend. Miscibility is governed by Gibbs free energy of mixing, ΔG_m, and its concentration dependence (Paul, 1978 a). For polymers to be miscible, it is necessary but not sufficient to satisfy the condition $\Delta G_m < 0$. The deciding factor is then the concentration dependence of ΔG_m. The Flory-Huggins (1962) theory shows that the contribution of the entropy of mixing ΔS_m is negative and very small but nevertheless promotes mixing even though to a much lesser extent than in low molecular weight compounds. In such a case the enthalpy of mixing, ΔH_m, becomes the overriding consideration. In the case of purely dispersive forces, ΔH_m is always positive. Consequently high molecular weight systems with this type of interactions are rarely miscible. If, however, there exists specific interactions e.g., ion-dipole interactions, hydrogen bonding of specific functional groups or complex formation stereoisomers, ΔH_m can be negative and the polymers become miscible.

In contrast to this rigorous thermodynamic definition of polymer miscibility, the practical polymer technologist considers two polymers as compatible if he gets useful properties from the polyblend (Deanin, 1974).

The Flory treatment does not allow for any volume change on mixing whereas many systems either dilate or contract on mixing. Since entropy depends on volume, such systems will have an additional contribution to the entropy of mixing. Theories developed later allow for this effect (Sanchez, 1978 a; 1978 b). The importance of enthalpic interactions in polyblends have been discussed in a recent paper by Barlow and Paul (1987).

2.4.1.2 Methods to Study Miscibility

There are a large number of methods for studying the miscibility of polymer blends. These include optical appearance, glass transition temperature, microscopy, small angle X-ray scattering, chemical and solution methods (Bhagawan, 1987; Paul, 1978 a; Olabishi, 1982; Gesner, 1969; Walsh, 1981).

If the blend is homogeneous, it will have a refractive index in between those of the individual polymers. If the system is heterogeneous with one polymer present as a discrete phase embedded in a second polymer it scatters light according to the size of the dispersed particles.

In the most commonly used method for studying the miscibility of polyblends, the T_g of the blend is determined and is compared to that of the individual constituents. T_g is determined by mechanical, dielectric, calorimetric, thermooptical, or radio-luminescence techniques. Regardless of the method used, T_g of any polymer is affected by its previous history, the experimental time scale and other factors that affect its intra- or intermolecular forces. Owing to the sensitivity of T_g to the disruption of the local structure that results from mixing two different polymers, the existence of the single and sharp or single and broad, or double and shifted or double and non-shifted T_g for a polyblend reveals the particular macroscopic characteristics of the blend. Broadening of the transition occurs in case of blends showing borderline miscibility whereas two separate transitions appear in case of total immiscibility. The T_g method is somewhat limited by very poor resolution when a quasi-binary polyblend contains polymers whose T_g values differ by less than 20°C.

Microscopic examination of polymer blends has become very important method in predicting the final properties of polyblends. Scanning electron microscope, phase contrast microscope, and transmission electron microscope are extensively used for studying the morphology of polymer blends.

Scattering methods include X-ray scattering, neutron scattering, light scattering, pulse induced critical scattering, and the cloud point curve. Less used are electron scattering and Rayleigh-Brillowin scattering. These methods are used in the characterization of chain conformation, local order and gross morphology.

Solution methods are used particularly in the field of paints, varnishes and lacquers. When determining the miscibility of polyblends a 50/50 mixture at low to medium concentration is dissolved and thoroughly mixed in mutual solvent. On standing for few days the polymers can be considered miscible if phase separation does not occur.

2.4.2 Rheology of Polymer Blends

Since end use of polymer blend is the ultimate aim of developing such a system, a knowledge about its processibility is essential. The processing and most of the times the mixing are carried out in molten state, and therefore study of rheological behaviour is of paramount importance. The two or more polymers used for making the blends may have difference in molecular structure and they may have molecular interactions. This may result in a different rheological behaviour for the blends.

Usachev et al.(1980) argued that the flow of polymer blends must be regarded as the combined flow of differing viscosity. Parasiewicz et al.(1979) found that polymers of similar chemical structure exhibit rheological behaviour deducible from additivity considerations and blends with polymers having different chemical structure generally have lower viscosity than the individual component of the blend. Utracki(1988) has considered (1) liquid mixtures and (2) homologous blends as models for study of flow of polymer blends. Plochocki(1989) argues that by making few simplifying assumptions, it is possible to develop a coherent engineering approach in selecting components and compositions of the polyblends to estimate their morphology and set up the mixing process as well as to assess the effects of processing on the morphology and the performance characteristics.

Polymer blends with a second polymer which is rubbery in nature and/or very high in molecular weight, can provide improvements in melt strength(Deanin, 1974). This improves processibility for blowing and thermoforming. Improvements also take place in post forming operations such as stretching, punching etc.

2.4.3 *Mechanical Properties*

Dynamic mechanical studies of polymer blends are commonly reported in the literature as it represents one of the primary methods of determining miscibility. By contrast ultimate mechanical properties of blends e.g., strength, toughness, elongation, fatigue resistance etc., are rarely reported even though these are of considerable interest for end applications (Robeson, 1982).

In miscible blends mechanical compatibility is assured. Modulus of rigidity is roughly intermediate between the two components and it depends fairly linearly on the ratios of the two (Deanin, 1974). When the two polymers exist in separate phases the relationship between the composition and modulus is not nearly as simple. In one view, the component that is present in larger amount should form the continuous matrix phase and should play the primary role in determining the modulus. A steep transition between the two components is expected in the region where both components are present in almost equal amounts. In another view, the dispersed phase may be considered as a filler and effect of such content on the modulus of the filled matrix can be calculated.

Strong exothermic interactions between components of miscible blends lead to denser packing and loss of free volume. Mechanical properties are expected to be higher than predicted by simple additivity rule. Experimental results in some systems generally conform to this expectation (Yee, 1977; Kleiner, 1979). Poor interfacial adhesion results in inferior ultimate properties compared to the expected average property of the constituents in totally incompatible blends.

In a polyblend where a moderate concentration of tiny rubber particles are dispersed in a glassy plastic matrix, tremendous improvement in impact strength results. A number of theories have been proposed for these behaviour and Deanin et al. (1974) have summarised these.

Polyblends containing "hard segment" domains and uncrosslinked rubbery phase may suffer from gradual creep due to the gradual relaxation of the hard segment and sliding of the rubber molecules past each other.

2.4.4 Optical Properties

Many of the polyblends are opaque or cloudy because of their multi-phase nature. When an incident light enters such a system the light has to pass through the polymer interphases number of times before it emerges from the other side of the sample. Each time the light passes through an interface it is scattered more and more. This converts even two transparent polymers into a translucent or opaque polymer system. The clarity of polyblends can be improved by lowering the size of the dispersed particles below that of wavelengths of visible light, but there is a limit if toughness is to be retained (Manson, 1977 a).

A better method of obtaining higher clarity is to properly select the refractive indices (RI) of two components. If both phases have same RI, a clear polyblend results. Gesner (1967) made a clear ABS type resin from a mixture of styrene-butadiene copolymer with a methyl methacrylate--styrene -butadiene copolymer. Petrich (1972) demonstrated a clear PVC-MBS system.

Conaghan and Rosen (1972) showed that unless the refractive indices do not show the same temperature dependence, clarity is dependent on temperature.

2.4.5 Morphology and Interactions

Morphology of blends is its organisation in supermolecular scale. It indicates the form, size, and orientation of blend's crystallites, structure of groups of molecules of the components and other boundaries and the degree of crystallinity. Morphology of the blends denotes the spatial arrangement of blend component phases. The major factors that govern morphology of the blend systems are i) viscosity of the components, ii) ratio of the components, iii) processing conditions such as shear rate and temperature and

iv) presence of additives. Additionally the morphology is also dependent on the thermodynamic properties of the components and the mixing process.

Danesi and Porter (1978) have reported that composition, processing history and difference in melt viscosities influence the morphology. Similar melt viscosities lead to uniform distribution of minor component in the major one with a very fine morphology. If the minor component has lower viscosity than the major, the minor will be finely and uniformly dispersed with domains oriented in the extrusion direction. The minor component gets coarsely dispersed in essentially spherical domains if its viscosity is higher than that of the major component.

Morphology of different polymers has been studied by many groups using a number of techniques (Yang, 1984; Baer, 1972; Dao, 1984; Jeng, 1989; Shen, 1989). Baer (1972) found the dynamic mechanical properties to be dependent mainly on particle size but independent of the processing methods used. Matsuo (1968; 1969 a) studied the temperature dependence of dynamic storage modulus E' and dynamic loss modulus E'' for PVC/NBR blends with varying acrylo nitrile content and concluded that these studies yield good insight into the structure and compatibility of polymer blends.

FTIR has been widely used in characterizing miscible polymer systems. FTIR technique gives evidence of the existence of specific interactions and elucidates the nature of such interactions (Macknight, 1989). Frequency shifts and band broadening for blends have been ascribed to intermolecular chemical interactions and to changes in polymer chain conformations. Coleman et al. (1979; 1984) have used digital subtraction and addition techniques on IR spectra and studied many blend systems. They concluded that blends of polymers containing a carbonyl group are particularly sensitive to intermolecular interactions. Harris et al. (1982) studied polyester-phenoxy blends and concluded that for achieving maximum miscibility through interactions with phenoxy, optimum density of ester groups are required.

2.4.6 Permeability Properties

Permeation through polymer films can be considered as the result of two distinct processes: solubility of the permeant in the polymer and diffusion. Permeation process in a polyblend can be understood with respect to the factors operative in two component systems (Manson, 1977 b). The type, shape, orientation of dispersed phase, the change in relaxation characteristics of the matrix phase, properties of the interface, solubility and diffusivity of permeant in both phases and interface are factors that govern permeability (Manson, 1973; Paul, 1972).

Permeation behaviour should also be sensitive to blend component interactions or loss in free volume. Studies by Paul et al. (1982) have shown that gas permeation rates through two miscible blends were well below any additive predictions. Bataille et al. (1988) studied polypropylene-polyethylene terepthalate blend systems and observed water vapour permeation similar to the observations made by Paul et al. They concluded that diffusion path of water molecules is made more complicated in the two component system.

2.5 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

From the preceeding sections it is apparent that polymers are widely used in medical applications and their use is on the rise. The role and importance of polymers in medicine can be understood by considering the variety of medical applications in which a large number of polymers are utilised. The size of medical polymers market will become larger in the near future since more and more attention is being given for health care all over the world.

In many of the medical applications, polymers used perform satisfactorily. But, in some other applications the polymers are far from ideal, though, presently better alternatives are not available. Disposable category of medical devices are very important since more number of people benefit from these. Among disposables PVC based products occupy the leading position. Plasticized PVC has a number of disadvantages associated with it. The important among these are i) plasticizer (DEHP) migration and ii) non-permanence in properties. Therefore, there is need to develop PVC formulations that can eliminate or reduce these problems.

Several approaches have been adopted to overcome the shortcomings of plasticized PVC. *'Polymer blend'* approach has the advantage of using the existing process technology and as a result product costs are not likely to be pushed up significantly. Impact modification and ease of processing has been the main emphasis of the studies done with PVC based polyblends so far.

From the survey of the existing literature it becomes obvious that there are no reports of PVC based polyblends being studied for medical application. Any polymer can be used in medical application only if it can be processed to the desired shape and size and it meets the properties required for the specific application. Studies on rheology, morphology and interaction and properties relevant to medical applications for PVC based polyblends are also scanty. Therefore, there is a need to study PVC based polyblends and investigate the possibility of considering these blends for medical application.

With the above background in mind, the present investigation was undertaken. The *core objective* of the study is to investigate the possibility of using PVC based polyblends in medical applications with more permanence imparted to the properties and the *scope of the work* has been limited to the following:

1. Selection of suitable polymers for blending with PVC based on desired blend property and existing information available on compatibility with PVC

2. Study on blending techniques and recommendation of suitable technique

3. Development of polyblend formulations

4. Studies on the polyblends formulated in respect of:
    - a) Rheological and processing characteristics
    - b) Mechanical properties
    - c) Low temperature behaviour
    - d) Permeability of gases
    - e) Extractibility and permanence
    - f) Blend morphology and interactions
    - g) Clarity and
    - h) Biological response

5. Correlation of properties to blend formulation and morphology, and

6. Modelling with an idea to predict blend property from those of 'pure' components.

EXPERIMENTAL TECHNIQUES

CHAPTER - III

EXPERIMENTAL TECHNIQUES

The details of materials used, sample preparation and perimental techniques adopted for the present investigation are scribed in this chapter.

3.1 MATERIALS USED

3.1.1 Poly(vinyl chloride)

Suspension grade PVC with K value of 66-69 from NOCIL, India was used for all the studies. The trade name for this polymer is S67-311. This free flowing resin is claimed to have been designed to provide good mechanical properties, easy processibility, and excellent plasticizer absorption characteristics with low fish eyes.

3.1.2 Poly(ethylene-vinyl acetate)-g-PVC

This is a graft polymer made by suspension polymerization of 50 parts of vinyl chloride and 50 parts of ethylene-vinyl acetate copolymer. The polymer was supplied by Wacker-Chemie GmbH, FRG and the trade name is Vinnol^R K 550. It is stated that the flexibility of Vinnol^R K 550 is comparable to PVC (K-value 70) containing 35% DEHP. The product is free flowing, despite its high elastomer content.

3.1.3 *Butadiene-Acrylonitrile Copolymer*

This polymer was procured from two sources. The product from Compagnie Francaise Goodyear is named as Chemigum P83 and the second product, named Hycar (1452 P-50), was procured from BF Goodrich. Chemigum P83 is particularly recommended for blends with PVC. In this thesis Chemigum P83 and Hycar (1452 P-50) will be referred to as NBR1 and NBR2 respectively.

3.1.4 *Polyesters*

Polyesters in liquid form were procured from ALA Chemicals Ltd., India. Plasflex PA, PB and PE are low molecular weight, medium molecular weight and high molecular weight products respectively. Kinematic viscosities at 60°C are 100-300, 375-475 and 600-750 centi-stokes respectively.

3.1.5 *Other Chemicals*

Other chemicals used for the study are tabulated with their trade names and sources in Table 3.1.1.

TABLE 3.1.1 Grades and Sources of Chemicals used

Sl. No.	Chemical	Trade name	Source
1.	Di(2-ethyl hexyl) phthalate	Di-octyl phthalate	Indo- Nippon Chemical Co.
2.	Epoxidised oil	Paraplex G-62	Indofil Chemicals Ltd.
3.	Ca-Zn stabilizer	ALA-152	ALA Chemicals Ltd.
4.	Phosphite chelator	ALA LE-109	ALA Chemicals Ltd.
5.	Calcium stearate, LR	-	New Modern Chem. Corpn.
6.	Refined ground nut oil	Postman	Local market
7.	Tetrahydrofuran, LR	-	BDH, England
8.	Methanol, AR	-	Glaxo Fine Chemicals
9.	Hydrochloric acid, LR	-	Glaxo Fine Chemicals
10.	Pepsin for Bacteriology	-	Romali
11.	Silica gel, Coarse	-	Glaxo Fine Chemicals
12.	Liquid soap	Laxbro	Laxbro Manufacturing Co.

.2 BLENDING METHODS

3.2.1 Mechano-thermal

3.2.1.1 Dry Blending

Master batches of dry blends were made in a high speed mixer (Papenmeyer TGEHK-20) with batch size of about 6.5 Kg. After charging the pre-weighed quantity of resins (PVC or EVA-g-PVC), the motor and the heater were switched on. The resin was made 'wet' with small quantity of plasticizer and motor speed was increased slowly to 1500-1600 rpm. Pre-weighed quantities of other ingredients were added slowly through a funnel. The more viscous additives were added first and wherever necessary they were diluted with plasticizer. In 5-6 minutes the temperature reached about 80°C. Jacket cooling by running tap water was started and the rate of plasticizer addition was increased so as to finish the addition by about 12 minutes time. The mixer was run at the same speed for another 3-4 minutes and the temperature at that stage came to about 115-120°C. Heater was put off and motor speed was reduced to 500-550 rpm and cooling was continued for about 15 minutes till the temperature came down to around 40°C. The free flowing dry blend was then discharged from the mixer and was collected in polyethylene bags.

3.2.1.2 Melt Blending

Melt blending was done in an oil-heated laboratory size (6 X 13 inch) two roll mill having a friction ratio of 1:1.2 (Bonanzo Enterprise, New Delhi). The mill was dry run for about an hour with the circulation of the heated oil. When the surface temperature of the rolls reached 160°C, the gap between the rolls was adjusted to the minimum and the PPVC compound was added. After masticating for about 4-5 minutes, when a band formed in the front roll, the gap between the rolls was increased. For binary/ternary blends, addition of other component(s) (EVAPVC, NBR1 or NBR2) was made at that stage. The band formed on the roll was cut and put back on the nip for having a better and quicker mixing. After mixing for 8-10 minutes when the melting and mixing were complete, the band was cut and removed from the roll.

3.2.2 Solution Blending

5 % solutions of the desired polymer/polymers were made in tetrahydrofuran at room temperature. While making blends, polymers were taken in the desired ratio. When no swollen polymer was visible, the solution was cast on glass petri dishes and solvent evaporation was allowed in a fume cupboard at room temperature till solvent smell disappeared completely.

covered with polyethylene films. Two roll mill was located in a class 1000 clean room which was maintained at slightly higher air pressure than the surroundings. This helped in avoiding unwanted contamination of the samples prepared.

3.4 RHEOLOGICAL STUDIES

3.4.1 Plasticorder Torque

Brabender plasticorder model PLV 151 was used for the present study. 'Roller type 30' mixer head was heated to the desired temperature by circulation of heated oil. Pre-weighed quantity of sample was added to the mixer chamber through the chute after switching on the mixer head. The speed of the rotor was varied. The torque and stock temperature were recorded.

3.4.2 Melt Flow Index (MFI)

The test samples were packed in the barrel of melt flow index tester (Karl Frank) which was designed in accordance with ASTM D 1238-73. The temperature of the electrically heated barrel was set and stabilized before adding samples. After a warmup period of 3 minutes, the molten samples were forced down through the nozzle by applying the desired load on the piston. The melt height in the barrel was kept the same for all experiments. Extruded samples for the 30 mm travel of the marked region of the piston were collected and the time for this travel was also measured with a digital stop watch. The MFI was obtained from

$$MFI = \frac{600w}{t} \qquad (3.1)$$

where, w is the extrudate weight and t is the extrusion time in second.

Other calculations were done using the equations:

$$Q = \frac{MFI}{600\rho} \qquad (3.2)$$

$$\tau_a = \frac{R_n F}{2\pi R_p^2 l} \qquad (3.3)$$

$$\dot{\gamma}_a = \frac{4Q}{\pi R_n^3} \qquad (3.4)$$

$$\dot{\gamma} = \frac{3n' + 1}{4n'} \times \frac{4Q}{\pi R_n^3} \qquad (3.5)$$

$$\eta = \frac{\tau_a}{\dot{\gamma}} \qquad (3.6)$$

where,

τ_a = apparent shear stress, dyne/cm^2

F = force due to weight of piston + applied load, dyne

R_n = radius of the nozzle, cm

R_p = radius of the piston, cm

l = length of the nozzle, cm

$Q = flow\ \ rate,\ \ cm^3/\sec$

$\dot{\gamma}_a = apparent\ \ shear\ \ rate,\ \ \sec^{-1}$

$\dot{\gamma} = corrected\ \ shear\ \ rate,\ \ \sec^{-1}$

$\rho = density,\ \ gm/cm^3$

$n' = flow\ \ behaviour\ \ index = d(\log \tau_a)/d(\log \dot{\gamma}_a)$

$\frac{3n'+1}{4n'} = Rabinowitch\ \ correction\ \ factor$

$\eta = viscosity,\ \ poise$

3.4.3 Die Swell Ratio

The extrudates from MFI experiments were collected and the length of these were measured by placing the samples on a graph paper with 1 mm graduations and kept on a flat surface. Care was taken to ensure that the samples were placed straight on the graph paper and they were not stretched. From the length, weight and density the extrudate dia was calculated by the equation

$$D_E = \sqrt{\frac{4w}{\pi L \rho}} \tag{3.7}$$

where, D_E, w, L, and ρ are extrudate diameter, and weight, length and density of the sample. Since, some of the blends had surface irregularities, this method enabled to get an average D_E. Direct measurements of D_E by optical or calliper method was found to be difficult and variations in the results were found to be more. Die swell ratio D_R was calculated from D_E and nozzle diameter D

$$D_R = \frac{D_E}{D} \tag{3.8}$$

Principal normal stress difference $(\tau_{11} - \tau_{22})$ was calculated from the die swell values and the shear stress τ_{12} according to Tanner's (1970) equation.

$$\tau_{11} - \tau_{22} = 2\tau_{12} \cdot \left(2D_R^6 - 2\right)^{0.5} \tag{3.9}$$

$$S_R = \frac{\tau_{11} - \tau_{22}}{2\tau_{12}} \tag{3.10}$$

$$G = \frac{\tau_{12}}{S_R} \tag{3.11}$$

where, S_R and G are recoverable shear strain and apparent elastic shear modulus and these were calculated from their relations with principal normal stress difference (Han, 1976).

3.4.4 *Extrusion Studies*

Haake Rheocord EU-5V with extruder head was used for this study. The single screw extruder had a 19 mm dia screw with L/D ratio of 26:1. Temperature was set at 150°C for all zones and hopper was cooled with running tap water. A capillary die of 3 mm dia and 45 mm length was fixed on the extruder head and pressure and torque in the metering zone for varying rpm were recorded. Output rate was measured by weighing the extrudate for a known period.

3.5 MECHANICAL PROPERTIES

3.5.1 Ultimate Elongation and Tensile Stress

Samples in the sheet form having thickness of about 0.25 mm, width of 22 mm and length of 100 mm were cut with a template at about -20°C in a cryostat (EC Model, Minotome Microtome, International Instrument Co.). Test procedure followed was ASTM D 882-81: Standard test methods for tensile properties of thin plastic sheeting. Thickness of each sample was measured with a digital micrometer. Testing was carried out in an Instron Universal Testing Machine, model 1193. Initial grip separation was maintained at 50 mm and rate of grip separation was maintained at 500 mm/min. Load and increase in length were recorded on a strip chart recorder. Stress was calculated from the load and original cross sectional area of the specimen. At least eight samples were used for each material. Calculations for ultimate elongation and tensile stress was done according to the procedure described in ASTM D 882.

3.5.2 *Modulus*

From the results of the tests done for ultimate elongation and tensile strength (Section 3.5.1), modulus values were calculated from the load values at 100% elongation of the samples.

3.5.3 *Tensile Energy to Break*

From the recorded values of load and increase in length (Section 3.5.1) stress and strain values were calculated at least in 20 points for each sample. Average stress vs. strain plot for each test material was made by taking the mean stress value (of at least 8 samples) at a particular strain. Ultimate strain for a material was taken as the mean of ultimate strain obtained by testing at least 8 samples. Tensile energy to break was calculated from the area under the average stress-strain curve as described in ASTM D 882.

3.5.4 *Creep*

Samples in sheet form with approximate thickness of 0.25 mm were cut into dumbbell shape with a metal template. The middle portion had a width of 20 mm and markings were made at 50 mm interval with a felt pen with soft tip in the middle portion of the sample. Clamping was done at the marked places with laboratory pinch cocks. 1.5 mm thick soft and plasticized PVC cushions were used between the samples and the pinch cocks to avoid pinching of the samples while clamping. One of the clamps was then fixed to a hook and from the lower side pinch cock appropriate load was applied such that the applied load could hang freely. The total weight of the lower pinch cock, weight of the cushion material and the dead load was taken as the applied load for a sample. The dead load was taken such that total load applied resulted in nominal stress level of 20% of the UTS of the sample as determined by test procedure ASTM D 882. The test was carried out at room temperature (30 ± 2°C). After the desired period, the load along with the lower clamp and cushion material were released. Measurement of the length of the marked portion of the sample was done at desired times with the help of a metal ruler. Extension at different times was calculated from

$$\%\ extension = \frac{L_t - L_0}{L_0} \cdot 100 \qquad (3.12)$$

where, L_t and L_o are the length of the marked portion of the specimens at a time 't' and 'O' (L_o = 50 mm).

3.5.5 Hardness

The hardness of the samples was measured according to the test procedure ASTM D 2240-81 using shore A durometer (Blue Steel Eng. Co).

3.6 DYNAMIC MECHANICAL ANALYSIS AND BRITTLENESS TEMPERATURE

3.6.1 Dynamic Mechanical Properties

Dynamic mechanical properties were determined by using Rheovibron Viscoelastometer DDV-III-C. 3 mm thick flat pieces of compression moulded sheets were cut to have approximate sample dimension of 70 X 10 X 3 mm. Dimensions of each sample were accurately measured before the experiment. Testing was carried out at a frequency of 35 Hz using a strain amplitude of 2.5×10^{-4}. Heating rate of the sample was approximately 1°C per minute. The instrument directly measures $\tan\delta$ (loss tangent) and complex modulus ($E*$). Storage modulus (E') and loss modulus (E'') were calculated using the following equations.

$$E* = \frac{L}{8AS(D-K)} \cdot 10^{11} N/m^2 \tag{3.13}$$

$$\text{Storage modulus, } E' = E* \cos\delta \tag{3.14}$$

$$\text{Loss modulus, } E'' = E* \sin\delta \tag{3.15}$$

where, L = length of the sample between the clamps
A = amplitude factor
D = dynamic force reading
S = sectional area of the sample
K = instrument error constant
δ = phase difference

Calculation of $E*$, E', and E'' were done with DCM, PC-AT computer, Turbo 2000 and other experimental details are as described by Bhagawan (1987).

3.6.2 Brittleness Temperature

For brittleness temperature studies, the samples of dimensions of 37.5 X 6 X 2 mm were punched from compression moulded pieces. Brittleness temperature was tested by following the test procedure ASTM D 746-79. Striker speed of 1.8 to 2.1 m/sec and acetone as the heat transfer medium were used for the tests. The tester used was from "Toyo Seiki", Japan (series No. 525).

3.7 MORPHOLOGY AND INTERACTIONS

3.7.1 Scanning Electron Microscope

For SEM studies, the samples prepared in two roll mill were collected with extreme care for cleanliness. Cast samples were prepared by dissolving the materials in tetra hydrofuran (BDH, HPLC grade) and casting in glass petri-dishes kept in a fume cupboard. The cast and rolled samples were gold coated in a sputter coating unit (EMSCOPE, Model No. AE-1231, England) for 3 minutes in Argon atmosphere. Sample stands were cooled by running water during the coating. The gold coated samples were stored in desiccator and SEM observations were made and pictures were taken by using JEOL JSM 35 C scanning electron microscope.

3.7.2 FTIR Studies

Milled samples of thickness approximately 0.1mm were used for recording of transmission spectra by FTIR (FTS 40, Biorad-Digilab Division). Average spectra of 64 scans were recorded after base line correction.

3.8 EXTRACTION AND WATER ABSORPTION

3.8.1 Extraction

3.8.1.1 Extraction in Vegetable Oil

Sheet samples prepared by two roll mill and having a thickness of about 0.25 mm were cut to have approximate dimensions of 80 X 22 mm. The samples were washed in 0.5% Laxbro soap solution, rinsed thrice with distilled water and dried at 70°C in an oven for 1 hour. After taking the weights, the samples were placed in a flat container having the vegetable oil. It was ensured that the samples did not touch each other and they were completely immersed in the oil. The container along with the samples were then kept in an incubator maintained at 70°C. After the specific intervals the samples were taken out from the oil and the surface oil was removed by washing with 1% Laxbro soap solution. The samples were then rinsed thrice in distilled water and dried at 70°C for 1 hour before taking the weights. Amount of extraction was calculated as follows:

$$\% \ extraction = \frac{W_0 - W_t}{W_0} \times 100 \tag{3.16}$$

where W_0 and W_t are the weights at zero time and at a particular time 't'.

3.8.1.2 Extraction in Simulated Gastric Fluid

The simulated fluid was prepared as described in US Pharmacopoeia (USP, 1985 a). 2 gm of NaCl and 3.2 gm of pepsin were dissolved in 7 ml conc. HCl and diluted in 1 litre of distilled water to have a solution with pH of 1.2.

Extruded rods from MFI experiments were cut to about 2.5 cm lengths and used for this study. The samples were cleaned in 0.5% Laxbro soap solution and rinsed in distilled water. After removing the water droplets by vigorous shaking, the samples were wiped dry with tissue paper and the initial weight was taken. 50 ml of the simulated juice was taken in each 100 ml beaker and the samples (about 3 gm) were added to it ensuring that the samples were completely immersed. The beakers containing the samples were then kept in an incubator set at 37°C. Samples were taken out at desired time, thoroughly rinsed in distilled water, wiped with tissue paper and the weights of the samples were recorded. Calculation for % extraction was done in the same manner as for vegetable oil.

3.8.2 Water Absorption

Compression moulded samples of dimensions 100 X 20 X 3 mm were used for this study. The samples were immersed in distilled water, wiped with tissue paper and the initial weights were taken. The samples were then kept immersed in distilled water which was changed every alternate day. Subsequent weights were taken at desired time intervals after removing the sample from the distilled water and wiping it with tissue paper to make the surface dry. The experiments were conducted at room temperature (about 30°C). Extraction of plasticizer by water is known to be very low (Prins, 1979) and was neglected and % water absorption (WA) was calculated as:

$$WA = \frac{W_t - W_0}{W_0} \times 100 \tag{3.17}$$

where W_0 and W_t are the weights at zero time and at a particular time '*t*'.

3.9 PERMEABILITY

3.9.1 Water Vapour

From the two roll milled sheets, small collapsible bags with only one 3 mm ID inlet/outlet tube were fabricated by high frequency welding (REC, Monga Electronics) technique. Two welding dies were required for the fabrication. Welding of the top side was done first after placing the tube with a mandrel between the two sheets. After removing the mandrel, welding of the bottom side having ‘U' shape was done. Aluminium welding dies were used. The shape of the collapsible bags was rectangular with dimension of 5.9 X 5.1 cm.

After filling the bags with distilled water, the inlet/outlet tube was sealed by high frequency welding and the initial weights were taken. The water filled bags were stored in desiccators containing silica gel desiccant. The desiccators were kept at appropriate temperatures (4°, 37°, and 60°C) in cold room or incubator. At desired intervals, the weights of the bags were noted. The loss of weight during two successive readings was taken as the amount of water vapour permeated during that interval. Permeability was calculated from the knowledge of water loss, its volume at the temperature of interest and other physical parameters of the barrier film. Equation (3.18) was used to calculate permeability constant.

3.9.2 Oxygen, Nitrogen and Carbon dioxide

Gas permeability was measured at 27 ± 2°C and 65 ± 2 % R.H. by using a permeability cell having 50 sq. cm. as the sample (film) area. Films were made by two roll mill. Thickness was measured with a gauge and average of ten readings was taken as the thickness for calculations. Helium was used as carrier gas. The amount of gas permeated was analysed using Gas Chromatograph after every 5 or 10 minutes. The apparatus used for gas permeability studies was "Lyssy Analytical Gas Permeability Fractometer model GPM-200". The steady difference between successive readings was taken as the amount of gas permeated within the interval. Average of 3-4 readings was used in all calculations. The details of the procedure have been described by Naik et al. (1990). Permeability was calculated from the equation

$$P = \frac{Qd}{pAt} \qquad (3.18)$$

where,

$$P = Permeability, \frac{cm^3/sec}{cm^2(cm\,Hg/cm\,of\,film)}$$

Q = volume, cm^3
A = area, cm^2
t = time, sec
p = driving force for permeating gas, cm Hg
d = thickness of film, cm

3.10 OTHER EXPERIMENTAL TECHNIQUES

3.10.1 Optical Clarity

% Transmission of light through the test material in the visible region was determined with a spectro photometer (Hitachi model 220). Milled samples having thickness between 0.20 and 0.30 mm were used for the test. Average thickness of each sample was determined from six measurements done by a digital micrometer (Micro 2000, Moore & Wright, England). The sample was placed between two pieces of slip gauges and the thickness difference of the slip gauges with and without the sample in position was taken as the sample thickness. The samples were placed in the light path with the help of a magnetic sample holder and the % transmission was recorded in the wave length region 700 - 400 nm.

In view of the difficulty of getting all samples with exactly the same thickness, initial experiments were done to verify whether within the range of sample thickness (0.25± 0.05 mm) of interest, the following relationship derived from Lambert Beer Law holds good or not for a particular test material.

$$\log \frac{P_0}{P} = A = a \cdot b \cdot c \qquad (3.19)$$

where,

P_0 = radiant power of incident light
P = radiant power of exit light
A = absorbance
a = constant for a material, absorptivity
b = length of the path (sample thickness)
c = concentration

The above relation was found to be valid and the deviation was within ± 5% for all the samples. Therefore, % transmission for all the samples was converted to % transmission for sample thickness of 0.25 mm. This was done to compare the transparency of the blends.

3.10.2 Haemolytic Potential

Tests for haemolytic potential of the materials were carried out by modifying the procedure described by O'Leary et al. (1969). The modification was minor and only change of the test procedure was that rabbit blood was used instead of human blood. 25 gm samples made by compression moulding were used for each test.

3.10.3 Density

Extruded samples of MFI experiment were cut into approximately 2.5 mm long pellets and were used for density measurements. Density measurements were carried out by immersion in liquid technique in 50 cc specific gravity bottles at 30± 2°C. Tri~~p~~ple distilled water was used for all samples excepting NBR1 and two blends containing high amount of NBR1, for which analytical grade methanol was used as the liquid. Care was taken to ensure removal of air bubbles while samples were immersed. At least 3 measurements were done for each sample. Density was calculated as shown below. Density with respect to methanol was multiplied with the density of methanol to get the density with respect to water.

$$\rho = \frac{w_2 - w_1}{(w_4 - w_1) - (w_3 - w_2)} \tag{3.20}$$

where,

ρ = density, gm/cc
w_1 = wt. of empty bottle, gm
w_2 = wt. of bottle + sample, gm
w_3 = wt. of bottle + sample + water, gm
w_4 = wt. of bottle + water/methanol, gm

RESULTS AND DISCUSSIONS

CHAPTER - IV

RHEOLOGICAL AND PROCESSING STUDIES

SECTION - 1

4.1 RHEOLOGICAL AND PROCESSING STUDIES

A material may have excellent properties like optical, mechanical, thermal and bio-compatibility, but it is useful for an end application only if it can be processed economically by traditional techniques. The knowledge about rheological and processing characteristics is therefore of paramount importance.

In this section, composition of the blends studied, observations made during compounding, and studies on melt flow index, Brabender Plasticorder and extruder are reported. The data collected have been analysed and discussions have been made for the observed behaviour.

4.1.1 Blend Compositions and Observations made during Blending

The blend compositions are given in Tables 4.1.1 to 4.1.3. The formulations for plasticized PVC samples (Table 4.1.1) were designed such that only plasticizer content varied and amount of all other ingredients remained constant. EVAPVC had minimum amount of additive to make it easily processible without decomposition.

Poly(ethylene-vinyl acetate)-g-PVC, polyesters and NBR were selected as the polymers to be blended with PPVC. The selection of these polymers was carried out based on the prior information available in the literature regarding the properties and miscibility of these components with PVC (Anderson, 1979; Paul, 1980; Ziska, 1981; Robeson, 1982; Wang, 1983; Dunn, 1982). The polyester blend formulations given in Table 4.1.2 were designed such that the blends had hardness values similar to control material, PPVC. This was done with the intention of having polyblends with flexibility similar to that of PPVC. Maintenance of similarity of formulations for three grades of polyesters enabled comparison of the performance of these polyesters.

The binary and ternary blend formulations, shown in Table 4.1.3, were chosen such that the characteristics of the entire range (0 to 100%) could be studied. Since objective of the work is to reduce the quantity of plasticized PVC by replacing it with another polymer(s) and not to substitute it, binary blends of NBR and EVAPVC were not formulated.

TABLE 4.1.1 Formulations for Samples of Plasticized PVC and EVAPVC

	Formulations, parts by wt.				
	Sample Codes				
Ingredients	PPVC	PPVC2	PPVC3	PPVC4	EVAPVC
PVC resin	100	100	100	100	-
Vinnol^{R} K-550 #	-	-	-	-	100
DEHP	55	30	20	5	5
Epoxidised oil	10	10	10	10	10
Ca-Zn stabilizer	2.5	2.5	2.5	2.5	2.5
Phosphite	0.5	0.5	0.5	0.5	0.5
Ca-stearate	0.2	0.2	0.2	0.2	0.2

Vinnol^{R} K 550 : Poly(ethylene-vinyl acetate)-g-PVC

TABLE 4.1.2 Formulations for PVC-Polyester Blends

Ingredients	Formulations, parts by wt.								
	Sample Codes								
	PE1	PE2	PE3	PE4	PE5	PE6	PE7	PE8	PE9
PVC resin	100	100	100	100	100	100	100	100	100
Polyester A #	35	20	10	-	-	-	-	-	-
Polyester B ##	-	-	-	35	20	10	-	-	-
Polyester E ###	-	-	-	-	-	-	35	20	10
DEHP	35	45	50	35	45	50	35	45	50
Epoxidised oil	10	10	10	10	10	10	10	10	10
Ca-Zn stabilizer	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Phosphite	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ca-stearate	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

\# Polyester A : Plasflex PA

\## Polyester B : Plasflex PB

\### Polyester E : Plasflex PE

TABLE 4.1.3 Formulations for other Binary and Ternary Blends

Sample Codes	Formulations, parts by wt.			
	Ingredients			
	PPVC	EVAPVC	NBR1	NBR2
BB1 91	90	10	-	-
BB1 73	70	30	-	-
BB1 55	50	50	-	-
BB1 37	30	70	-	-
BB1 19	10	90	-	-
BB2 91	90	-	10	-
BB2 73	70	-	30	-
BB2 55	50	-	50	-
BB2 37	30	-	70	-
BB2 19	10	-	90	-
BB3 91	90	-	-	10
BB3 73	70	-	-	30
BB3 55	50	-	-	50
BB3 37	30	-	-	70
BB3 19	10	-	-	90
TB111	33.33	33.33	33.33	-
TB211	50	25	25	-
TB311	60	20	20	-
TB811	80	10	10	-
TB121	25	50	25	-
TB131	20	60	20	-
TB181	10	80	10	-
TB112	25	25	50	-
TB113	20	20	60	-
TB118	10	10	80	-

4.1.1.1 Dry Blending

Generally, no difficulty was encountered during the dry blending excepting the blends containing NBR2 which was lumpy in nature. These blends were therefore blended with PPVC only in molten state in two roll mill. The dry blends were free flowing powders.

4.1.1.2 Blending in Two Roll Mill

Initially attempts were made to blend PPVC4 with different proportions of EVAPVC, NBR1 and NBR2. PPVC4 powders did not form any band on the two roll mill even at 190°C. Attempts were therefore made to make a band first with the EVAPVC, NBR1 or NBR2 and then add PPVC4. However, extensive milling at 180°C for about 15 minutes also did not produce well dispersed blend. PVC particles were still clearly seen visually and the matrix polymer started degrading as was evidenced by the colour change. This behaviour is due to the fact that PPVC4 is hardly plasticized. Since, blending PPVC4 with a second polymer was not possible it was therefore decided to use PPVC, which is more plasticized, for further studies.

Another notable observation made during the milling was that of all the 'pure' components, NBR2 offered the maximum resistance to the movement of the rolls. Extensive milling was required to breakdown this product before PPVC could be added.

Like typical rubbers, the milled samples of both NBR1 and NBR2 and blends containing about 90% of these were found to be very sticky.

Milled films of plasticized PVC samples and NBR1 had more transparent appearance than EVAPVC. The blends generally became more and more opaque as the relative amount of the components became closer. For example BB2 91 or BB2 19 were more transparent than BB2 55. Ternary blends were generally more opaque than binary blends.

PPVC-NBR2 blends containing 30% NBR2 had distinct brownish appearance. The colour was more intense for blends of NBR2 containing more than that amount. PPVC-NBR1 blends containing 50% or more NBR1 also had a pale brown appearance.

All milled samples were smooth in appearance of the surface, excepting the blends containing more than 10% of NBR2.

4.1.1.3 Solution Blending

No difficulty was encountered for co-dissolving PPVC and EVAPVC in THF and casting films. However, both NBR1 and NBR2 did not dissolve fully. Both had visible swollen polymer left even after days of adding solvent. Undissolved swollen polymer was more for NBR2 than for NBR1.

4.1.2 *Melt Flow Index*

Shenoy et al. (1983 a) advocate the use of an inexpensive apparatus, melt flow indexer, for elucidating the flow behaviour of materials.

Melt flow index (MFI) for binary and ternary blends at one representative temperature and shear stress are shown in Figs. 4.1.1 to 4.1.3 and the complete MFI data for all the blends studied for different temperatures and shear stress conditions have been given in Table A.1 in the Appendix-A. MFI of 'pure' NBR1, BB2 37 and BB2 19 could not be properly determined due to degradation of the materials because of very low flow rate and high residence time in the barrel.

The samples of the PE series generally show lower MFI values compared to PPVC (Fig. 4.1.3). This is expected due to the fact that these formulations have lower amount of DEHP than PPVC. PE1 has the polyester (Plasflex PA) with lowest molecular weight and therefore, among the liquid polyesters used, this polyester acts as better plasticizer than the others. The effective plasticizer content is higher in PE1 compared to PPVC and other PE blends and this results in higher MFI for this blend.

The binary blends containing NBR1 (Fig. 4.1.1) show a rapidly decreasing trend with the addition of NBR1, though, the values could not be determined beyond a 50-50 weight percent composition.

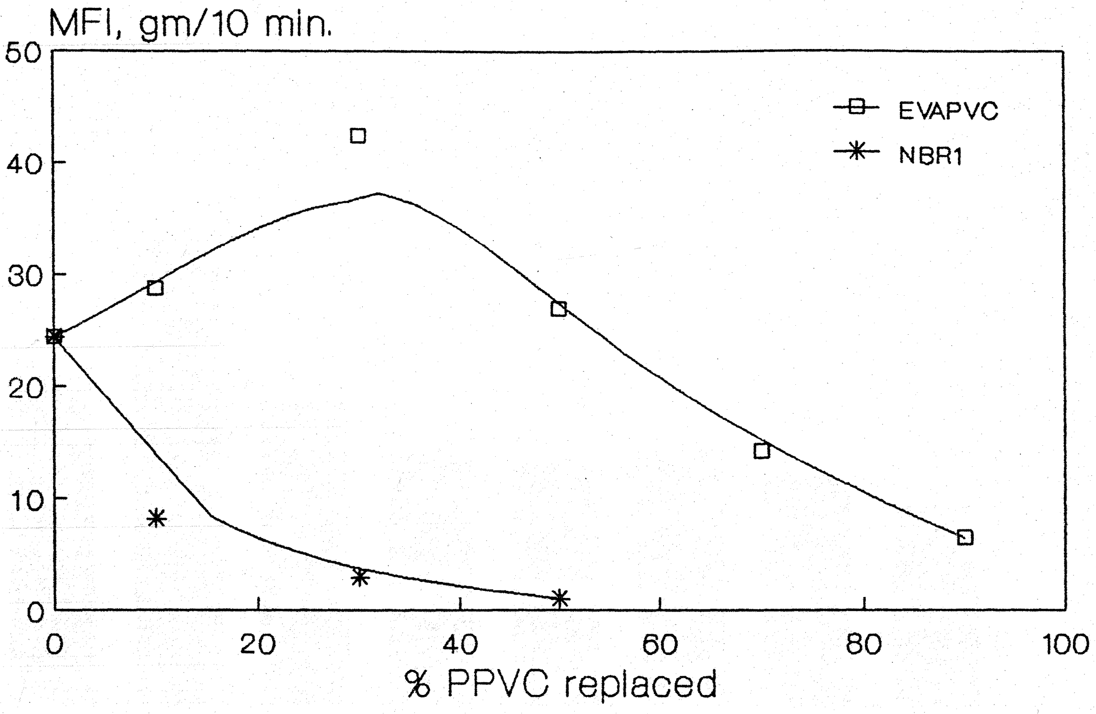


Fig. 4.1.1 MFI of binary blends at 170°C and shear stress of 1.26E+5 N/m^2

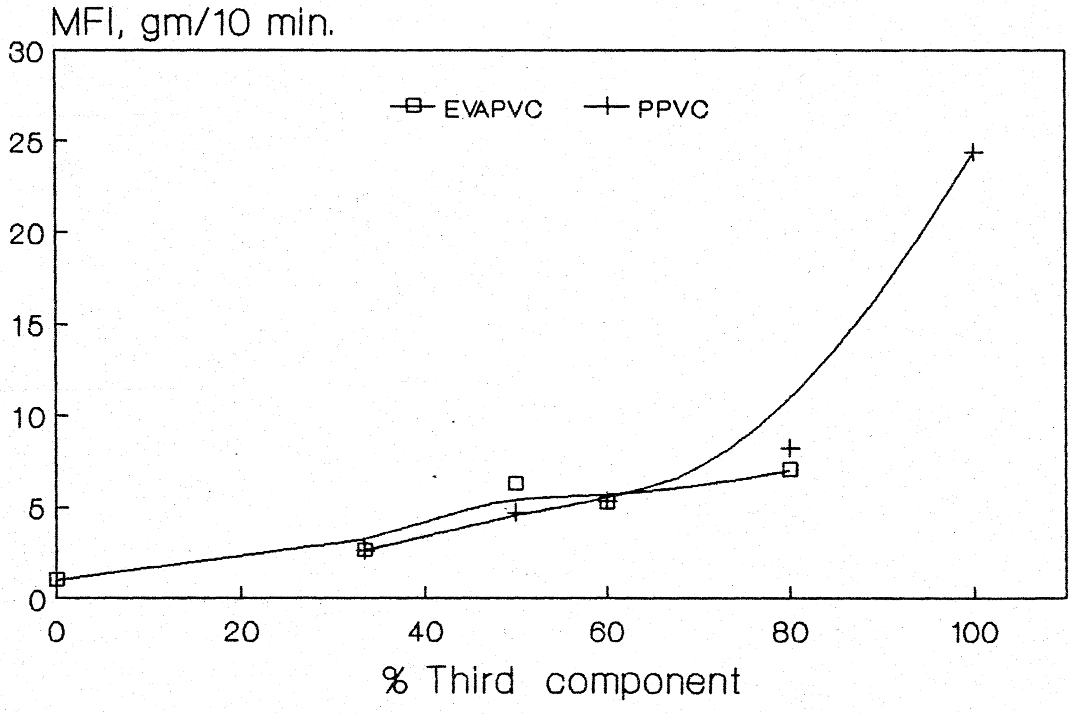


Fig. 4.1.2 MFI of ternary blends at 170°C and shear stress of 1.26E+5 N/m^2

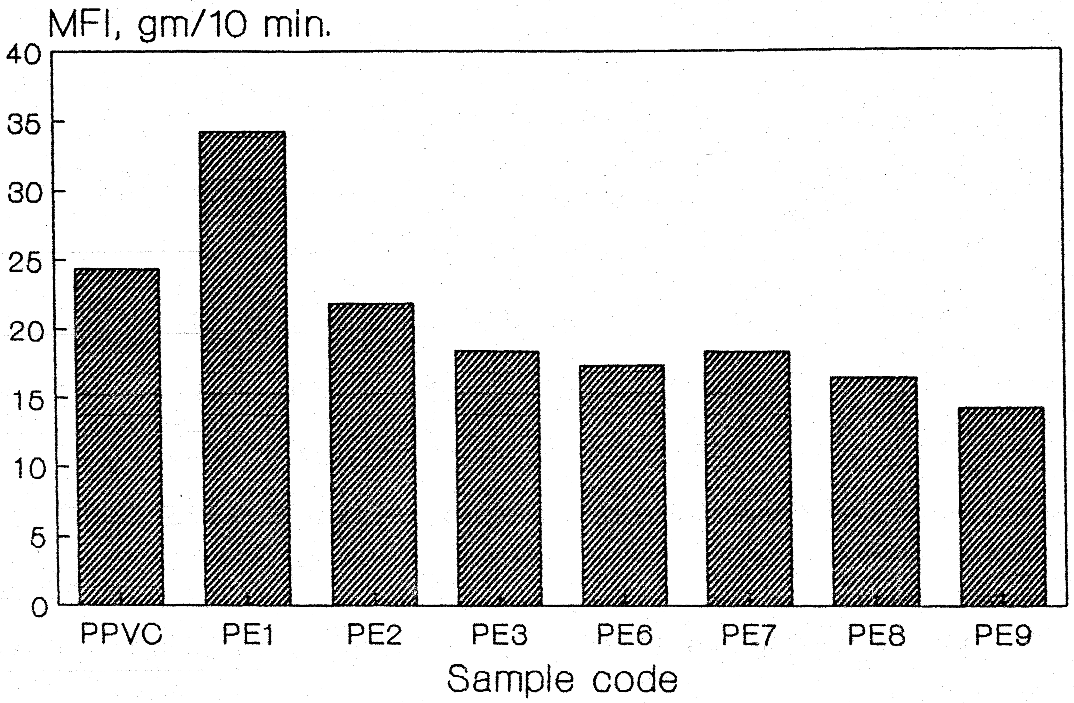


Fig. 4.1.3 MFI of PPVC and PE blends for shear stress of 1.26E+5 N/m^2 at 170°C

The binary blends of PPVC with EVAPVC however, show higher MFI values than PPVC upto a weight percent of 50, though, EVAPVC itself has a much lower MFI value than PPVC (Fig. 4.1.1). All compositions show a good expected dependency on temperature. These observations are interesting and are of great practical significance from processing point of view.

The noted behaviour of PPVC-EVAPVC and PPVC-NBR1 binary blends are reflected in ternary blends. The trend for ternary blends are (i) addition of PPVC to a blend containing equal amount of EVAPVC and NBR1 increases MFI, (ii) addition of NBR1 to a binary blend of equal fractions of PPVC and EVAPVC results in decreased MFI values, and (iii) addition of EVAPVC to a 50-50 PPVC-NBR1 binary blend increases MFI values. The 'very low flow' characteristic of PPVC-NBR1 binary blends containing more than 50 % NBR1 can thus be improved by formulating a ternary blend containing EVAPVC .

4.1.3 Viscosity

Compared to MFI, viscosity is a more important and direct flow property. More purposeful analysis and detailed description of the flow properties can be done from viscosity data. The experimental data on the MFI vs. load are converted to viscosity vs. shear rate using the relationships given in section 3.4.2. Bagley correction was not carried out for true shear stress, since only one nozzle could be used for the MFI experiments. The idea was to compare the flow properties of various blends under similar conditions. It is presumed that the error for not correcting for the entrance-exit effect for blends containing similar materials (though in different proportion) would be marginal, at least for comparative purposes. Apparent shear stress has therefore been used for further calculations. Values of shear stress, corrected shear rate and viscosity are given in Table A.1 in Appendix-A.

4.1.3.1 Variation with Blend Formulation

The general approach to the description of the dependence of the viscosities of two (or three) component systems on the composition hinges on the analysis of the behaviour of simple models. Though such an approach allows one to obtain equations for the viscosity of a blend in which one polymer is dispersed in the continuous matrix of the other, the assignment of the components as dispersed and continuous must be understood depending on any phase inversion likely to take place at a critical value of the composition.

A simple empirical model applicable to blends of polymers has been suggested as

$$\log \eta = w_2^2 \log \eta_2 + \left(1 - w_2^2\right) \log \eta_1 \tag{4.1}$$

where, w_2 is the weight fraction of the dispersed phase of the blend. Though, most of the published literatures refer to volume fraction (Heitmiller, 1964; Vinogradov, 1980), the consideration of weight fraction also seems to give reasonably accurate predictions for PPVC-EVAPVC blend system as is seen in Fig. 4.1.4. Hayashida et al. (1970) also considered weight fractions instead of volume fractions in an inverse additivity model and found better interpolation. The assignment of subscript 1 or 2 must be changed for phase inversion, which depends not only on the properties of the pure components but also on the mode of dispersion. For phase inversion, equation (4.1) becomes

$$\log \eta = w_1^2 \log \eta_1 + \left(1 - w_1^2\right) \log \eta_2 \tag{4.2}$$

A simpler empirical model of logarithmic additivity, suggested by Bersted et al. (1981) (equation 4.3) is also tested for the blends.

$$\log \eta = w_1 \log \eta_1 + w_2 \log \eta_2 \tag{4.3}$$

Viscosity value of the pure component NBR1 could not be determined in the experimental range of shear stress and therefore viscosity values of only PPVC-EVAPVC blends could be predicted and are shown in Fig. 4.1.4. All three equations give predicted viscosity values that are quite close to experimental ones. For the blends BB1 73, BB1 55 and BB1 37 equation (4.2) gives viscosity values that are closer to experimental ones compared to equation (4.3). This indicates that in this range of composition, EVAPVC is predominantly the matrix phase. This is also confirmed from the SEM studies (Section 4.4.1.2).

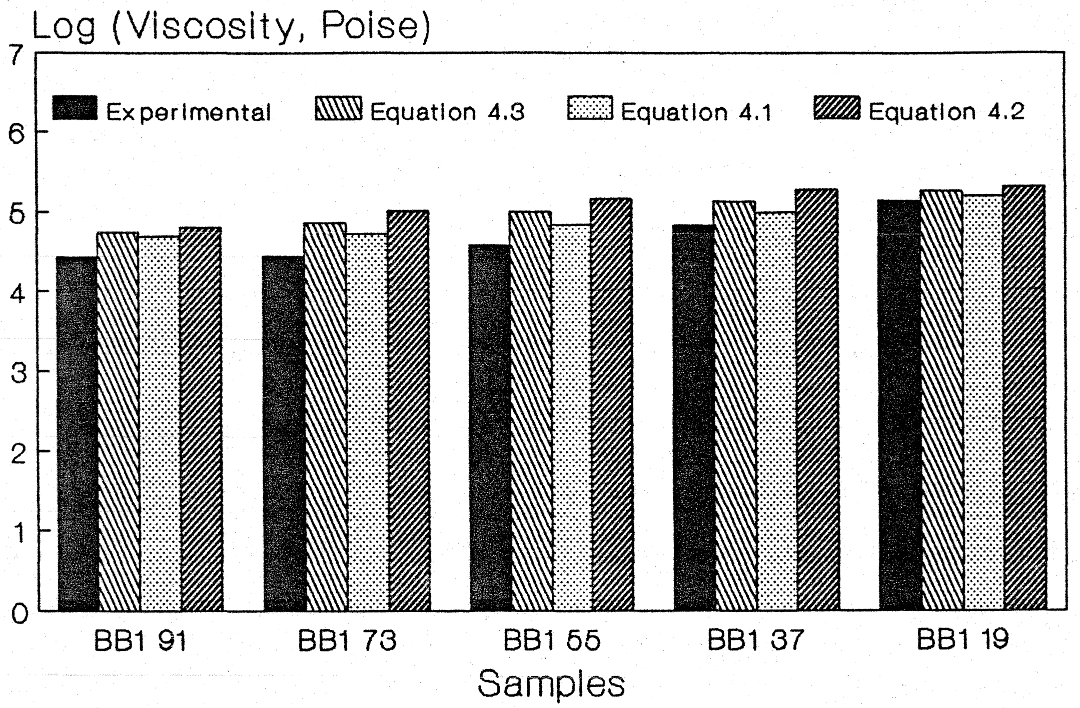


Fig. 4.1.4 Experimental and predicted viscosity values at 160°C and shear stress of 1.37E+5 N/m^2

4.1.3.2 Shear Stress (Shear Rate) Effects

Although, for several applications, the raw data of $\eta(\tau)$ or $\eta(\dot{\gamma})$ are quite sufficient, it is useful and desirable to make calculations and derivations of specific and simple analytical expressions for $\eta(\dot{\gamma})$ that describe the experimental data with sufficient accuracy. While several such equations are given in the literature, the behaviour shown in plots of $\eta(\dot{\gamma})$ vs. $\dot{\gamma}$ in Figs. 4.1.5 to 4.1.7 indicate that the "power law" as given in equation (4.4) is applicable to all samples in the region of experimental $\dot{\gamma}$ and temperature values. Viscosity is least affected by change in temperature (within the range of experiment) for blends containing more of NBR1. This is of course expected due to its elastomeric nature and characteristic absence of sharp melting region for an elastomer.

$$\eta = m\dot{\gamma}^{n'-1} \tag{4.4}$$

The values of *m* and the power law index *n'* for the best fit straight lines in the log log plots are given in Table 4.1.4. For the power law fluids, this index is the same as the flow behaviour index in equation (3.5) given in section 3.4.2.

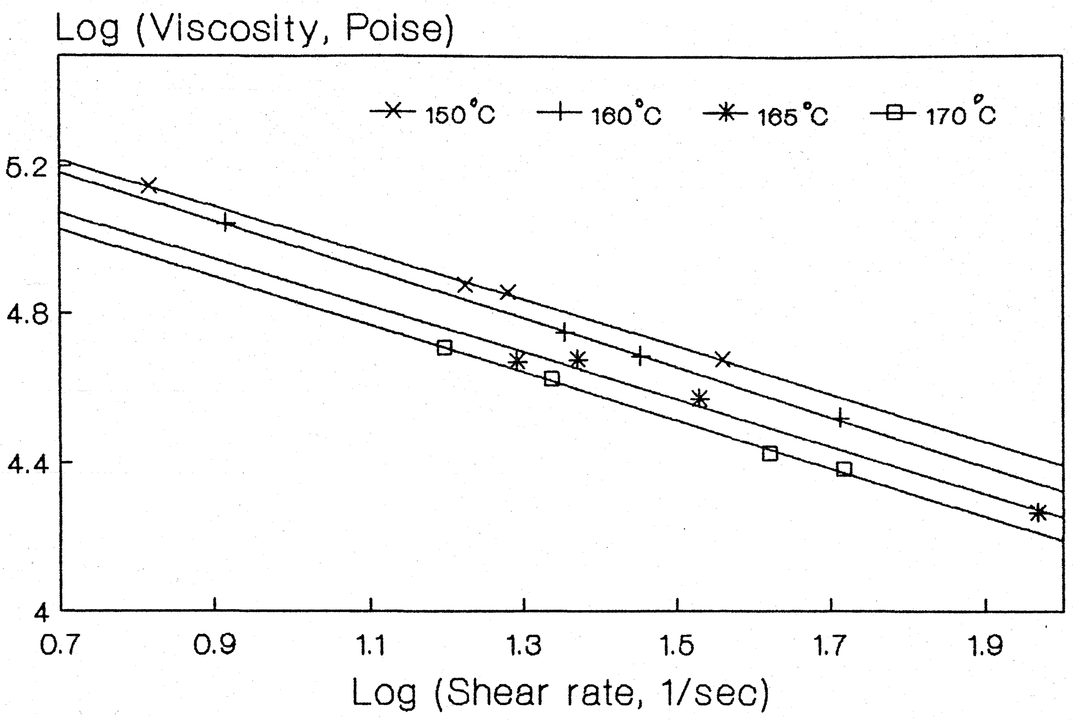


Fig. 4.1.5 Viscosity as a function of shear rate for PPVC

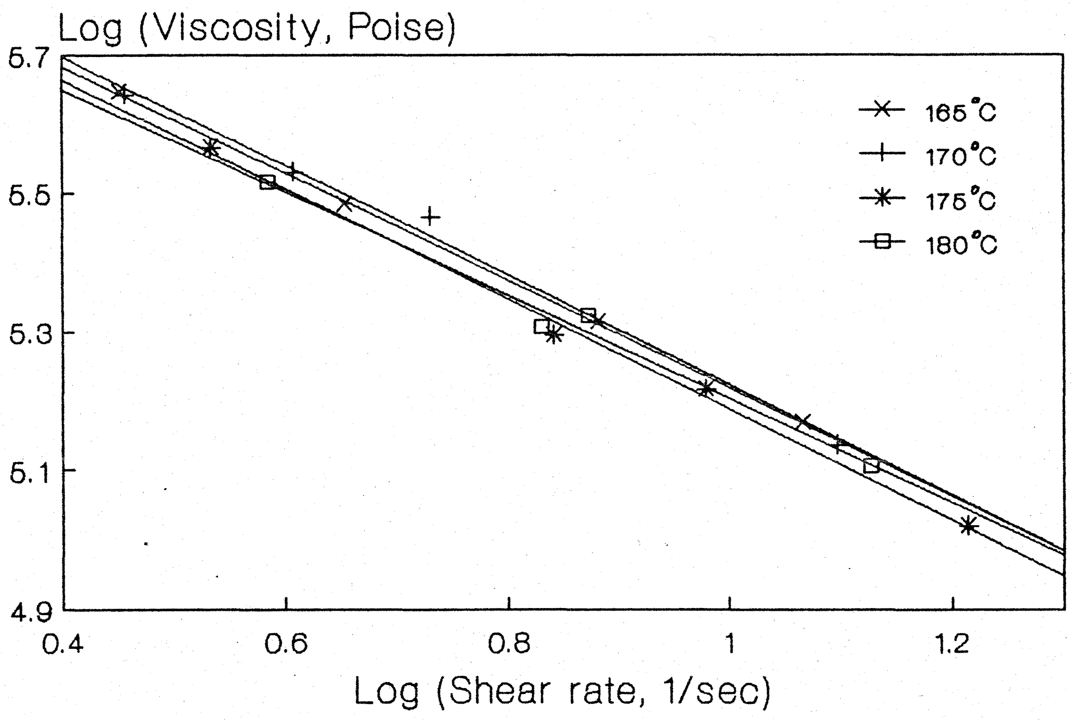


Fig. 4.1.6 Viscosity as a function of shear rate for BB2 55

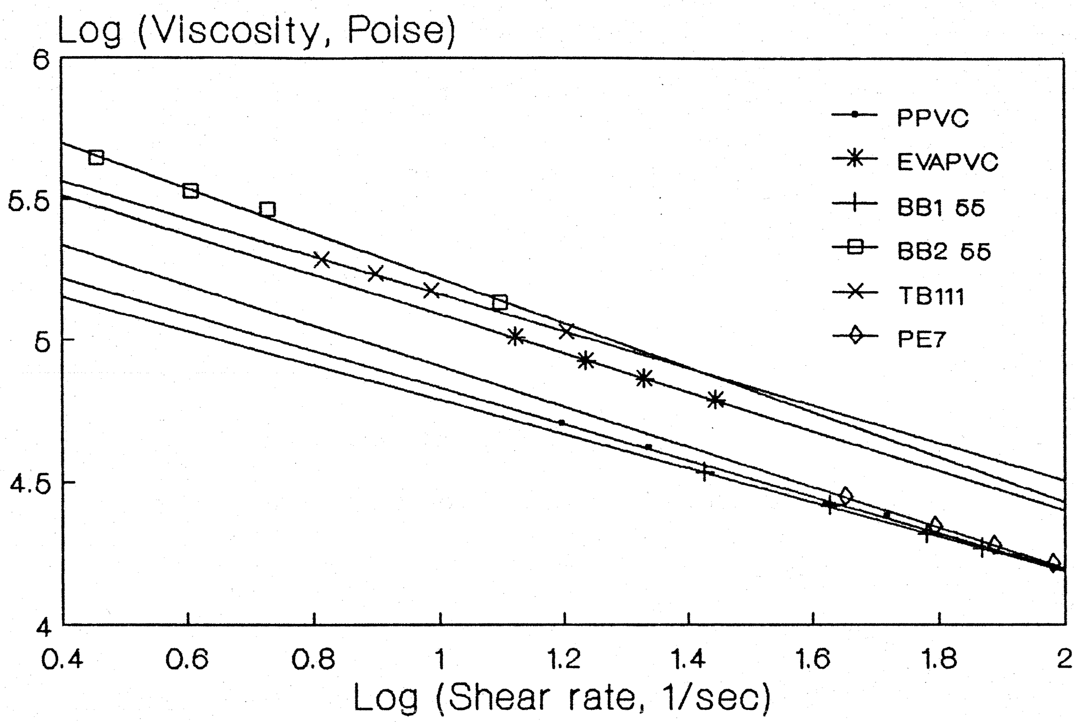


Fig. 4.1.7 Viscosity as a function of shear rate at 170°C

4.1.3.3 Temperature Effect

From the Arrhenius-Frenkel-Eyring (AFE) theory, the variation of viscosity with temperature is given by

$$\eta = K\exp(E/RT) \tag{4.5}$$

where, E is the activation energy and K is a constant. The existence of non-Newtonian behaviour gives rise to the fact that the viscosity is a function of shear rate $\dot{\gamma}$ (or the shear stress τ) in addition to being a function of melt temperature. The temperature dependence of viscosity can be considered at constant $\dot{\gamma}$ or at constant τ. Constant τ is preferred as $E_{\dot{\gamma}}$ varies with $\dot{\gamma}$ and little variation of E_τ is seen with τ.

Using the AFE equation and choosing one of the experimental temperatures (170°C or 443°K) as a reference temperature T_r, at constant τ,

$$\frac{\eta_T}{\eta_{T_r}} = \frac{\eta}{\eta_r} = a_T = \exp\frac{E_\tau}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)$$

$$= K'(T_r)\exp\frac{E_\tau}{RT} \tag{4.6}$$

where, $$K'(T_r) = \exp\left(-\frac{E_\tau}{RT_r}\right)$$

a_T is the shift factor and values of a_T are obtained either from the plots of $\log\eta$ vs. $\log\dot{\gamma}$ for different melt temperatures or as average values of the ratios at different load conditions.

An expression for a_T as a function of temperature of the form in equation (4.6) for all the samples can be obtained as

$$\log a_T = A + B/T \tag{4.7}$$

where,

$$A = \log K'(T_r), \quad B = \frac{E_\tau}{2.303R} \tag{4.8}$$

Values of a_T, A and B are given in Table 4.1.4 from the best fit of (log a_T) vs. ($1/T$) graphs.

TABLE 4.1.4 Calculated Values of n', m, a_T, A, B, a and b

Sample Codes	Temp °C	n'	Log m	a_T	A	B	Log a	b
PPVC	150	0.368	5.658	3.623	-11.18	4966	5.48	-0.639
	160	0.351	5.630	1.941				
	165	0.343	5.556	1.435				
	170	0.391	5.429	1.069				
PPVC2	170	0.208	5.971		-27.42	12159	5.95	-0.825
	175	0.354	5.743					
	180	0.298	5.694					
	185	0.310	5.405					
PPVC3	175	0.247	5.940					
	180	0.164	5.961					
	185	0.424	5.582					
	190	0.220	5.748					
PE1	150	0.204	5.853	3.009	-9.64	4282	5.71	-0.771
	160	0.303	5.674	1.756				
	165	0.263	5.677	1.354				
	170	0.532	5.139	1.051				
PE2	150	0.518	5.466	3.575	-11.06	4914	5.59	-0.700
	160	0.258	5.750	1.927				
	165	0.335	5.586	1.430				
	170	0.325	5.545	1.068				
PE3	150	0.441	5.563	2.849	-9.31	4129	5.56	-0.668
	160	0.438	5.491	1.695				
	165	0.301	5.652	1.319				
	170	0.368	5.499	1.033				

Sample Codes	Temp °C	n'	Log m	a_T	A	B	Log a	b
PE7	150	0.424	5.652	5.347	-13.46	6002	5.80	-0.811
	160	0.386	5.646	2.514				
	165	0.301	5.679	1.746				
	170	0.291	5.616	1.223				
PE8	150	0.336	5.784	4.909	-14.27	6329	5.68	-0.735
	160	0.271	5.768	2.216				
	165	0.260	5.738	1.509				
	170	0.296	5.626	1.037				
PE9	150	0.320	5.771	3.467	-10.75	4777	5.67	-0.720
	160	0.306	5.717	1.902				
	165	0.324	5.656	1.423				
	170	0.303	5.633	1.072				
EVAPVC	160	0.402	5.811	2.215	-13.32	5916	5.77	-0.678
	170	0.306	5.789	1.089				
	175	0.358	5.686	0.773				
	180	0.384	5.595	0.552				
BB1 91	160	0.375	5.499	2.049	-7.37	3268	5.41	-0.611
	165	0.406	5.412	1.386				
	170	0.384	5.414	0.946				
	175	0.528	5.137	0.651				
BB1 55	160	0.361	5.578	1.514	-12.56	5578	5.43	-0.625
	170	0.395	5.398	1.242				
	175	0.384	5.373	1.023				
	180	0.431	5.241	0.846				

Sample Codes	Temp °C	n'	Log m	a_T	A	B	Log a	b
BB1 73	160	0.374	5.490	2.108	-14.57	6443	5.38	-0.629
	165	0.429	5.344	1.079				
	170	0.437	5.263	0.781				
	175	0.453	5.142	0.569				
BB1 37	160	0.336	5.699	2.080	-11.93	5304	5.53	-0.623
	170	0.381	5.522	1.100				
	175	0.395	5.468	0.809				
	180	0.449	5.333	0.599				
BB1 19	160	0.344	5.803	2.122	-11.84	5269	5.68	-0.655
	170	0.332	5.698	1.128				
	175	0.448	5.522	0.831				
	180	0.430	5.494	0.616				
BB2 91	165	0.276	5.756	1.364	-19.94	8794	5.72	-0.710
	170	0.319	5.685	0.809				
	175	0.296	5.617	0.486				
	180	0.370	5.419	0.295				
BB2 73	165	0.188	5.977	1.570	-15.82	7014	5.92	-0.793
	170	0.260	5.884	1.036				
	175	0.231	5.853	0.690				
	180	0.276	5.784	0.463				
BB2 55	165	0.221	5.997	0.959	-4.01	1749	6.01	-0.790
	170	0.264	5.975	0.864				
	175	0.231	5.960	0.781				
	180	0.435	5.795	0.707				

Sample Codes	Temp °C	n'	Log m	a_T	A	B	Log a	b
TB111	170	0.348	5.816	1.020	-11.07	4907	5.80	-0.638
	175	0.335	5.794	0.768				
	180	0.440	5.632	0.581				
	185	0.384	5.642	0.443				
TB211	170	0.363	5.716	1.000	-12.03	5331	5.71	-0.635
	175	0.385	5.639	0.734				
	180	0.374	5.601	0.542				
	185	0.385	5.538	0.403				
TB311	165	0.402	5.684	1.355	-10.51	4661	5.66	-0.620
	170	0.331	5.723	1.028				
	175	0.398	5.598	0.784				
	180	0.469	5.436	0.602				
TB811	165	0.399	5.629	1.359	-11.07	4906	5.61	-0.624
	170	0.349	5.646	1.016				
	175	0.407	5.511	0.764				
	180	0.405	5.471	0.578				
TB121	165	0.357	5.709	1.144	-7.85	3464	5.71	-0.649
	170	0.437	5.596	0.931				
	175	0.471	5.511	0.762				
	180	0.410	5.535	0.626				
TB131	165	0.374	5.720	1.408	-11.92	5285	5.70	-0.654
	170	0.315	5.738	1.029				
	175	0.336	5.666	0.757				
	180	0.386	5.551	0.561				

Sample Codes	Temp °C	n'	Log m	a_T	A	B	Log a	b
TB181	165	0.432	5.646	1.407	-11.73	5204	5.66	-0.628
	170	0.378	5.652	1.033				
	175	0.366	5.626	0.764				
	180	0.383	5.552	0.569				
TB112	170	0.413	5.742	0.987	-7.70	3410	5.82	-0.661
	175	0.369	5.758	0.810				
	180	0.339	5.747	0.667				
	185	0.375	5.694	0.552				
TB113	170	0.372	5.820	1.072	-7.40	3293	5.88	-0.692
	175	0.433	5.761	0.886				
	180	0.349	5.792	0.735				
	185	0.337	5.780	0.612				
TB118	175	0.330	5.918					
	180	0.248	5.956					
	185	0.224	5.952					

4.1.4 *Master Plots*

Introducing equation (4.4), equation (4.6) can be modified as

$$\eta = a_T \eta_r = a_T m_{T_r} (a_T \dot{\gamma})^{n'-1}$$

$$\text{or} \quad \frac{\eta}{a_T} = m_{T_r} (a_T \dot{\gamma})^{n'-1} \tag{4.9}$$

or generally as

$$\frac{\eta}{a_T} = a \cdot (a_T \dot{\gamma})^{b} \tag{4.10}$$

Using the experimental values of viscosities at different shear rates and the a_T values from the expression (4.7), the values of *a* and *b* for the best fit are given in Table 4.1.4. Equation (4.10) is called the expression for a "*master curve*", dependent on the chosen reference temperature T_r. The plots for representative samples are given in Figs. 4.1.8 and 4.1.9. Shenoy et al. (1983 b) utilised MFI data and from the knowledge of T_g values generated temperature independent unified curve by plotting $\eta \cdot MFI$ versus $\dot{\gamma}/MFI$. They have extended this method of estimating rheograms of pure polymer melts to polymer blends (Shenoy, 1984). Teh et al. (1984) also made shear rate temperature superimposition plot (τ versus $a_T\dot{\gamma}$) for linear low density polyethylene.

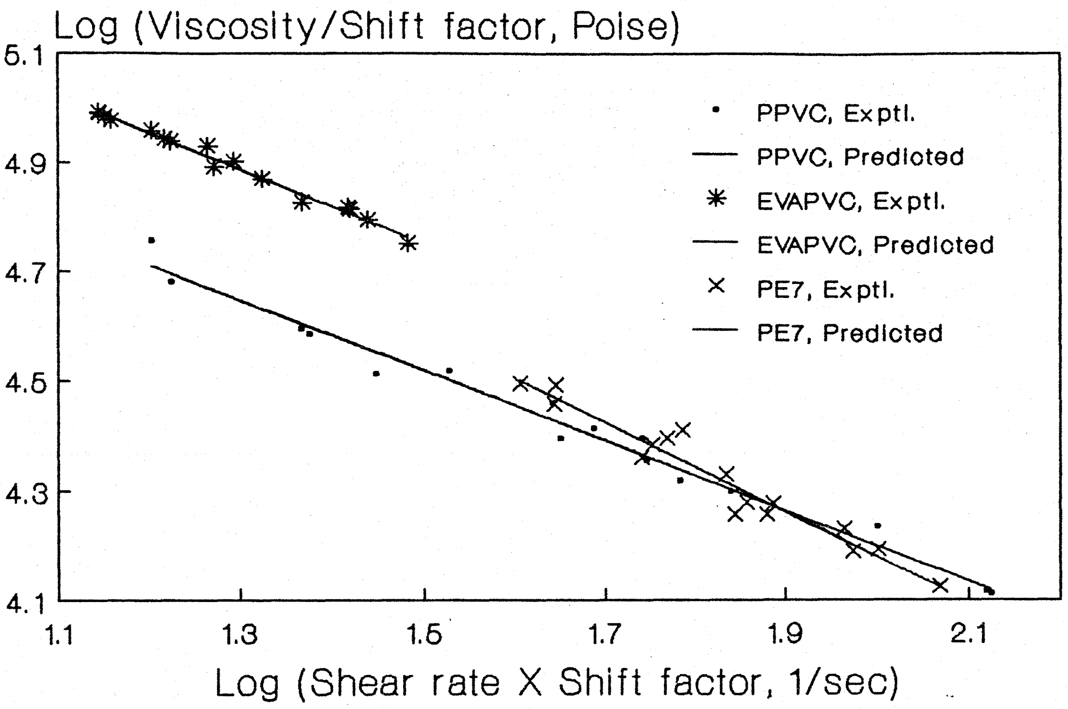


Fig. 4.1.8 Master plots for PPVC, EVAPVC and PE7

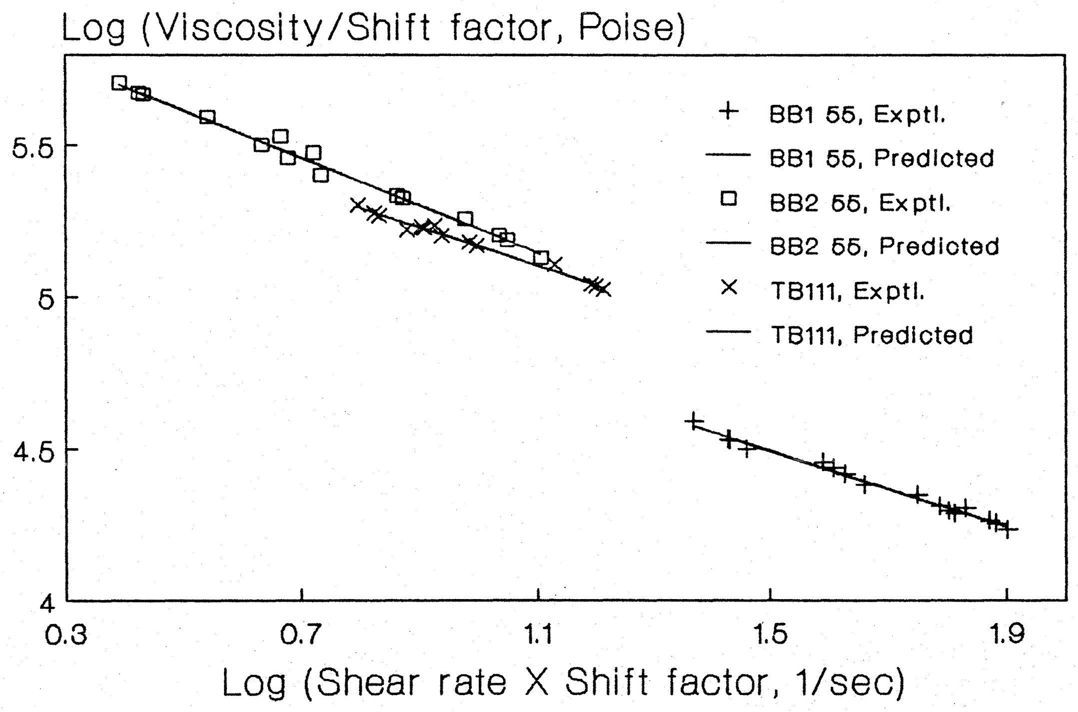


Fig. 4.1.9 Master plots for BB1 55, BB2 55 and TB111

The master plot is helpful thus: with the expression for a_T for a particular sample, at a temperature T from equation (4.7), for any shear rate value, the value of $a_T\dot{\gamma}$ and hence η/a_T and ultimately the value of η can be obtained.

4.1.5 *Composition Dependence of A, B, a and b*

Values of A and B in equation (4.8) indicate that B is a measure of activation energy, at constant τ. A and B are related by $B/A = -T_r$, and thus A is once again indicative of the activation energy.

Values of b (the index in equation 4.10) are the averages of $(n'-1)$ in the range of temperature studied. Values of a in equation (4.10) are indicative of the viscosity levels at the reference temperature for the various samples studied; they are approximately the m values of equation (4.4) at that temperature.

In the PE series replacement of DEHP by polyesters shows a gradual decrease in b or flow behaviour index n'. Most significant is the large decrease from PPVC to PPVC2 (PPVC2 has lesser quantity of DEHP).

In case of PPVC-EVAPVC binary blends, no significant change is observed, whereas in the PPVC-NBR1 binary blends, addition of NBR1 shows a significant decrease in the values of b (or the flow behaviour index).

For ternary blends, the behaviour is reflected as (i) gradual addition of NBR1 to TB111 shows a gradual decreasing trend and (ii) addition of EVAPVC and PPVC to TB111 shows no significant trend for the values of *b*.

Values of *B* (or otherwise the activation energy levels, that are indicative of the temperature dependence of viscosity) are not significantly affected when there is a gradual replacement of DEHP by Plasflex PA but show an increase if the replacement is done by Plasflex PE (Plasflex PE has higher molecular weight than Plasflex PA). Here again PPVC2 shows a high activation energy level.

The binary blends of series BB1 show an intermediate behaviour between PPVC and EVAPVC (with minor deviations), and EVAPVC has a higher *B* value than that of PPVC. Nothing notable can be said about the behaviour of series BB2 blends as there is a sudden increase for one with 10% of NBR1, but is followed by a drop to a very low value for 50% NBR1 blend. As MFI itself could not be determined for NBR1, no cognisance is taken of this behaviour. A better observation is made in case of ternary blends: (i) addition of PPVC to TB111 does not show significant change, (ii) addition of NBR1 to TB111 gradually reduces the value and it is expected that NBR1 has the least dependence on temperature and (iii) addition of EVAPVC has no significant change.

Values of *a*, indicative of the viscosity levels, as mentioned earlier, increase with gradual replacement of DEHP by polyesters. Also there is a significant increase for PPVC2 compared to PPVC.

The dependence on composition of the viscosities of the binary blends is discussed in section 4.1.3.1. The values of BB1 blends are intermediate between the 'pure' components PPVC and EVAPVC, with the latter having a marginally higher value. As expected, increase in the content of NBR1 in the blends (series BB2) shows significant increase in the viscosity and hence the value of *a*. The ternary blends reflect the same trend in that: (i) addition of PPVC to TB111 has a decreasing trend, (ii) addition of NBR1 to TB111 has an increasing trend, and (iii) addition of EVAPVC to TB111 has a decreasing effect on the value of *a* or the viscosity.

4.1.6 *Die Swell*

4.1.6.1 Extrudate Swell Ratio

Extrudate swell ratio (D_R) is indicative of the existence of normal stress in the material during processing and is usually dependent on the shear rate and temperature. These data are therefore analysed with the composite relation

$$D_R = a'\exp\left(\frac{b'}{T}\right)\dot{\gamma}^c \tag{4.11}$$

or

$$\ln D_R = \ln a' + \frac{b'}{T} + c\ln\dot{\gamma} \tag{4.12}$$

The coefficients *a'*, *b'* and *c* are evaluated by fitting the experimental data and the values of *a'* and *b'* are shown in Figs. 4.1.10 to 4.1.13 and Table 4.1.5. The values of *b'* are always negative indicating that the die swell increases with temperature. This anomalous melt elasticity behaviour of PVC based polyblends was also noted by Varughese (1990) for PVC-epoxidized natural rubber system.

To isolate the effect of shear rate, the equation is rewritten as

$$D_R\exp\left(-\frac{b'}{T}\right) = a'\dot{\gamma}^c \tag{4.13}$$

or

$$\ln D_R - \frac{b'}{T} = \ln a' + c\ln\dot{\gamma} \tag{4.14}$$

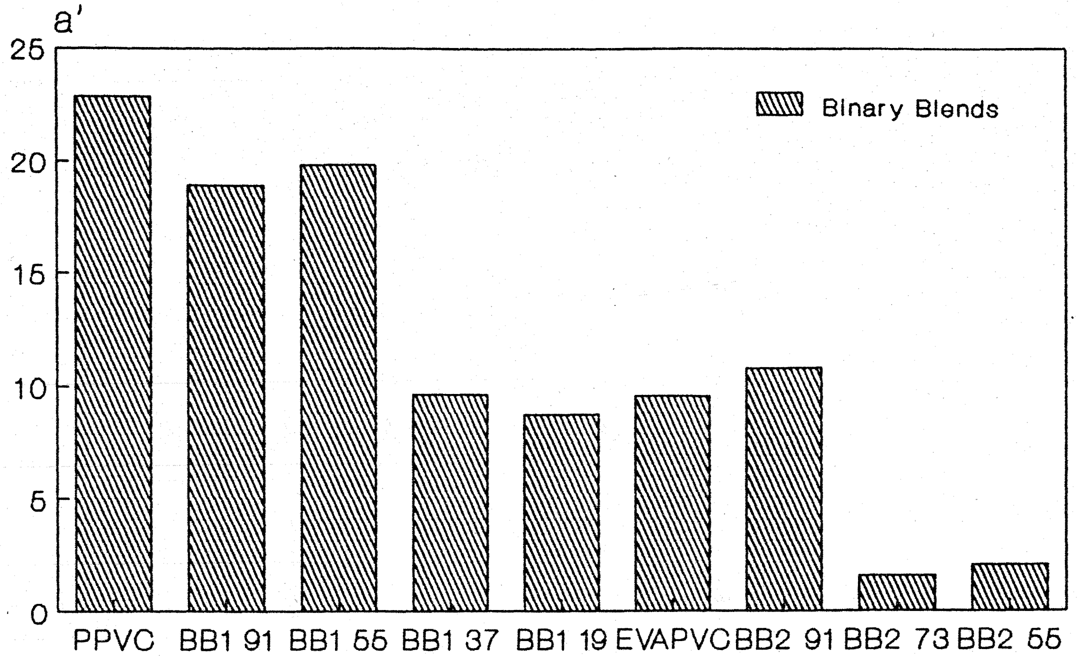


Fig. 4.1.10 Variation of the coefficient a' with blend composition

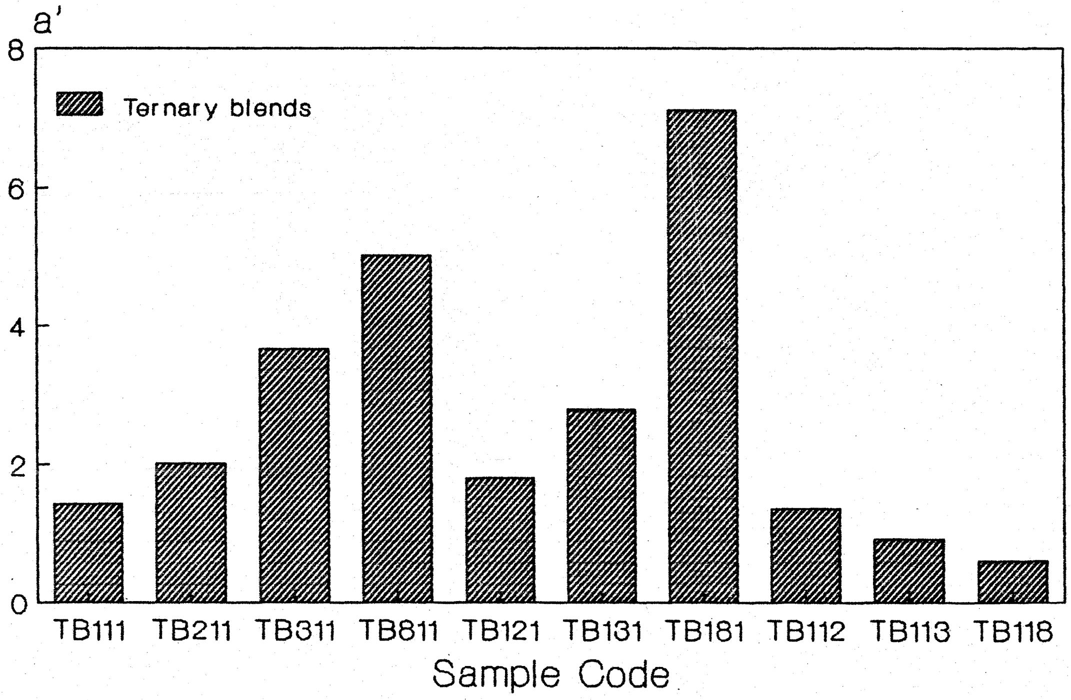


Fig. 4.1.11 Variation of the coefficient a' with blend composition

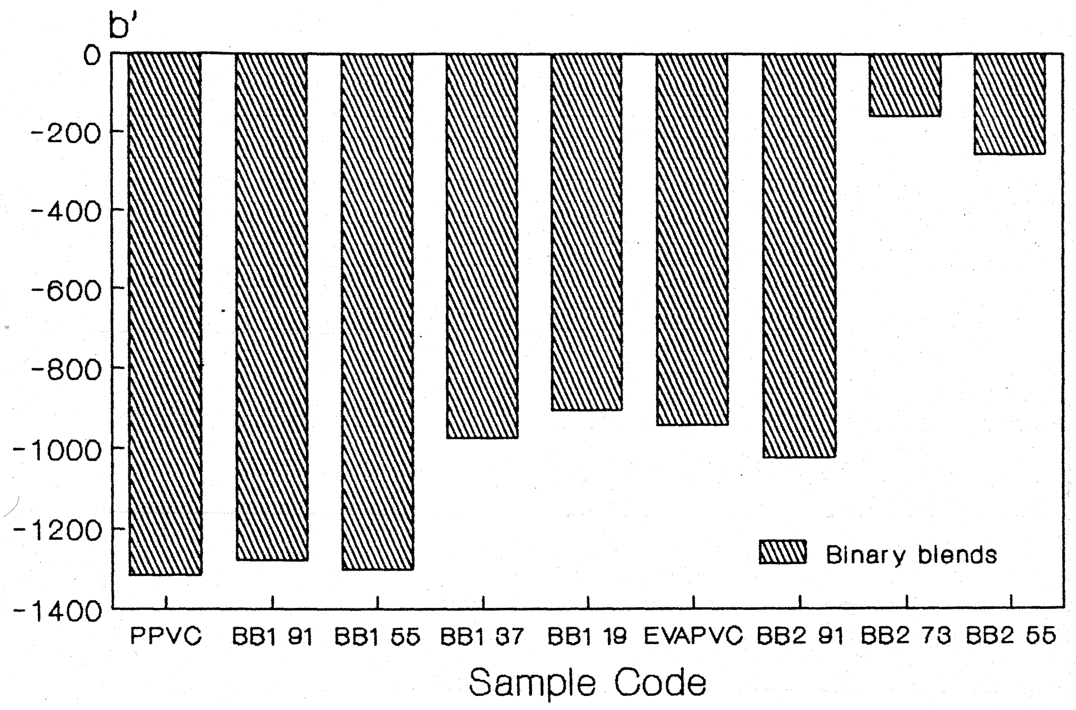


Fig. 4.1.12 Variation in the values of coefficient b' with blend composition

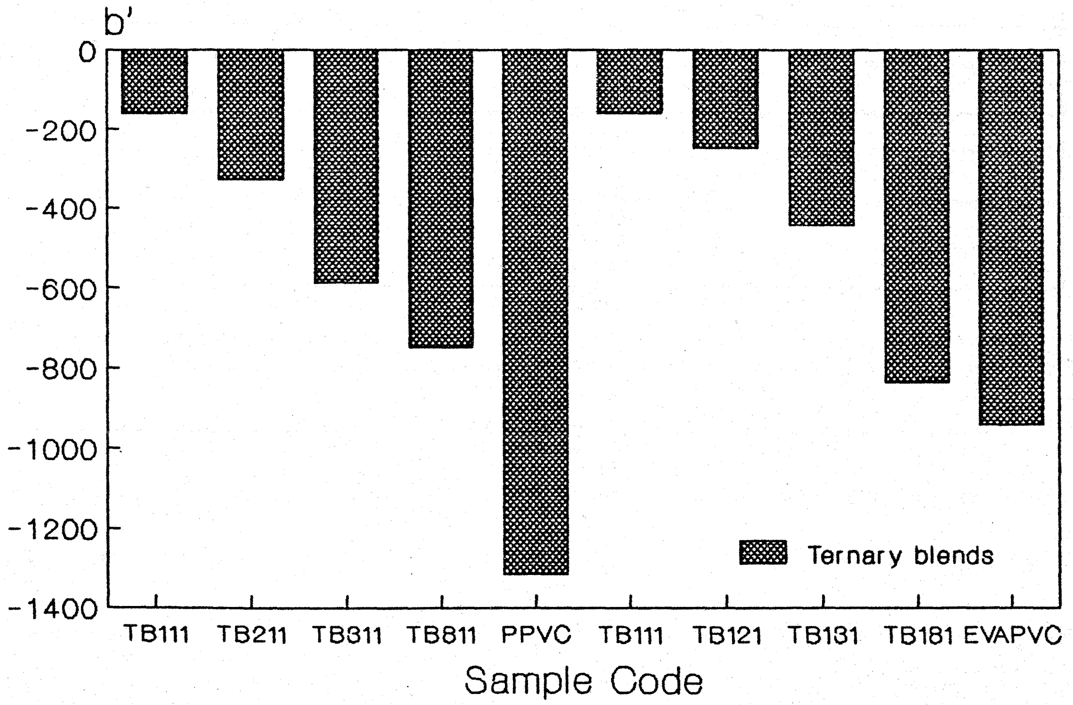


Fig. 4.1.13 Variation in the values of coefficient b' with blend composition

TABLE 4.1.5 Values of the Coefficients *a′* and *b′* for Polyester Blends

	Coefficients	
Sample code	*a′*	*b′*
PPVC	2.29E+01	-1.32E+03
PE1	5.07E+01	-1.67E+03
PE2	3.06E+01	-1.46E+03
PE3	4.15E+01	-1.57E+03
PE7	1.67E+01	-1.23E+03
PE8	2.21E+01	-1.32E+03
PE9	3.55E+01	-1.49E+03

Figs. 4.1.14 and 4.1.15 show the variation of $\ln D_R - b'/T$ vs. $\ln\dot{\gamma}$. The nearly horizontal lines indicate little pronounced effect of shear rate. The values of *c* are small and are less than 0.04 for all samples indicating very little effect of shear rate (for the experimental range).

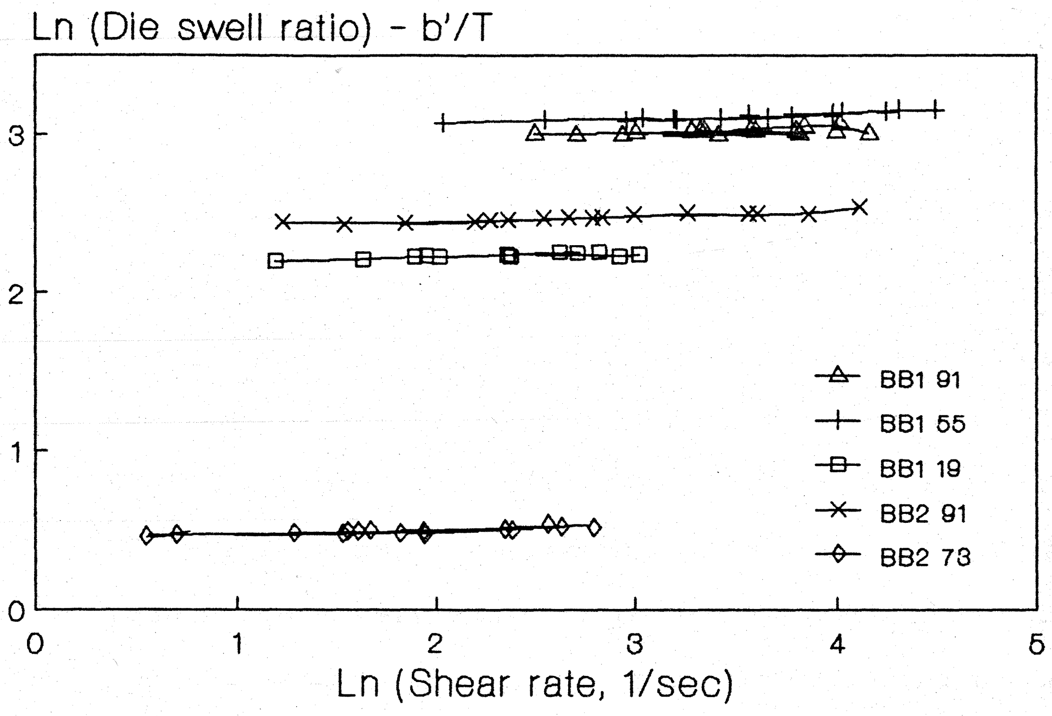


Fig. 4.1.14 Variation of die swell ratio with shear rate for binary blends

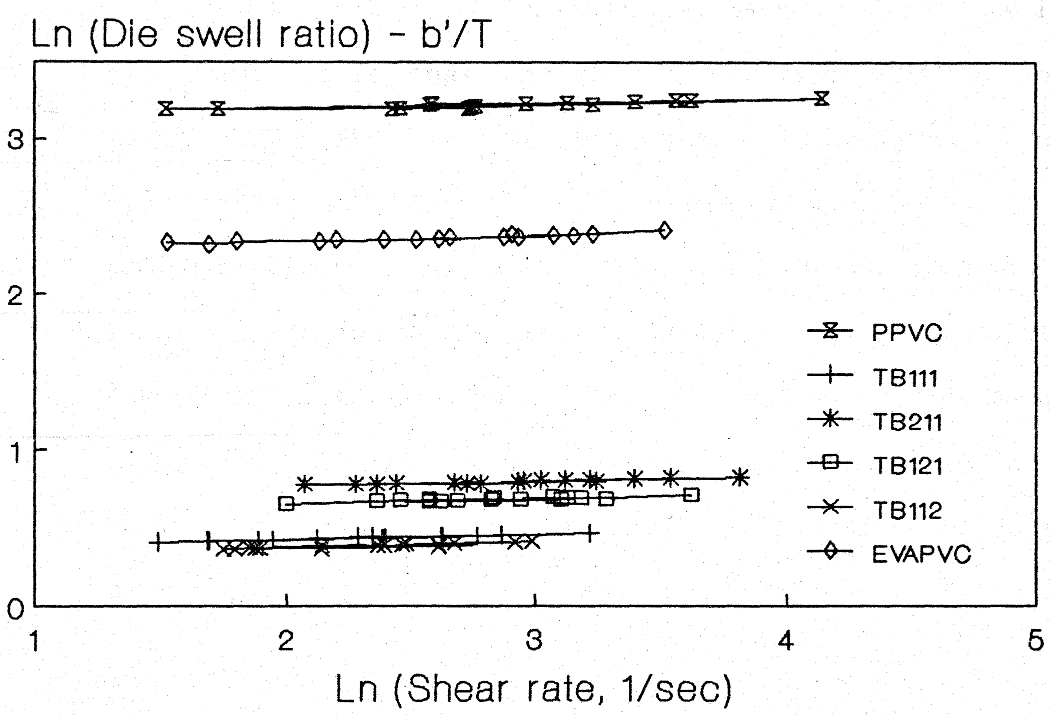


Fig. 4.1.15 Variation of die swell ratio with shear rate for ternary blends, PPVC and EVAPVC

The temperature dependence of the die swell as indicated by the values of *b'* is little affected in the binary blends of polyesters. For the PPVC-EVAPVC blends, the temperature dependence remains the same for upto 50% EVAPVC and decreases on further addition of EVAPVC. For PPVC-NBR1 blends, the temperature dependence is drastically reduced to a very small value for 30% replacement of PPVC. For the ternary blends, this trend is reflected by the fact that addition of EVAPVC to TB111 only gradually increases *b'* values. The later observation is also applicable to the addition of PPVC to TB111.

The values of *a'* indicate the level of die swell. From Fig. 4.1.10, it is observed that addition of EVAPVC and NBR1 reduces the die swell ratio of PPVC. The reduction is more drastic for addition of NBR1. Inter-polymer chain entanglement and reduced al~~l~~ignment are the reasons for such behaviour. In the ternary blends also (Fig. 4.1.11) it is observed that addition of PPVC or EVAPVC to TB111 has the effect of increasing the die swell, while addition of NBR1 results in reduction in die swell. In the PE series, however, no specific trend is observed, as is shown in Table 4.1.5.

4.1.6.2 Principal Normal Stress Difference

The principal or first normal stress difference (equation 3.9) is defined as the difference between the components τ_{11} and τ_{22} of the stress tensor. For the rheological flow properties of a melt in a simple shear flow to be described completely, it is necessary to determine the functions-the shear stress τ_{12} and the first normal stress difference ($\tau_{11}-\tau_{22}$) as functions of the shear rate $\dot{\gamma}$. While dependence of the shear stress τ_{12} has been dealt with in detail in section 4.1.3.2, this section deals with $\tau_{11}-\tau_{22}$.

Normally, in the region of low shear rates, τ_{12} is proportional to $\dot{\gamma}$ and $\tau_{11}-\tau_{22}$ to $\dot{\gamma}^2$. As shear rate increases, both these stresses increase, but, the rate of growth of normal stress difference is faster and so the $\tau_{11}-\tau_{22}$ becomes greater than τ_{12} , the relation between the two being dependent on the non-Newtonian behaviour of the fluid. Variation of $\tau_{11}-\tau_{22}$ with τ_{12} are given in Figs. 4.1.16 to 4.1.18 showing clearly that the former is larger than the latter in the range of shear rates involved in the experiment.

There is an invariable increase of $\tau_{11}-\tau_{22}$ with increase in temperature for all the samples. A representative result for a binary blend BB1 55 is shown in Fig. 4.1.18. The effect of composition on $\tau_{11}-\tau_{22}$ is analysed in the next section along with the recoverable strain.

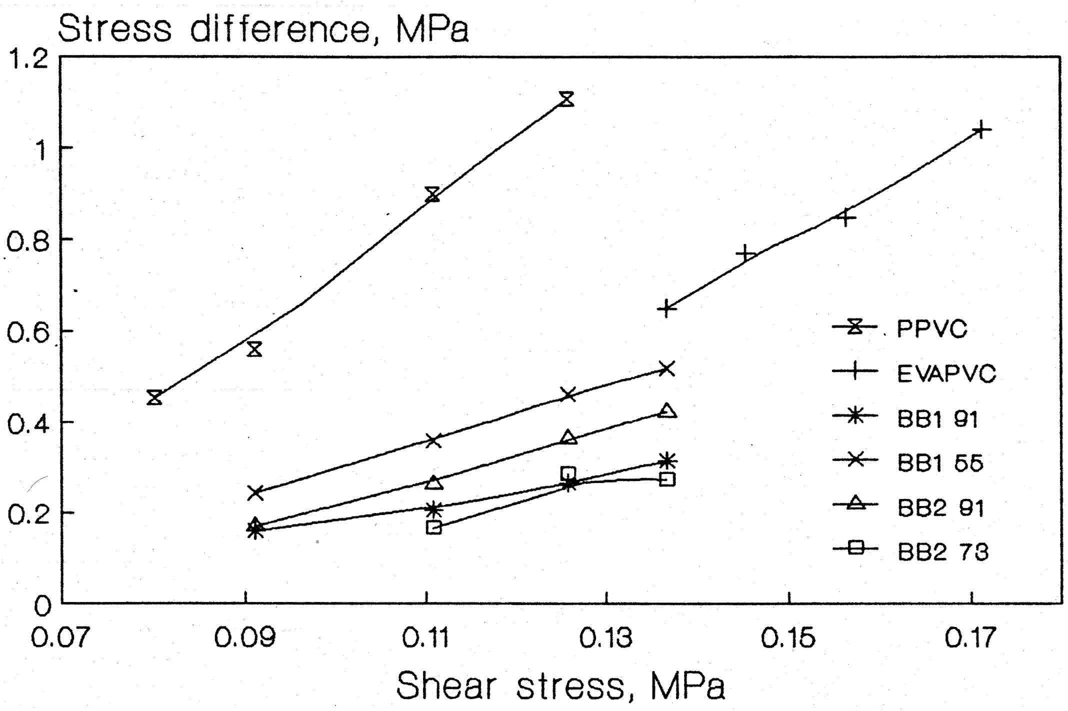


Fig. 4.1.16 Principal normal stress difference as a function of shear stress at 170°C

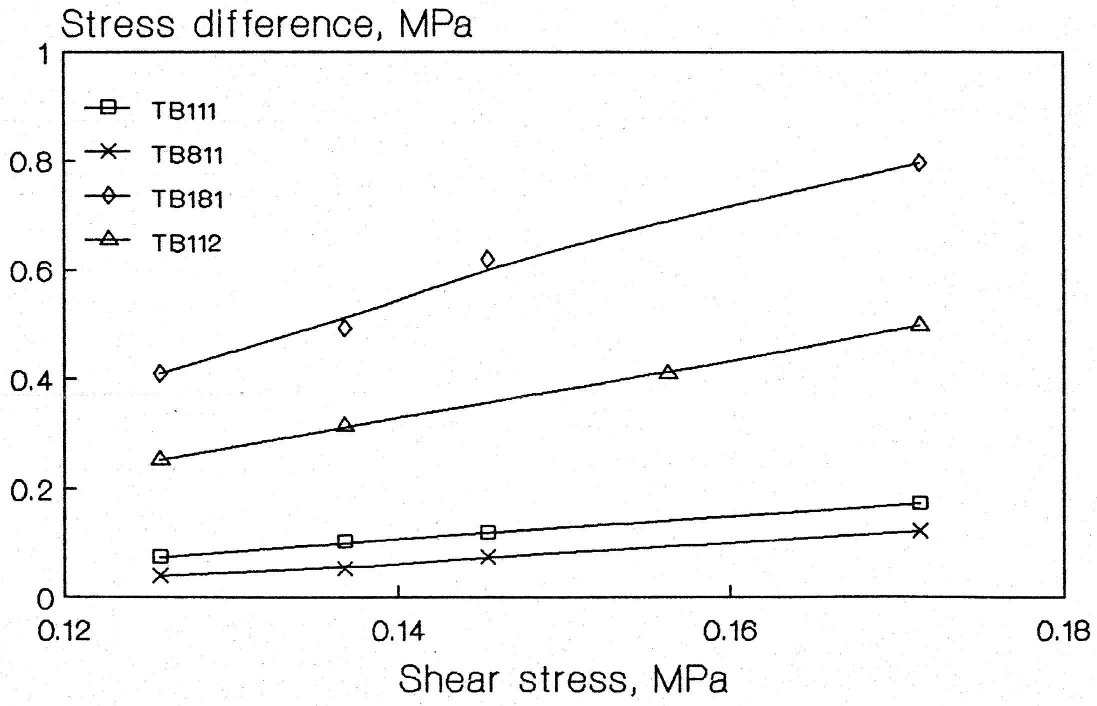


Fig. 4.1.17 Principal normal stress difference as a function of shear stress at 170°C for ternary blends

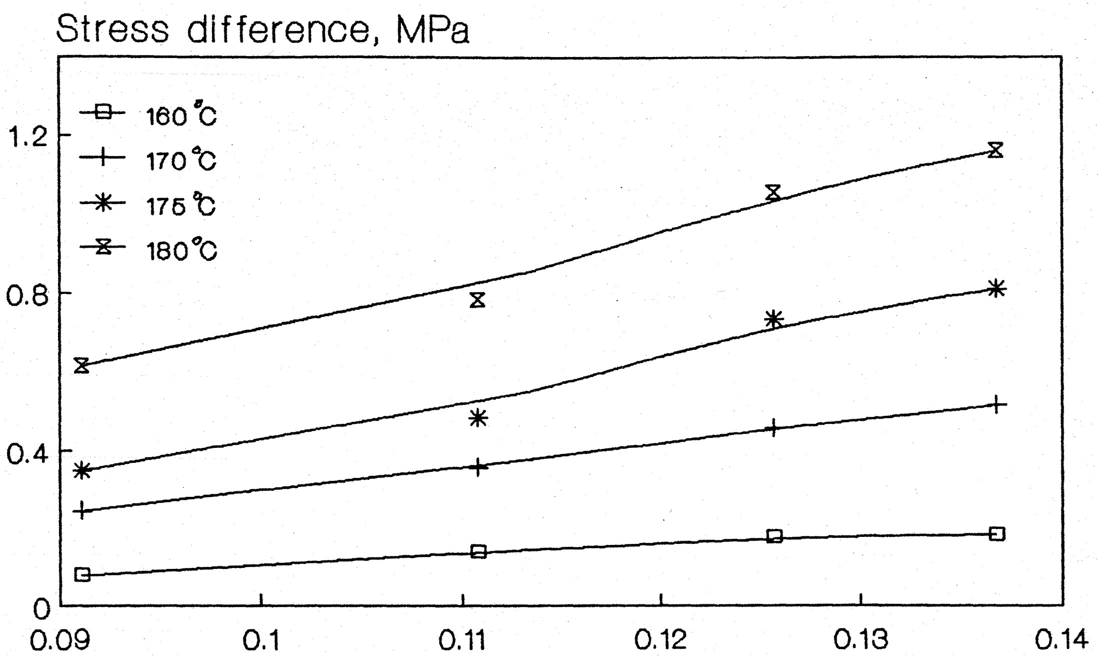


Fig. 4.1.18 Principal normal stress difference as a function of shear stress for the sample BB1 55

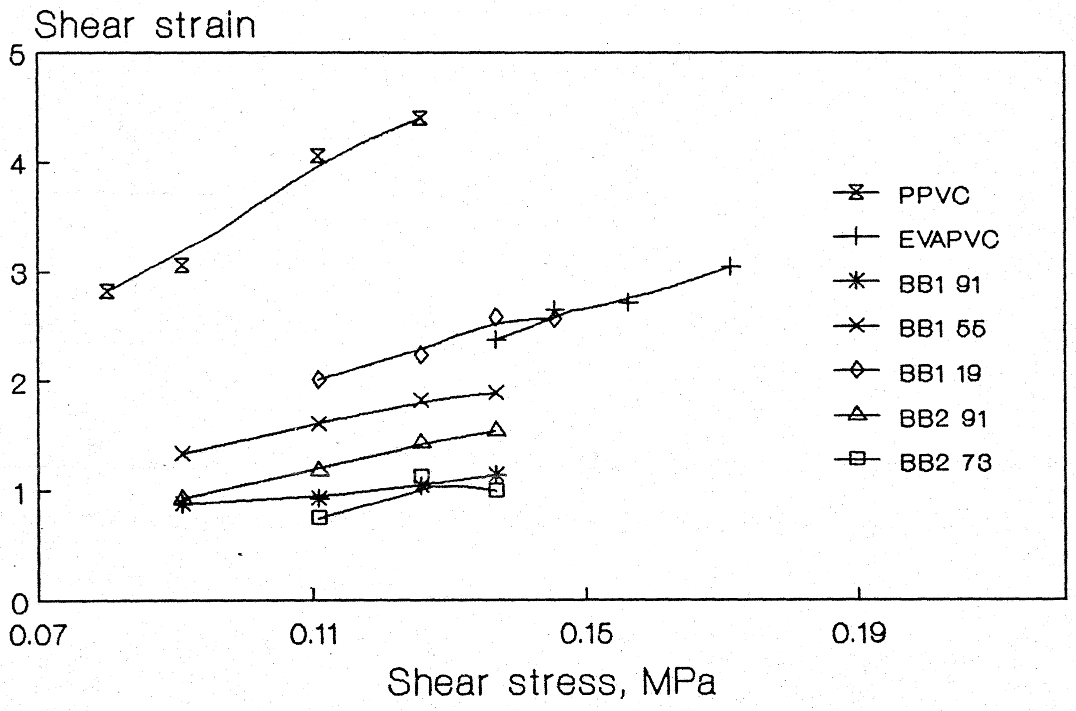


Fig. 4.1.19 Recoverable shear strain as a function of shear stress at 170°C

4.1.6.3 Recoverable Elastic Shear Strain

The ability to develop recoverable deformation (strain) is not only an important feature of the mechanical properties of the polymeric materials, but also typical of polymers in fluid state. For polymer melts in flow, the total strain is composed of the irrecoverable one of viscous flow and the rubber-like strain (deformation) which recovers after the cessation of the flow. Under steady state flow, for each shear rate and stress, there corresponds a definite quasi-equilibrium rubbery deformation which is retained in the system for any straining period. After the stress is removed, when the polymer extrudate emerges from the nozzle, it gives rise to die swell, due to the release of the elastic energy stored during flow.

The values of recoverable deformation or strain (S_R) for the representative compositions and temperature are shown in Figs 4.1.19 to 4.1.21. as function of shear stress.

While EVAPVC shows less $\tau_{11}-\tau_{22}$ and S_R values compared to PPVC, the binary blends of these two show a mixed but similar trend. There is a sudden decrease on addition of EVAPVC to PPVC (a minimum value is observed for BB1 91). A gradual increase in the values are observed upto 90% replacement of PPVC (BB1 19) and the value for BB1 19 is nearly that of 'pure' EVAPVC. (Fig. 4.1.19)

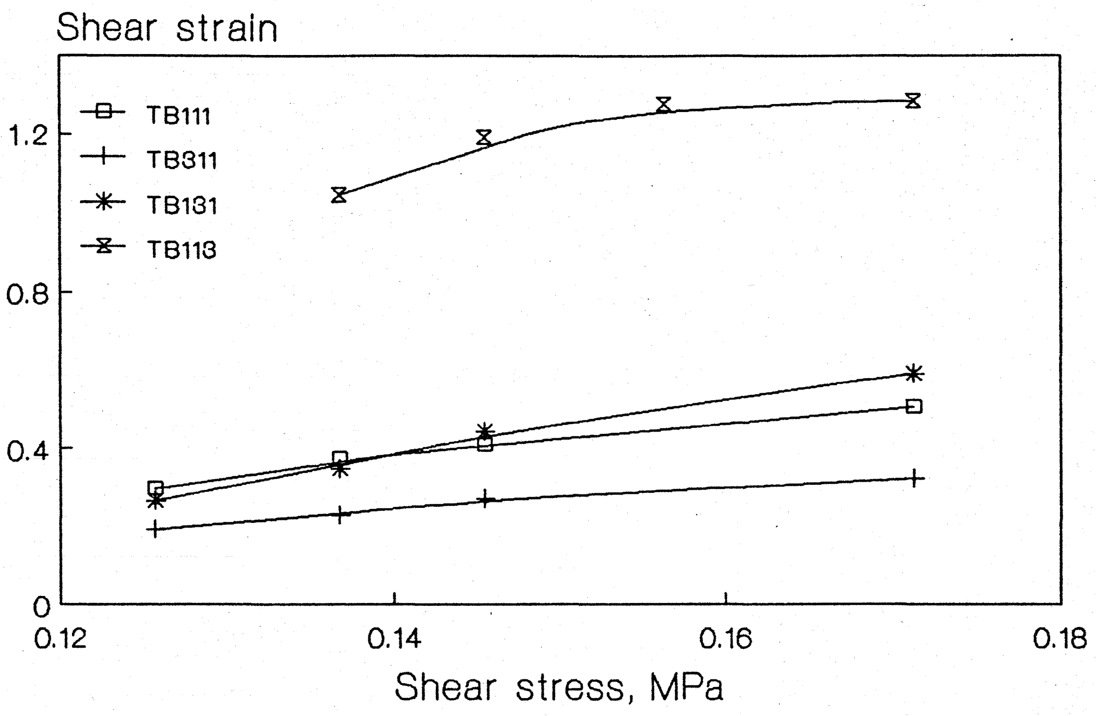


Fig. 4.1.20 Recoverable shear strain as a function of shear stress at 170°C

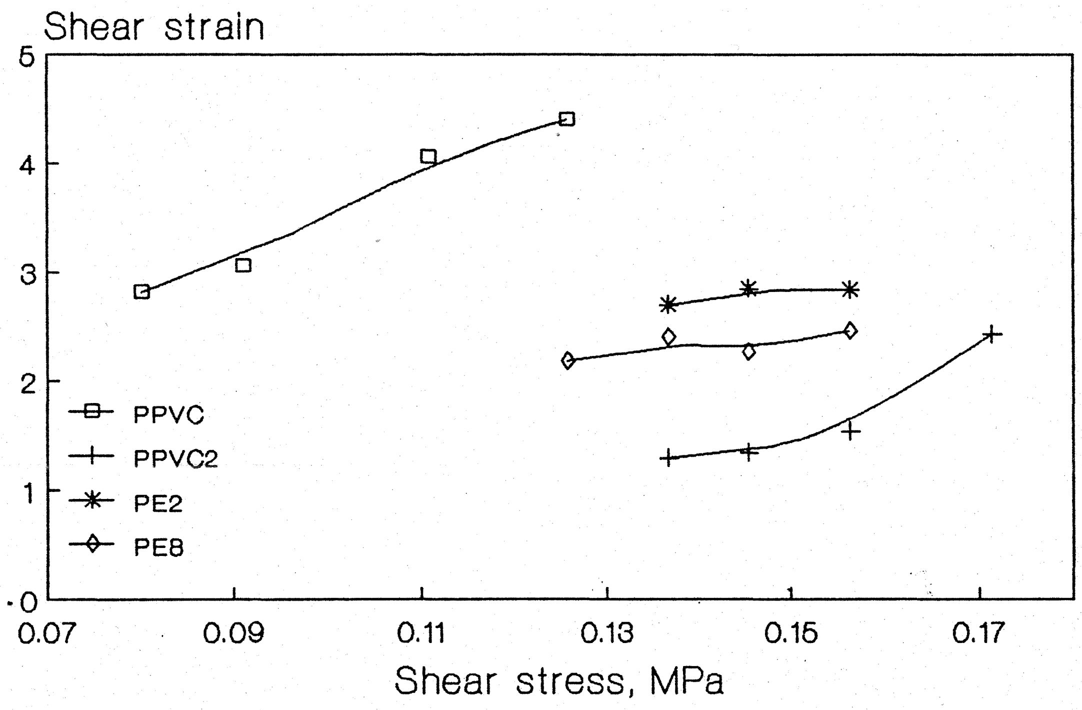


Fig. 4.1.21 Recoverable shear strain as a function of shear stress at 170°C

With respect to the second binary blend system, addition of NBR1 invariably reduces the value of both $\tau_{11}-\tau_{22}$ and S_R, as shown in Figs. 4.1.16 and 4.1.19. Regarding the PE series formulations, there is a reduction in both the values for increasing amount of Plasflex PA and PE and S_R values are shown in Fig. 4.1.21. PPVC2 has also S_R values less than those of PPVC (Fig. 4.1.21)

S_R values of representative samples of ternary blends are shown in Fig. 4.1.20. From Figs 4.1.17 and 4.1.20 it is seen that the ternary blends follow the trends: addition of EVAPVC and NBR1 to TB111 increases $\tau_{11}-\tau_{22}$ and S_R whereas addition of PPVC reduces these values.

Thus the trends in both the properties are similar with respect to composition. Temperature dependence of S_R, is also similar to that of $\tau_{11}-\tau_{22}$ indicated in the previous section i.e., an increase with increase in temperature.

4.1.6.4 Shear Modulus

The amount of elastic recovery discussed above is characterized by the modulus of elastic recovery (*G*) defined in section 3.4.3. Figs. 4.1.22 to 4.1.24 give the values of *G* as a function of shear stress for representative samples. There appears to be negligible dependence on shear stress. It is observed that increase in temperature has a decreasing effect on the values of *G* for all the samples and the plots for a representative sample TB111 are shown in Fig. 4.1.24. *G* value of PPVC is less than that of EVAPVC (Fig. 4.1.22) The binary blend system PPVC-EVAPVC show a trend in reverse to that of the $\tau_{11}-\tau_{22}$ and S_R in that there is a sudden increase on addition of EVAPVC (a maximum value is shown for BB1 91). Further increase in EVAPVC content decreases the *G* value upto BB1 19, whose value is nearly that of 'pure' EVAPVC (Fig. 4.1.22). Addition of NBR1 to PPVC invariably increases the value of *G*.

Like the binary blends, the trends for *G* in case of ternary blends are in reverse to the trends observed for $\tau_{11}-\tau_{22}$ and S_R.

It is therefore concluded that PPVC has the least value of *G* due to large values of recoverable strain and die swell.

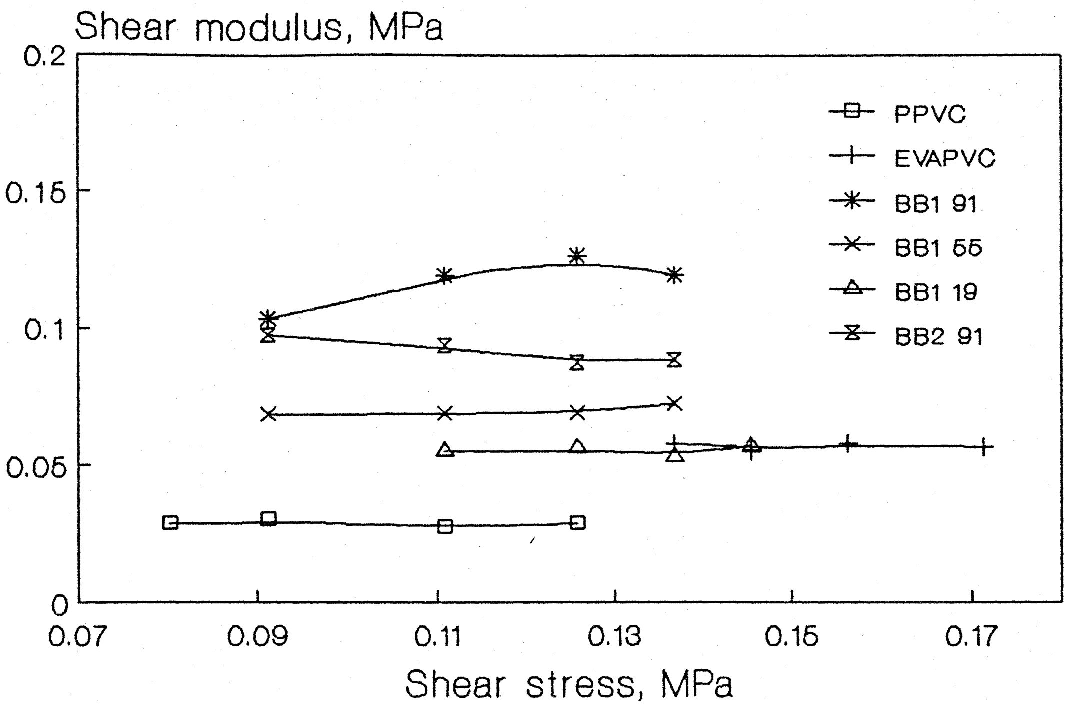


Fig. 4.1.22 Elastic shear modulus as a function of shear stress at 170°C

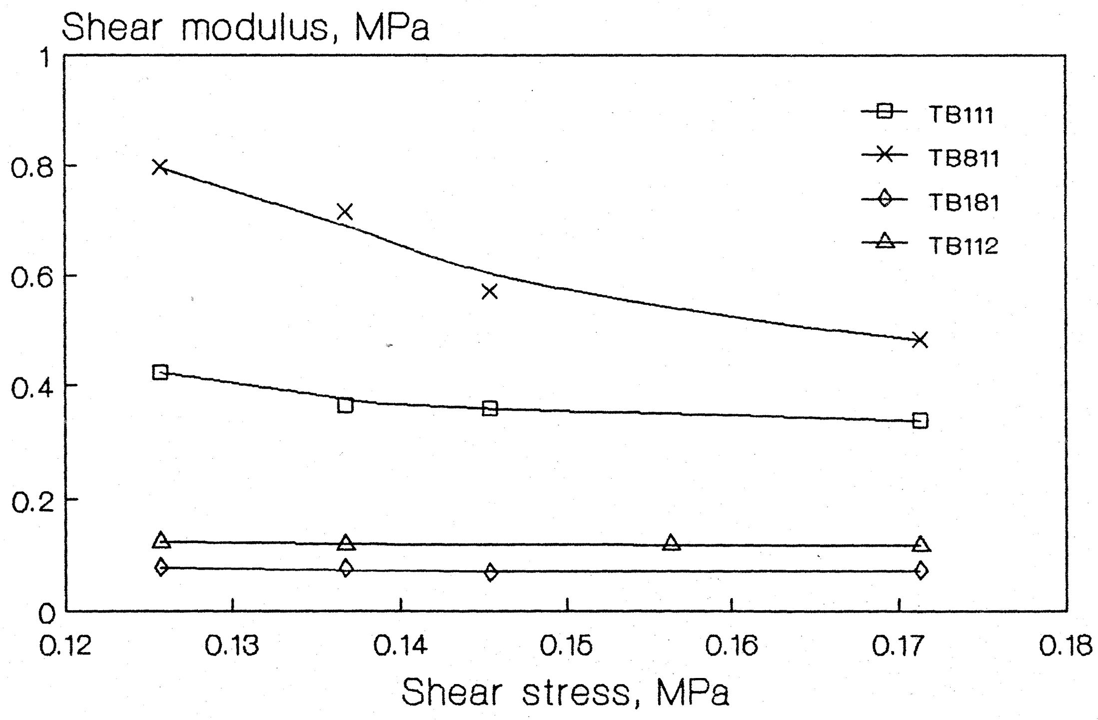


Fig. 4.1.23 Elastic shear modulus as a function of shear stress at 170°C

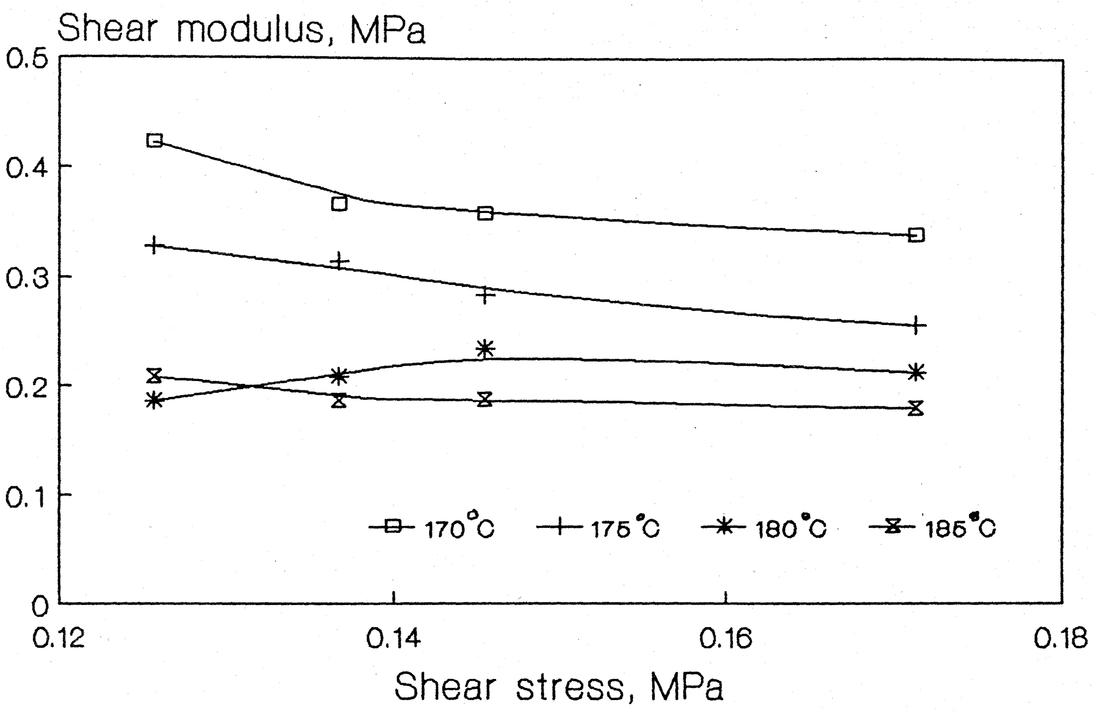


Fig. 4.1.24 Elastic shear modulus as a function of shear stress for TB111

4.1.7 *Torque Data from Plasticorder*

Brabender Plasticorder has been extensively used to study rheological characteristics of thermoplastics. Goodrich et al. (1967), Blyer et al. (1967) and Lee et al. (1969), among others, reported the use of Plasticorder in the sixties. The importance of tests carried out with this instrument lies in the fact that test conditions are close to the actual processing conditions and the data can more reliably be translated for actual practice.

The effects of various rotor speeds and the mixer temperatures on the equilibrium torque are given in Table 4.1.6. The torque recorded in all cases are quite low and processing problems are not anticipated in any of the polyblends. As is expected, rise in test temperature results in reduction in equilibrium torque for all samples. Polyester blends have generally equilibrium torque similar and marginally lower than that of PPVC. This is because, the liquid polyesters used plasticize PVC further. Difference in the molecular weight of the polyesters used in the study is not significant enough to give significant difference in torque values.

TABLE 4.1.6 Effect of Rotor Speed and Temperature on Equilibrium Torque

Sample Codes	Equilibrium Torque, m.gm								
	Temperature and Rotor Speed								
	33 rpm			50 rpm			66 rpm		
	A*	B*	C*	A	B	C	A	B	C
PPVC	540	440	340	530	485	400	510	440	380
PE4	350	330	300	360	330	295	410	350	300
PE5	440	340	300	490	330	280	380	300	210
PE6	545	440	355	480	450	370	480	420	330
PE8	450	390	310	490	400	300			
PE9	390	360	300	490	360	310			
Test1#	620	560	480	680	500	430	620	540	460
Test2#	760	640	470	640	620	440	720	600	500

* A: 150°C, B: 160°C, and C: 180°C

\# *PPVC formulation with only change being : Test1 has 50 parts of DEHP and additional 10 parts of Chemigum P-83 (NBR1) and Test2 has 40 parts of DEHP and additional 30 parts of NBR1.*

However, blends containing NBR1 (Test1 and Test2) show higher equilibrium torque. Being an elastomer with much higher molecular weight than the polyesters, blends containing NBR1 exhibit higher torque. Similar behaviour is also noted in MFI studies for polyblends containing polyester and NBR1 (Section 4.1.2).

4.1.8 *Processing Studies*

Any polyblend developed has to be processed by conventional processing technique for its end application. It is therefore important to study the behaviour of the material(s) under actual processing conditions. Extrusiometer has been widely used to study the rheological behaviour of polymer melts, by developing a shear stress-shear rate data from experimental torque-screw speed data. The developed data had been found to be consistent with those found in capillary rheometer (Rojers, 1970).

In experimental studies, data are obtained for the pure components mainly with the intention of finding out whether modifications in the processing equipments, if any, are necessary for processing the components and the resulting blends. Results of the extrusiometer experiments carried out for three 'pure' components PPVC, EVAPVC and NBR1 are shown in Figs. 4.1.25 and 4.1.26. Log-log plots of pressure vs. output give straight lines and these also indirectly indicate the shear stress-shear rate relations. Pressure generated in the die head for a specific rate of output is in the order PPVC<EVAPVC<NBR1. This was expected from the results of MFI and Plasticorder studies.

Expectedly, exactly similar is the trend for equilibrium torque with respect to variation in screw speed (Fig. 4.1.25).

The straight line plots for PPVC, EVAPVC and NBR1 have slopes of 0.374, 0.369 and 0.143 respectively. It is interesting to note that the slope for PPVC is very similar to the power law exponent (flow behaviour index, *n'*) which has a value of 0.368 (Table 4.1.4). Unfortunately, *n'* could not be obtained from MFI experiments for NBR1 for reasons explained earlier (Section 4.1.2) and data for EVAPVC is not available at 150°C, the temperature at which the experiment was conducted for extrusiometer. From the MFI and the extrusiometer data for 'pure' components, it can be expected that binary blends containing NBR1 would require higher energy for processing compared to PPVC. However, the torque for NBR1, though higher than PPVC, is still not so high as to pose a problem for processing and no modification is required for processing these blends in conventional processing equipments .

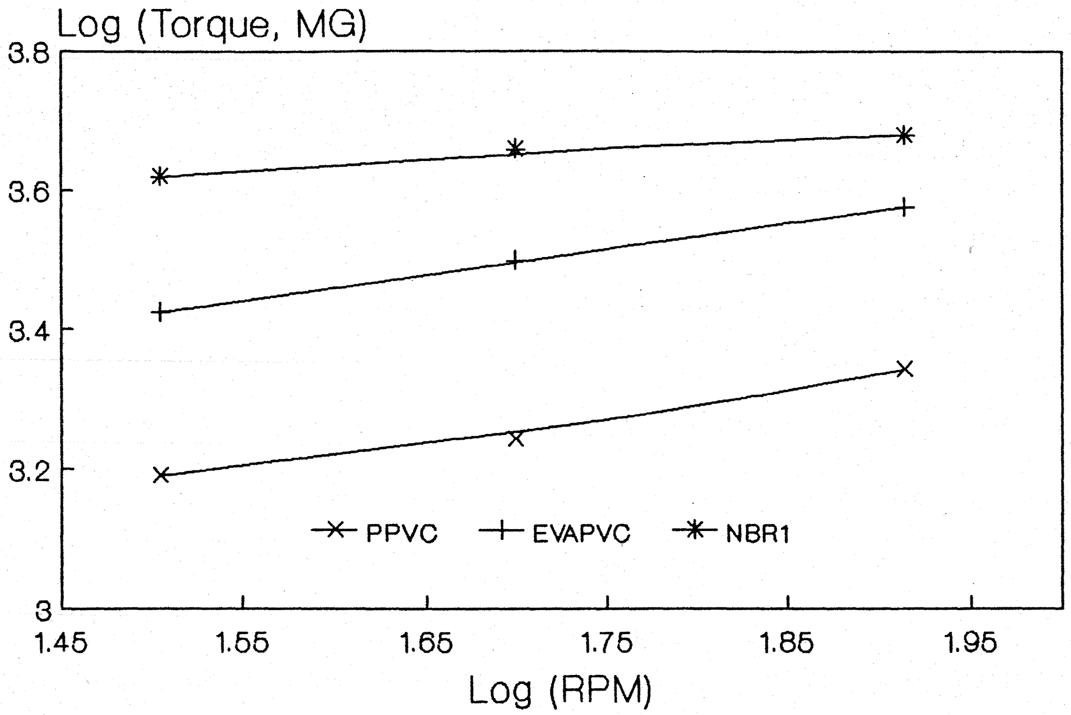


Fig. 4.1.25 Torque vs. screw speed plots for a single screw extruder

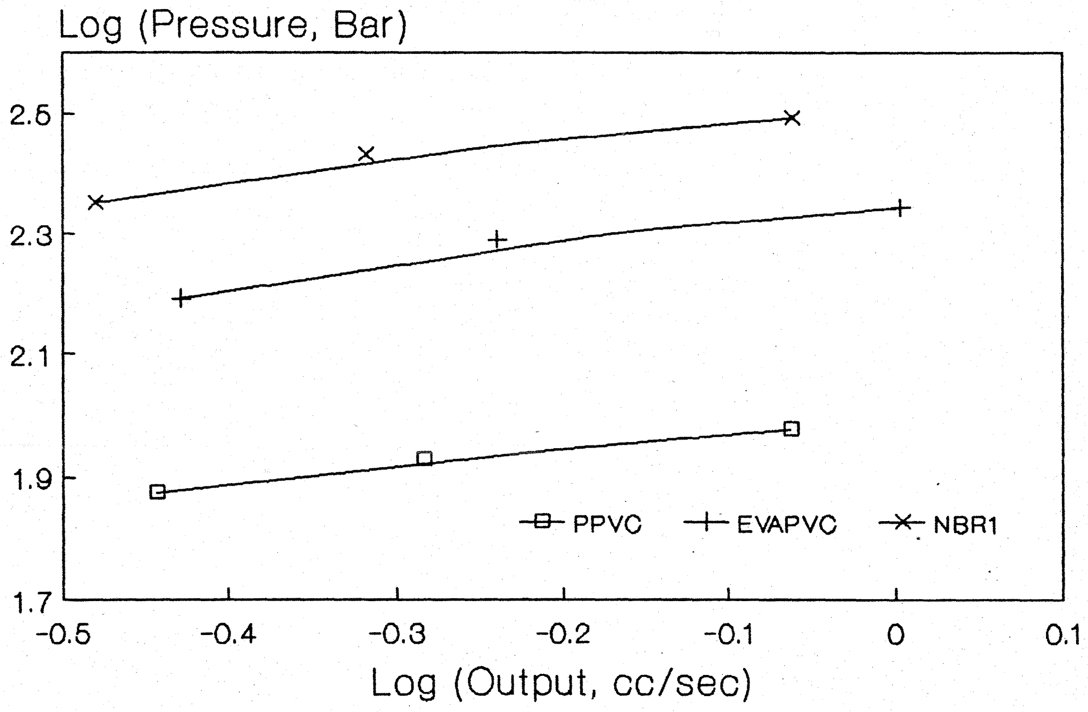


Fig. 4.1.26 Pressure vs. output plots for a single screw extruder

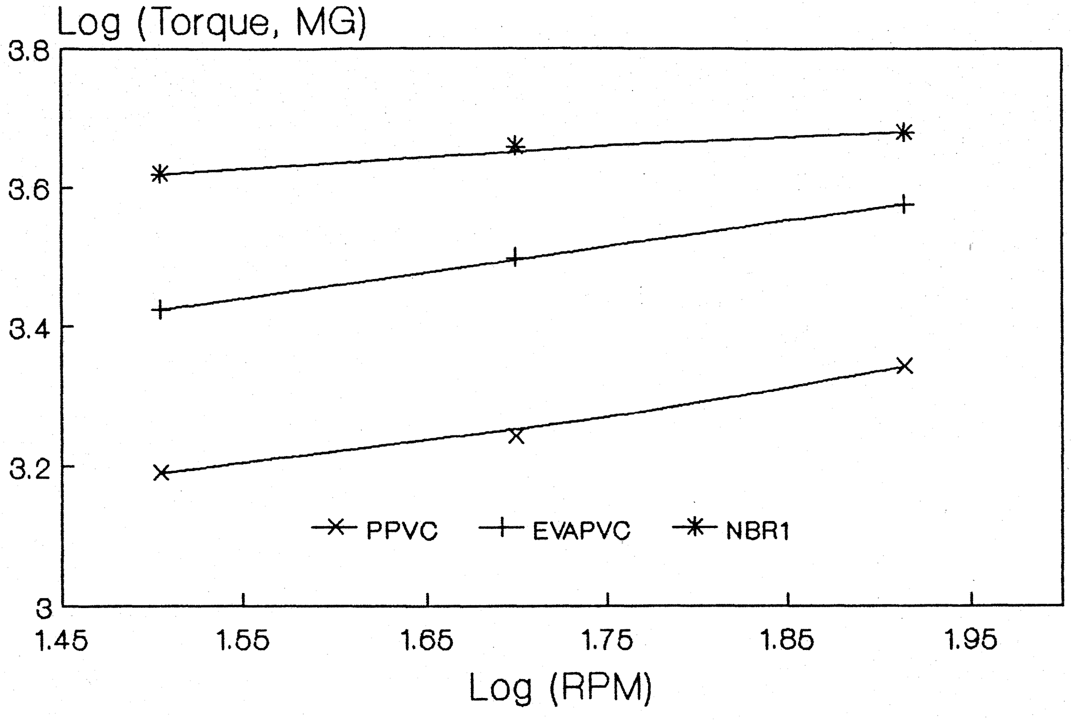


Fig. 4.1.25 Torque vs. screw speed plots for a single screw extruder

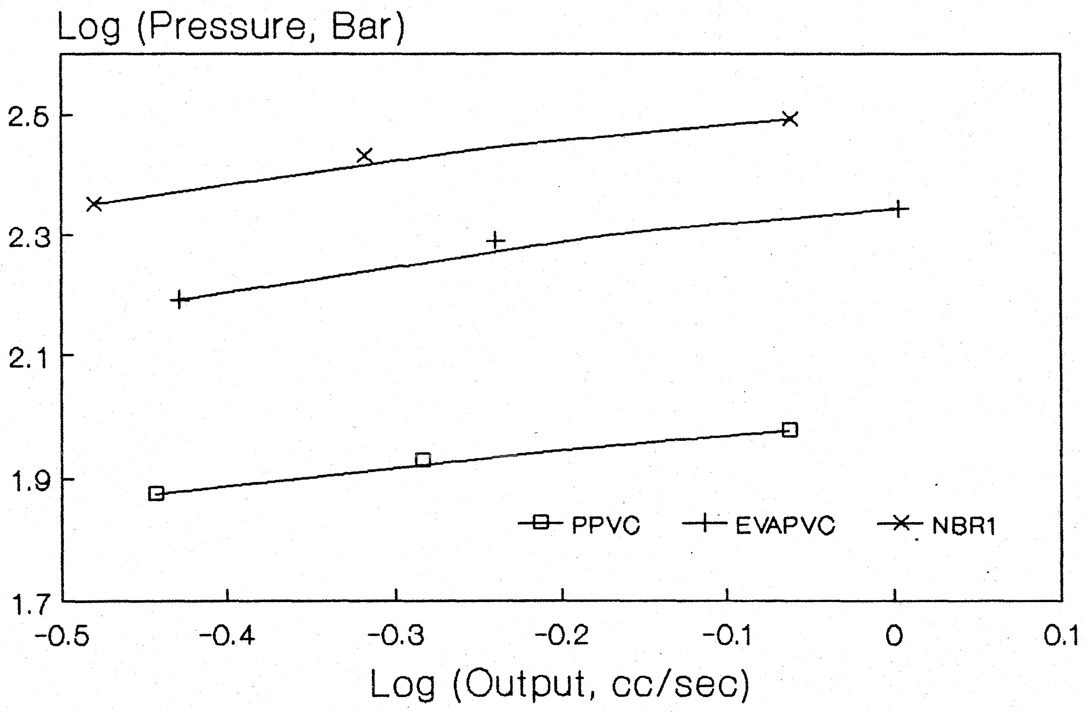


Fig. 4.1.26 Pressure vs. output plots for a single screw extruder

Visual examination indicates smooth surface for PPVC and EVAPVC extrudates. Pure NBR1 however, produces some amount of surface roughness. PPVC-NBR1 blends containing around 30% or less of NBR1 are unlikely to give rough surface. Examination of the extrudates of MFI experiment also indicates that higher temperature and formulations having 50% or higher NBR1 lead to rough surfaces. Rough surfaces of finished products are not acceptable for cosmetic and technical reasons. 50% replacement of PPVC by NBR1 is not intended and this problem should not occur. However, according to the report of Schwarz and Bley (1988), partial replacement of linear NBR with a crosslinked NBR should eliminate this problem, if at all present.

MECHANICAL PROPERTIES

SECTION - 2

4.2 MECHANICAL PROPERTIES

The response of a material to applied stress is reflected in mechanical properties. In majority of the medical applications, mechanical properties are of great importance and are considered while selecting a material for a specific application. Therefore, characterizing the mechanical properties of polyblends, intended for medical applications, becomes a must.

In this section, mechanical properties of PVC based polyblends are discussed in terms of stress-strain behaviour, ultimate elongation and tensile stress, modulus, tensile energy to break and hardness. Models have been proposed for ultimate elongation and tensile stress, tensile energy to break and modulus.

4.2.1 Stress-Strain Behaviour

Stress-strain plots of PPVC, NBR1 and EVAPVC are shown in Figs. 4.2.1 and 4.2.2. It is evident that the three materials behave quite differently when a stress is applied. PPVC has the characteristics of a relatively high modulus plastic and hence for a specific deformation PPVC needs much larger stress than NBR1. EVAPVC shows intermediate behaviour. NBR1 is characterized by low modulus rubbery nature and EVAPVC has high modulus with tendency to yield.

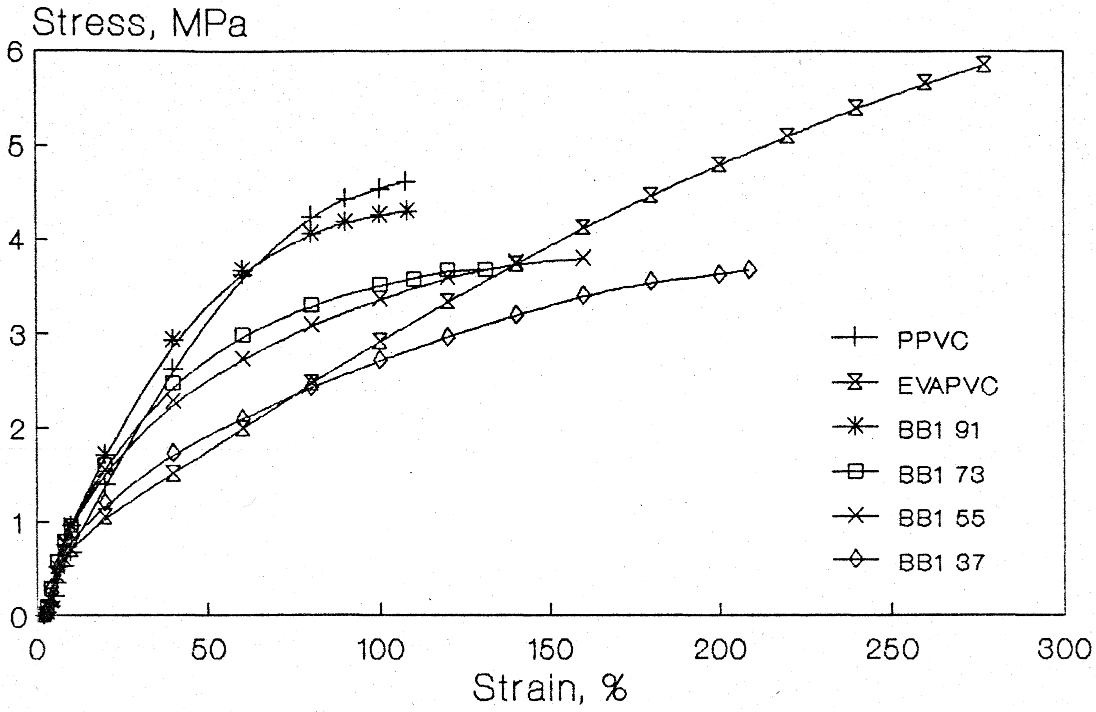


Fig. 4.2.1 Stress-Strain plots for binary blends of PPVC and EVAPVC

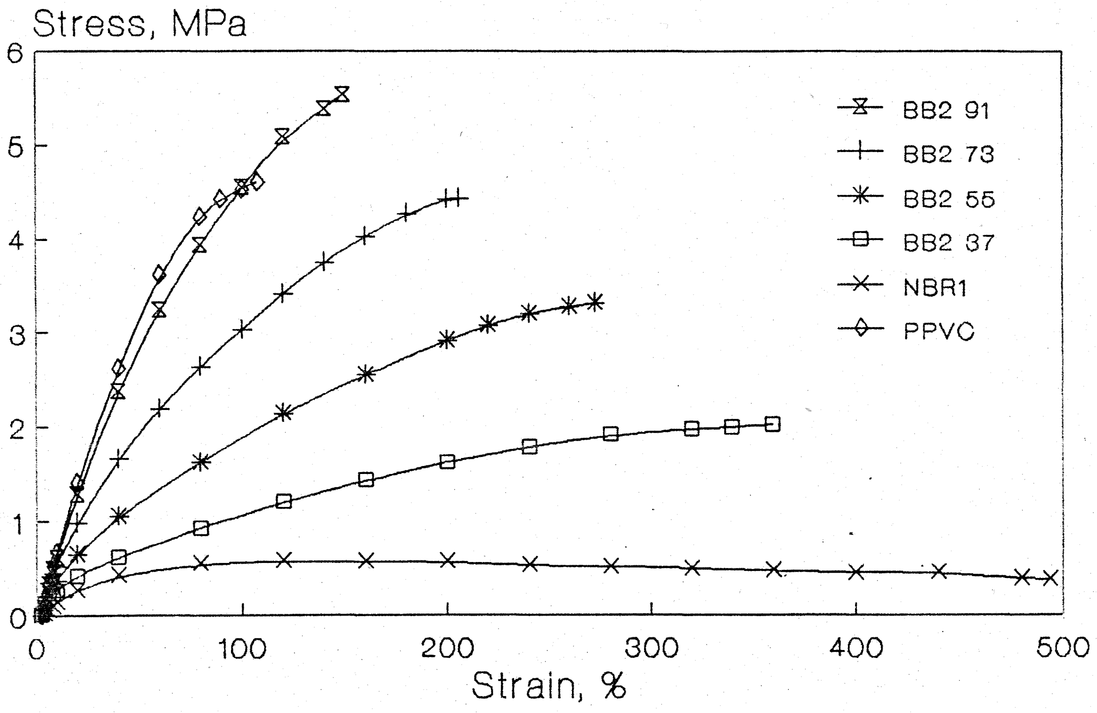


Fig. 4.2.2 Stress-Strain plots for binary blends of PPVC and NBR1

There are distinct differences in the nature of the plots. PPVC exhibits linearity and stiff rise for the major portion of the plot and after the yield point a small region of plastic flow occurs before failure. EVAPVC has very small region of stiff linear plot like PPVC and then large portion of plastic flow before deformation. NBR1 deforms very easily with much lesser stress and at failure, stress is lesser than the maximum stress. Ultimate deformation is much higher for NBR1 than PPVC and EVAPVC has intermediate value.

The behaviour of binary blends of PPVC and EVAPVC is given in Fig. 4.2.1. Initial portions of the plots are similar for all the blends. It is interesting to note that BB1 91 has almost similar characteristics as that of PPVC with marginally stiffer slope of the plot in the initial region. BB1 73, BB1 55 and BB1 37 show lower ultimate stress values than both PPVC and EVAPVC. Ultimate strain, for these binary blends are higher than PPVC and lower than EVAPVC. As expected, stress required for a specific deformation becomes progressively lower with increase in the content of EVAPVC. The other interesting point to note is that though all the binary blends have stiffer rise in stress for a specific strain in the initial stage compared to EVAPVC, but before the failure, all the blends can be deformed more easily than EVAPVC itself. This is probably because the polyblends are not completely miscible and limited compatibility is achieved due to interactions like hydrogen bonding. Compatibility is best for BB1 91. FTIR studies (Section 4.4.2.3) also confirm this. In the initial stages the blends show stiffer rise in stress due to the inter polymer interactions. However, once the applied stress overcomes these resistances it becomes like an inhomogeneous blend and deformation becomes easier.

Close look at Fig. 4.2.2 indicates that BB2 91 has similarity with BB1 91 (Fig. 4.2.1) in terms of the slope of the plot, though BB2 91 has higher ultimate elongation and stress. As expected, BB2 73, BB2 55 and BB2 37 have behaviour intermediate between PPVC and NBR1. From this observation it would appear that interaction between PPVC and NBR/EVAPVC is of synergistic nature when PPVC is replaced with 10% of NBR or EVAPVC.

Fig. 4.2.3 depicts the stress-strain plots for ternary blends. Generally, the blends have intermediate characteristics and as the content of third component increases from TB111, the properties approach to that of the 'pure' component. This is because in TB111 all three components are present in equal proportions and probably this is the most inhomogeneous blend. The component that is present in larger quantity forms the matrix phase and the property of the matrix is reflected with increase in the content of any particular component.

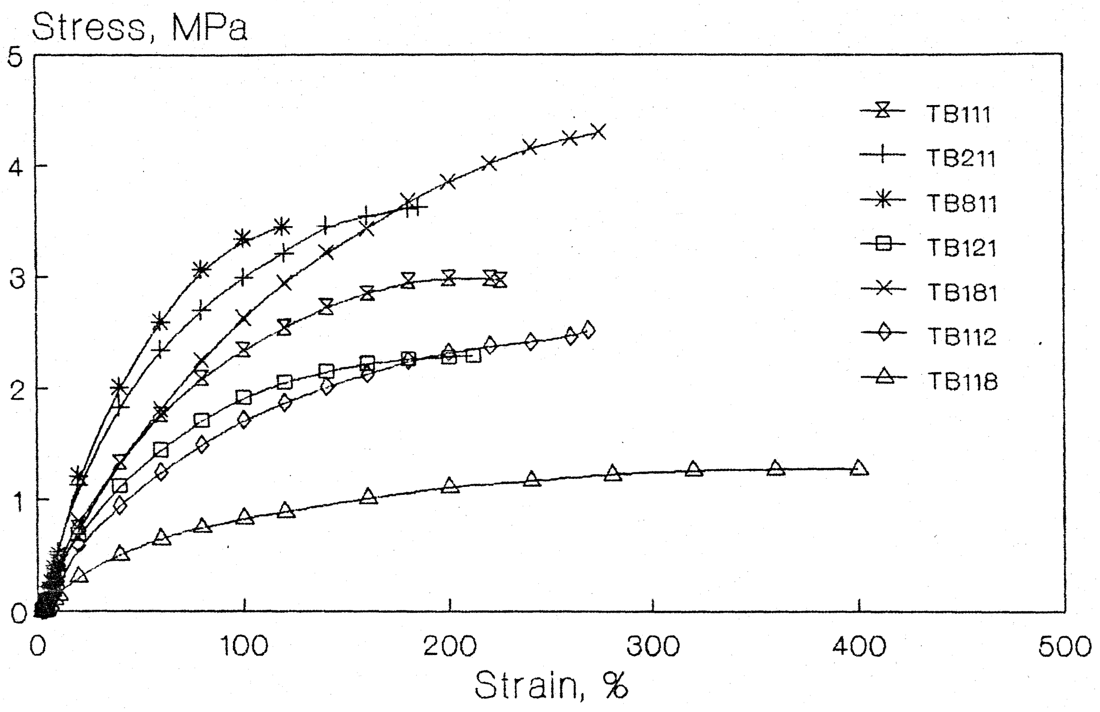


Fig. 4.2.3 Stress-Strain plots for ternary blends of PPVC, EVAPVC and NBR1

4.2.2 *Ultimate Elongation*

Ultimate elongation (UE) of binary and ternary blends are shown in Figs. 4.2.4 and 4.2.5. For binary blends with EVAPVC, the UE increases gradually as PPVC is replaced. For PPVC-EVAPVC blends, the UE is marginally lower than the additive values derived from the values of 'pure' components. For blends with NBRs, the UE values are marginally higher than the additive values. This indicates that both the NBRs form synergistic alloys with PPVC and PPVC-NBR blends are having better compatibility and specific interactions.

UE of ternary blends also generally show marginally lower values than the values obtained by additivity rule. This indicates that the ternary blends are not having synergistic effects as in PPVC-NBR1 binary blends, though, there are no drastic falls in the UE values. Ternary blends are therefore likely to be less homogeneous than PPVC-NBR1 binary blend system.

4.2.3 *Ultimate Tensile Stress*

From Figs. 4.2.6 and 4.2.7 it is seen that ultimate tensile stress (UTS) of binary and ternary blends have generally the same trend as for ultimate elongation (Figs. 4.2.4 and 4.2.5). The reasons for such behaviour are the same as discussed for the UE behaviour (Section 4.2.2). PPVC-NBR1 blends have UTS higher than the additive values.

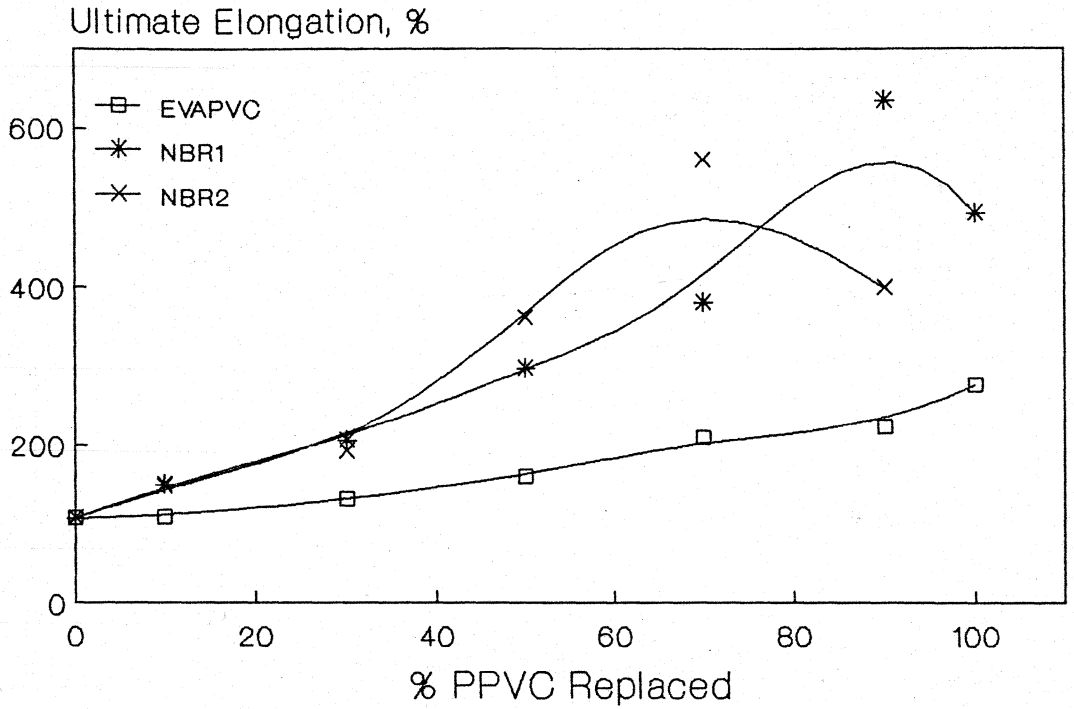


Fig. 4.2.4 Ultimate Elongation vs PPVC replaced for binary blends of PPVC with NBR1, NBR2 and EVAPVC

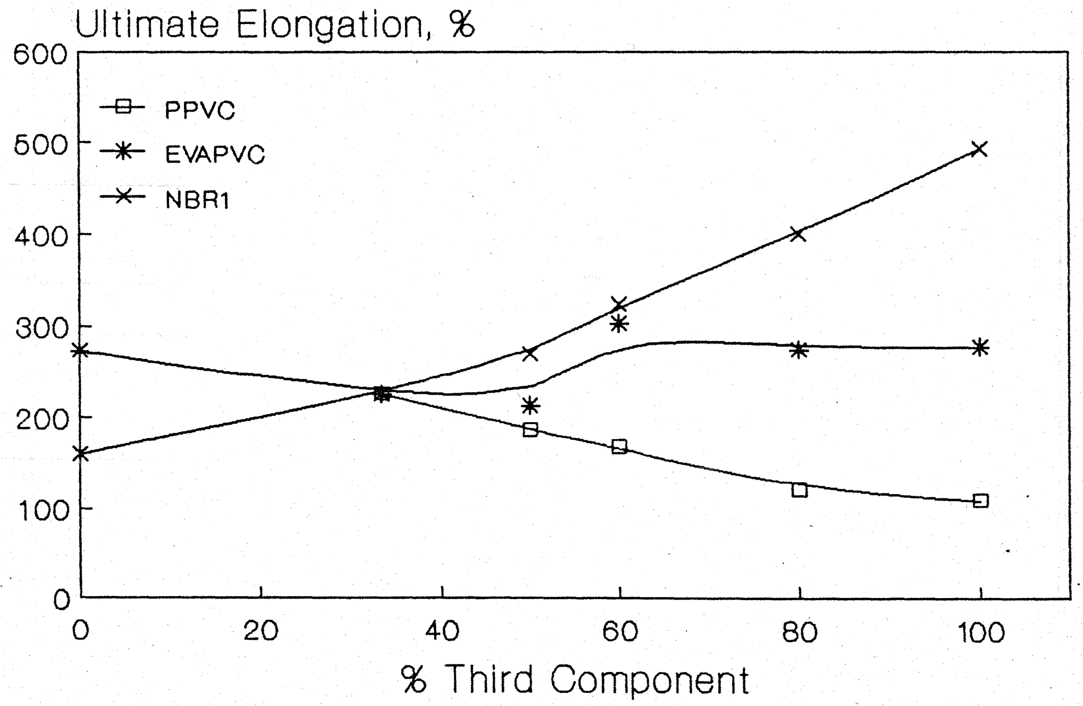


Fig. 4.2.5 Ultimate Elongation of ternary blends, third component added to equal fractions of other two components

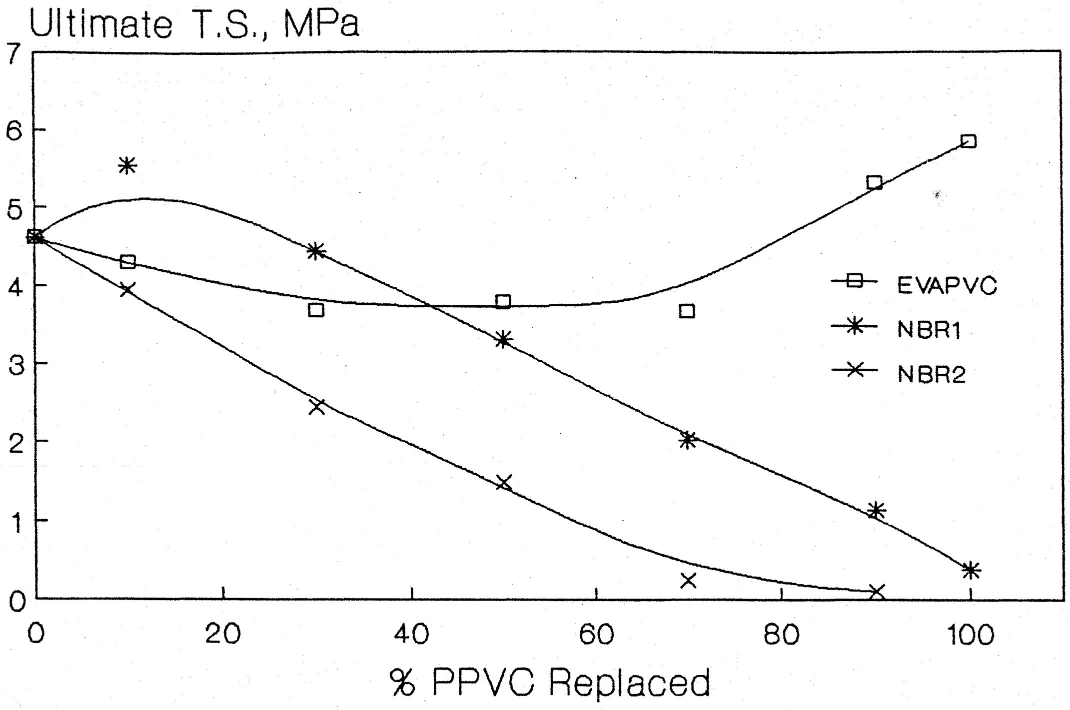


Fig. 4.2.6 Ultimate Tensile Stress vs. % PPVC replaced for binary blends with EVAPVC, NBR1 and NBR2

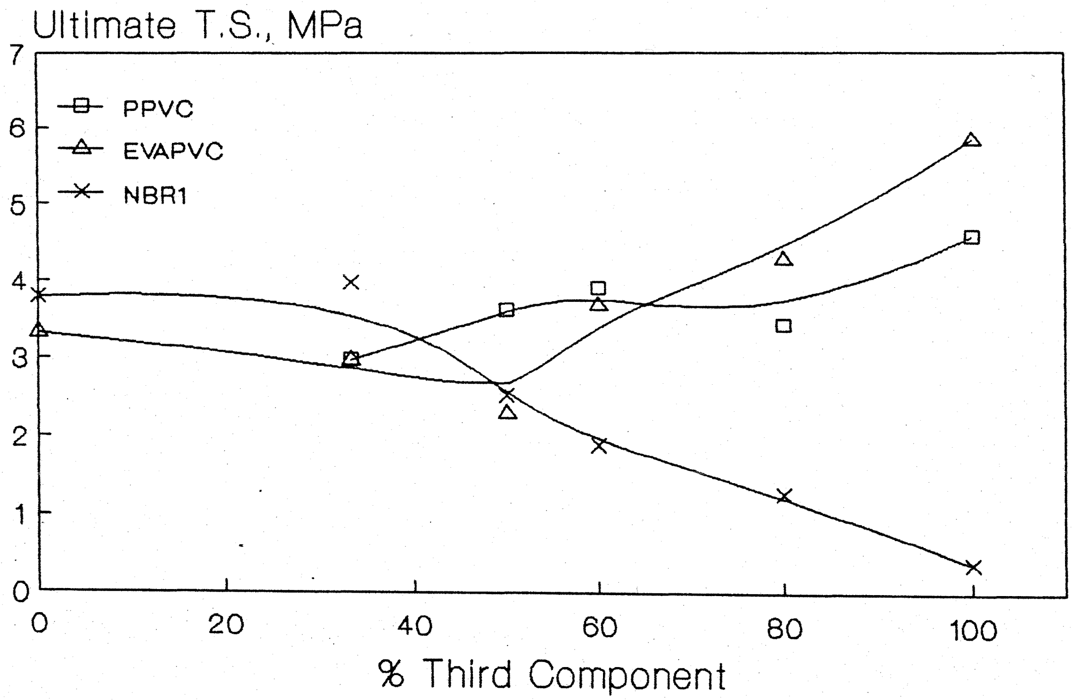


Fig. 4.2.7 Ultimate Tensile Stress of ternary blends, third component added to equal fractions of other two components

In fact 10% replacement of PPVC with NBR1 results in significant increase in UTS over even PPVC, though NBR1 itself has much lower UTS. This further reinforces that PPVC-NBR1 blends have appreciable intermolecular interactions.

The possible reasons of NBR2 not exhibiting same behaviour as that of NBR1 could be due to higher molecular weight and lower acrylonitrile content of NBR2 compared to NBR1. Both these factors result in lesser compatibility.

4.2.4 Modulus

Modulus of blends at 100 % elongation are shown in Figs. 4.2.8 and 4.2.9. In case of binary blends modulus values show gradual fall in all cases when PPVC is replaced. NBR1 and NBR2 have modulus values much lower than those of PPVC and EVAPVC. This is reflected in the modulus values of blends. However, the fall in modulus for about 25% replacement of PPVC with NBR1/EVAPVC is not very significant. The practical implication of this is that if 25% replacement of PPVC results in improvement in some other desirable properties e.g., UE, the fall in modulus values will not pose a big problem for an end use.

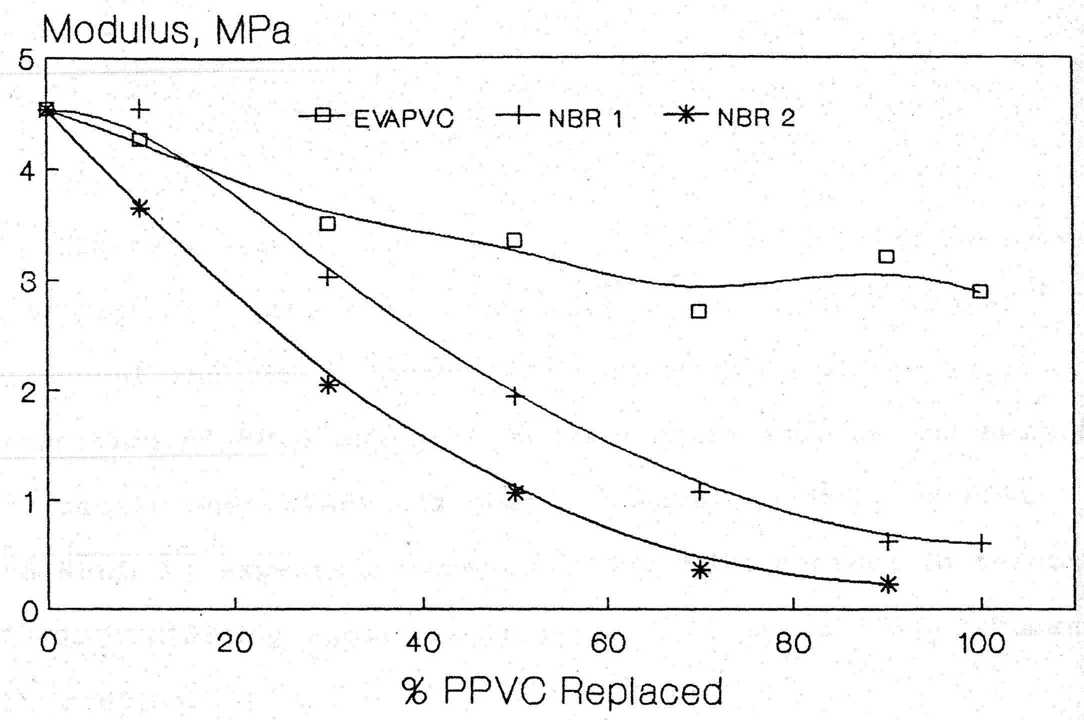


Fig. 4.2.8 Modulus of binary blends at 100 % elongation

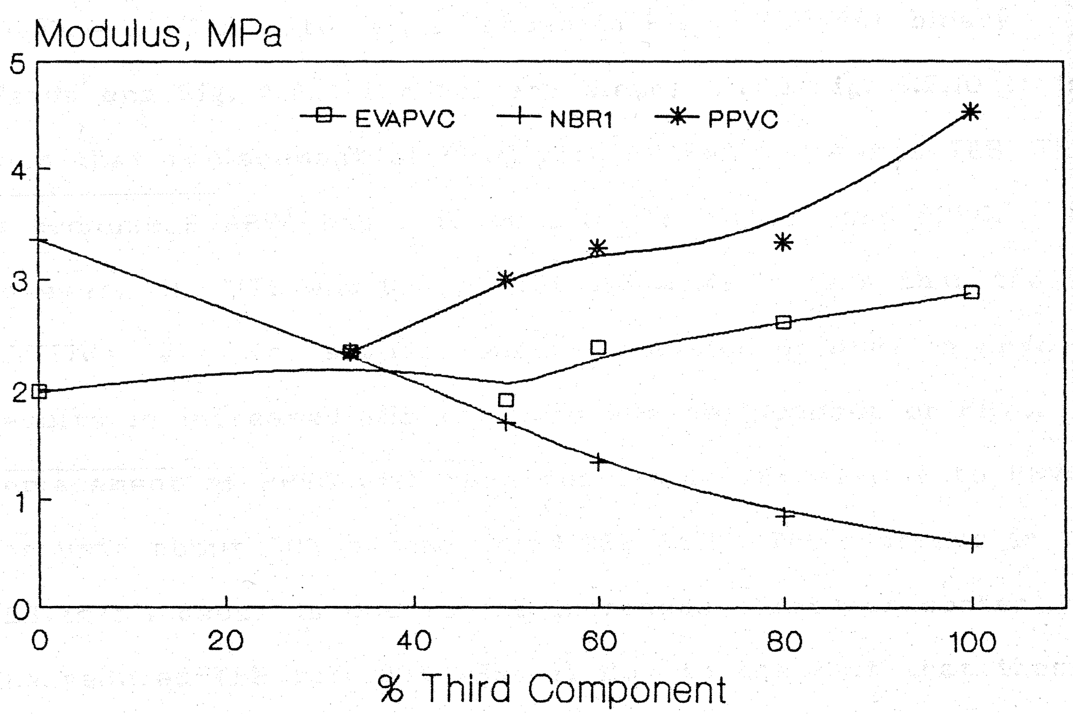


Fig. 4.2.9 Modulus of ternary blends at 100 % elongation

Ternary blends (Fig. 4.2.9) generally have modulus values very similar to the ones expected from the values of 'pure' component and binary blends. Addition of PPVC to the equal proportion of PPVC and NBR1 increases the modulus and same is the result when EVAPVC is added to equal quantity of PPVC and NBR1. As expected, increase in the NBR1 content in ternary blends containing equal fractions of PPVC and EVAPVC reduces the modulus.

4.2.5 Tensile Energy to Break

Tensile energy to break (TEB), which is a measure of toughness of a material, is shown in Fig. 4.2.10 for binary blends and Fig. 4.2.11 for ternary blends. From Fig. 4.2.10 it is seen that replacement of PPVC with EVAPVC increases TEB. This is because EVAPVC has both UE and UTS higher than PPVC. However, like UTS and UE the TEB ~~increase~~ is less than the additive value for similar reasons. Addition of NBR1 to PPVC results in increased TEB for upto 90% replacement of PPVC. Replacement of PPVC with NBR2 results in TEB similar to PPVC for upto about 50% beyond which TEB falls. The increase in TEB in all cases is due to the increased elastomer content. The reduced TEB for 100% NBRs is due to the fact that these uncrosslinked elastomers have very low ultimate tensile strength and therefore the area under the stress-strain

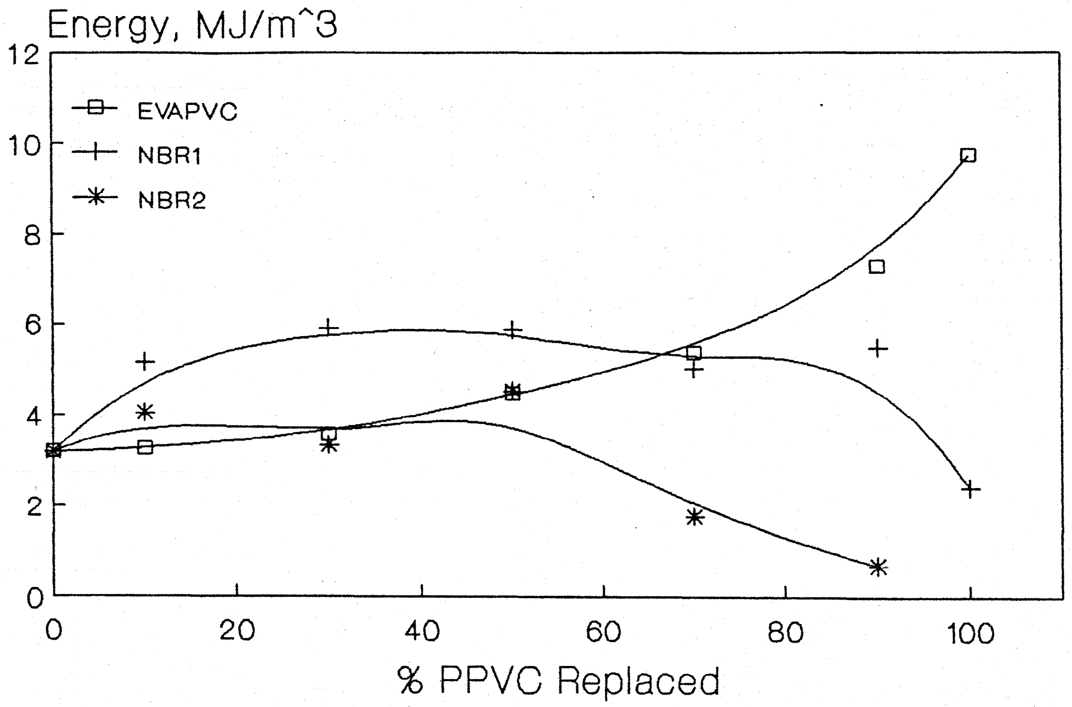


Fig. 4.2.10 Tensile Energy to Break for binary blends with EVAPVC, NBR1 and NBR2

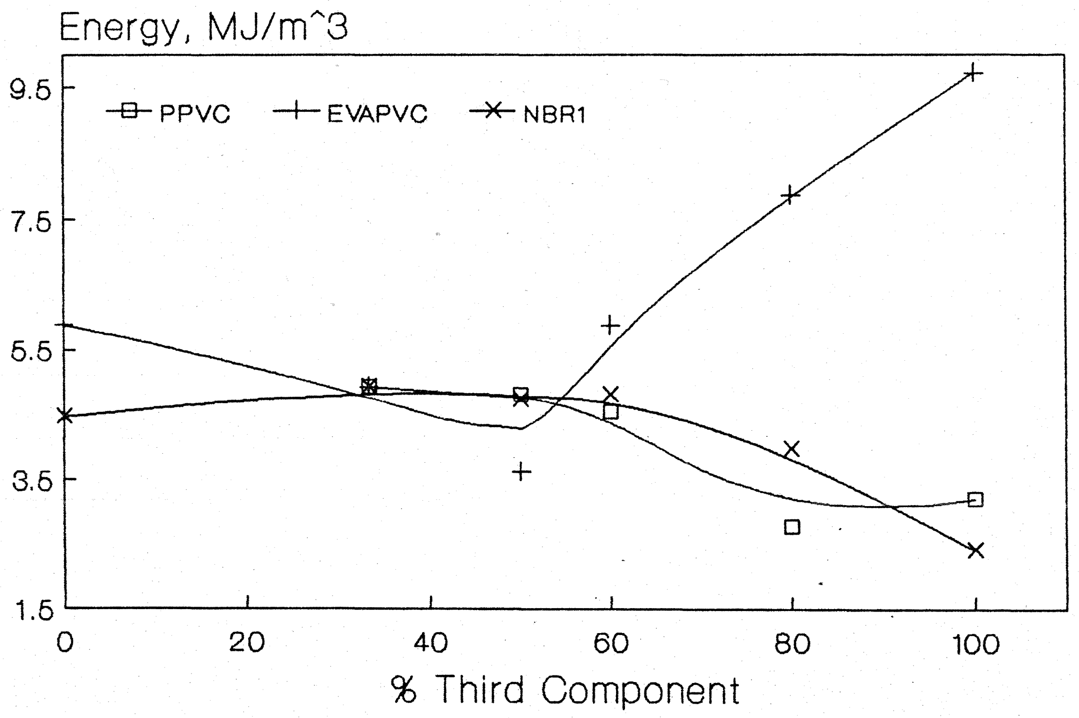


Fig. 4.2.11 Tensile Energy to Break for ternary blends

curve becomes smaller. Since PPVC-NBR1 blends have synergistic effect on both UE and UTS, similar behaviour is also seen for TEB.

Ternary blends in which NBR1 is added to equal fractions of PPVC-EVAPVC show increased TEB for upto 60% addition of NBR1. Reduction in TEB beyond 60% NBR1 is due to its own poor UTS and hence TEB. When the third component is PPVC, TEB reduces because PPVC has much lower UE and hence TEB than EVAPVC and reduction in EVAPVC results in lower TEB. Addition of EVAPVC results in reduced TEB for upto 50%, and beyond 50% TEB increases. The reason for this can be explained by looking at the plots of binary blends (Fig. 4.2.10). 50-50 blend of PPVC-NBR1 has higher TEB than 50-50 blend of PPVC-EVAPVC and therefore addition of EVAPVC to a 50-50 blend of PPVC-NBR1 results in immediate reduction in TEB. However, since EVAPVC itself has the highest TEB, further addition of EVAPVC results in increase in TEB.

The ability to improve the TEB values of PPVC by blending it with other polymer(s) has important practical utility in medical application. In application like blood bag, where the bags are centrifuged at high rpm (5000 g) and are supported during the centrifugation, the failure of bags (bursting) is due to poor TEB values. In such applications it is the TEB that is more important parameter to be considered than individually UTS or UE. 25-30% replacement of PPVC by NBR1 should result in substantial improvement in TEB and thus should reduce the instances of failure due to centrifugation.

4.2.6 Models for Mechanical Properties

Models are useful in predicting the behaviour of a system. Chuang et al. (1985) in a somewhat recent paper observed that though many theories have been advanced for predicting mechanical properties of polyblends, there is no comprehensive theory which can predict the mechanical/physical properties.

An ideal blend behaviour should be shown by a straight line relationship with compositions. This is true also for a ternary blend.

i.e., $$P = P_1 x_1 + P_2 x_2 \tag{4.15}$$

or $$P = P_1 x_1 + P_2 x_2 + P_3 x_3 \tag{4.16}$$

where,

P = predicted value of a property of the blend
P_1, P_2, P_3 = values of a property of 'pure' components
x_1, x_2, x_3 = wt. fractions of component 1, 2 and 3

The difference between the actual property of a blend and that of an ideal blend is conveniently termed as an 'excess property', which is the effect of differences in inter-elemental effects, and therefore is expressed as a function of composition.

A general equation for expressing this excess property of the blend is developed statistically (using the method of Wohl's equation for excess free energy) in terms of composition of the separate components. Written in a form suitable for the present context,

$$P - \Sigma P_i x_i = K_1 x_1 x_2 + K_2 x_1 x_3 + K_3 x_2 x_3 + K_4 x_1 x_2 x_3 \qquad (4.17)$$

where, K_1, K_2, K_3 and K_4 are empirical constants. The first three terms on the right hand side represent the contributions due to interactions of unlike components in groups of two and the last term represent interactions of the components in groups of three. Though terms containing $x_1^2x_2$, $x_1^2x_3$, $x_2^2x_3$, $x_2^2x_1$, $x_3^2x_1$ and $x_3^2x_2$ should normally be included, very little improvement in prediction takes place with their inclusion. Hence, for predicting mechanical properies, a simpler model is proposed and this is in the form :

$$P = P_1 x_1 + P_2 x_2 + P_3 x_3 + k_1 x_1 x_2 + k_2 x_1 x_3 + k_3 x_2 x_3 + k_4 x_1 x_2 x_3 \qquad (4.18)$$

where,

$k_1, k_2, k_3, k_4,$ = constants

subscripts 1,2,3 for P and x refer to PPVC, EVAPVC and NBR1 respectively

The constants can be calculated from the known experimental values of a property for 'pure' components, 1:1 binary blends and 1:1:1 ternary blends. Calculating in the above manner the models for different properties are:

$$UE = 107.66x_1 + 277x_2 + 493.6x_3 - 129.32x_1x_2 - 111.88x_1x_3 - 1105.74x_1x_2x_3 \qquad (4.19)$$

$$UTS = 4.60x_1 + 5.85x_2 + 0.378x_3 - 5.74x_1x_2 + 3.33x_1x_3 - 9.97x_1x_2x_3 \quad (4.20)$$

$$Modulus = 4.53x_1 + 2.88x_2 + 0.6x_3 - 1.38x_1x_2 - 2.46x_1x_3 - 2.59x_1x_2x_3 \quad (4.21)$$

$$TEB = 3.19x_1 + 9.73x_2 + 2.40x_3 - 7.95x_1x_2 + 12.35x_1x_3 - 18.24x_1x_2x_3 \quad (4.22)$$

Kleiner et al.(1979) also used a similar empirical simple equation to predict the modulus of PPO-polystyrene blends.

The predicted and experimental values of the various mechanical properties are shown in Tables 4.2.1 and 4.2.2. Since the models were derived from experimental values of 'pure' components and 1:1 and 1:1:1 binary and ternary blends, the deviations from non-linearity and the interactions among the polymers are also included in the proposed models. As can be seen from the Tables, the models can predict values which are quite close to the experimental ones with only few exceptions. Since the objective of the present investigation was to study the effect of replacement of PPVC with another polymer, no studies were conducted with 1:1 blend of EVAPVC-NBR1. The constant k_3 could not therefore be calculated. This did not affect the predictions of binary blends. For ternary blends the term containing k_3 and therefore the interactions between EVAPVC and NBR1 have been neglected. Prediction for ternary blends would have been more accurate if this term also would have been considered. Surprisingly, the predictions are still quite good. This indicates that blends do not behave abruptly due to change in formulations and such simple models can be used to design formulations based on the requirements of end use.

TABLE 4.2.1 Predicted and Experimental Values of Ultimate Elongation and Tensile Stress

Sample No.	Ultimate Elongation			Ultimate Tensile Stress		
	E* (%)	P# (%)	D** (%)	E (MPa)	P (MPa)	D (%)
BB1 91	108.00	112.96	4.39	4.29	4.21	1.76
BB1 73	131.12	131.30	0.14	3.67	3.78	2.69
BB1 37	208.85	199.04	4.93	3.66	4.28	14.25
BB1 19	223.33	248.43	10.10	5.34	5.21	2.35
BB2 91	149.20	136.18	9.56	5.54	5.86	23.53
BB2 73	205.71	199.95	2.88	4.43	4.04	9.88
BB2 37	359.66	354.32	1.51	2.02	2.34	13.83
BB2 19	636.00	444.94	42.94	1.14	1.10	3.13
TB211	185.00	181.78	1.77	3.63	3.25	11.88
TB311	167.00	163.23	2.31	3.92	3.48	12.55
TB811	119.20	135.05	11.73	3.45	4.03	14.61
TB121	211.70	231.10	8.40	2.31	3.35	31.22
TB131	302.60	239.92	26.13	3.70	3.72	0.28
TB181	274.25	261.42	4.91	4.30	4.68	8.10
TB112	268.66	286.34	6.18	2.53	2.55	0.77
TB113	322.80	327.96	1.57	1.90	2.25	15.68
TB118	400.00	414.26	3.44	1.27	1.48	13.84

* E = Experimental
\# P = Predicted
** D = Deviation

TABLE 4.2.2 Predicted and Experimental Values of Modulus at 100% Elongation and Tensile Energy at Break

Sample No.	Tensile Energy at Break			Modulus at 100% Elongation		
	E* (MJ/m³)	P# (MJ/m³)	D** (%)	E (MPa)	P (MPa)	D (%)
BB1 91	3.26	3.13	4.17	4.26	4.24	0.45
BB1 73	3.57	3.48	2.59	3.51	3.75	6.28
BB1 37	5.37	6.10	13.59	2.71	3.09	12.16
BB1 19	7.26	8.36	15.13	3.19	2.92	9.22
BB2 91	5.14	4.22	17.91	4.55	3.92	16.20
BB2 73	5.91	5.55	6.10	3.03	2.83	6.90
BB2 37	5.04	5.23	3.88	1.08	1.26	14.45
BB2 19	5.48	3.59	34.55	0.62	0.77	19.65
TB211	4.79	4.61	3.92	3.00	2.74	9.65
TB311	4.54	4.43	2.38	3.28	3.02	8.77
TB811	2.76	3.97	43.79	3.34	3.69	9.38
TB121	3.62	5.47	51.11	1.90	2.48	23.30
TB131	5.86	6.06	2.93	2.38	2.55	6.75
TB181	7.86	7.68	2.24	2.61	2.70	3.43
TB112	4.73	4.91	3.68	1.70	1.84	7.60
TB113	4.80	4.75	1.03	1.34	1.55	13.76
TB118	3.96	3.98	0.36	0.84	1.03	18.54

* E = Experimental
\# P = Predicted
** D = Deviation

4.2.7 *Creep*

From Fig 4.2.12 it is seen that on application of stress (20% of UTS), extension is minimum for PPVC and maximum for EVAPVC. NBR1 has extension which is almost comparable to PPVC till about 30 minutes, after which extension increases at a faster rate and finally breaks at an extension of about 60%. EVAPVC also breaks at an extension of 135 %. PPVC does not break during the experimental period (24 hour). It is interesting to note that the deformation behaviour seen for the 'pure' components in this experiment where constant stress (nominal) is applied for long durations is different than the results of the experiment done by following ASTM D 882, where constant and fast (500 mm/min) strain rate was applied (Figs. 4.2.1 and 4.2.2). The possible reason for EVAPVC showing higher ultimate extension than NBR1 in this experiment is probably due to the fact that EVAPVC can yield and undergoes plastic flow till it breaks and offers less resistance to deformation. This possibility is also further supported from the fact that the extension rate for EVAPVC remains more or less unchanged till break. NBR1 on the other hand behaves like a typical elastomer and offers resistance to deformation initially. However, once some increase in length has taken place, the thickness comes down and the stress level goes up higher than 20% of UTS (nominal) and this results in higher rate of extension and finally failure takes place.

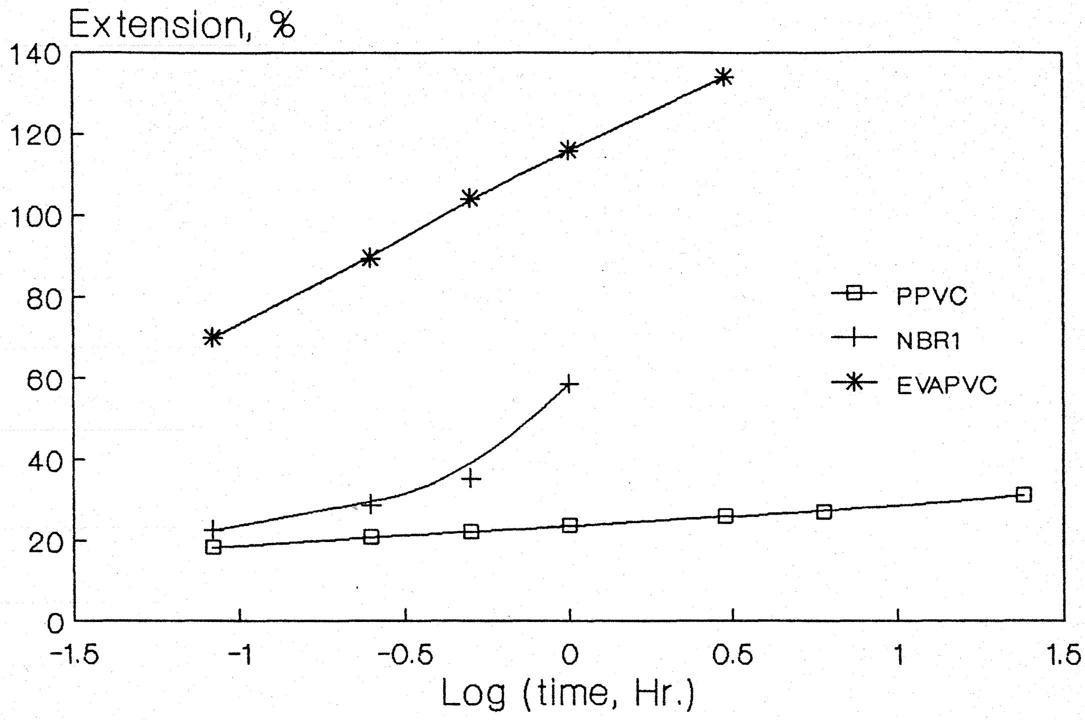


Fig. 4.2.12 Extension vs. Time for fixed stress = 20 % of UTS

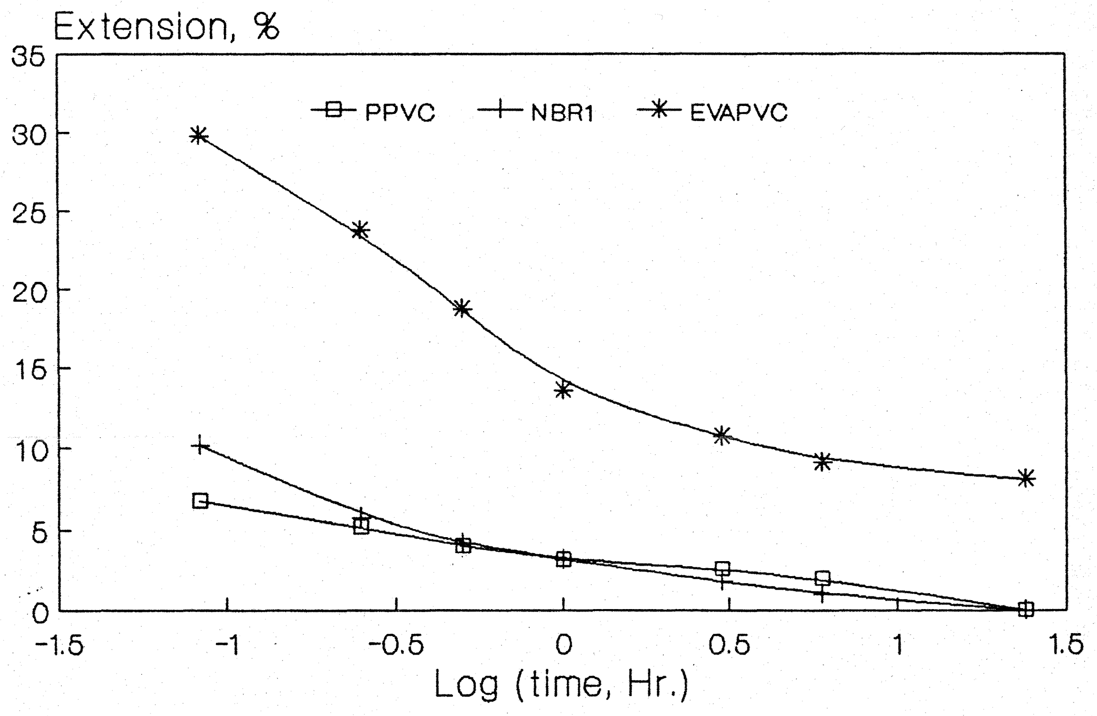


Fig. 4.2.13 Extension after release of applied stress (20% UTS)

On release of stress PPVC and NBR1 come back to the original length over a period of 24 hours (Fig. 4.2.13) and EVAPVC has still an extension of about 8%. On release of load the initial retraction rate is quite fast for both NBR1 and EVAPVC compared to PPVC. However, retraction rate slows down for EVAPVC when extension comes down to about 15%. Further retraction is very slow and a permanent deformation is evident. The permanent deformation (creep) of EVAPVC is due to the stretching of crystalline ethylene part of EVAPVC and this also explains the higher extension at break for EVAPVC compared to NBR1.

From the results of 'pure' components it can be expected that the polyblends containing EVAPVC should exhibit creep behaviour. From Tables 4.2.3 and 4.2.4 it is seen that BB2 91 has extension at break higher than PPVC. However, when the load is released it retracts much faster in first 5 minutes. This is because NBR1 is elastomeric and this has a faster initial retraction than PPVC and moreover PPVC-NBR1 blends have synergistic UE and UTS behaviour (Fig. 4.2.4 and Fig. 4.2.6). Binary blends of PPVC-EVAPVC could not be studied because the samples used to break in a short period of time (within 30 minutes). The ternary blends reflect the behaviour of 'pure' components. Blends with EVAPVC as the major component have more extension on application of load and creep behaviour is also apparent when load is removed. These blends show more permanent distortion than EVAPVC itself. This could be due to the fact that the other two polymers present in the blend physically restrict the movement and retraction of the EVAPVC chains. Ternary blends with PPVC as the major component have less extension and no permanent set and blends having NBR1 as the major component show more extension than PPVC but less than EVAPVC and as expected permanent set gets reduced as the amount of NBR1 goes up.

Some of the PVC based medical products like CAPD and crystalloid containers containing 500 ml to 3000 ml of fluid are stored by stacking for fairly long durations. In such cases the containers at the bottom experience continuous load for long durations. While selecting materials for these applications, creep behaviour becomes one of the important considerations. From the results of this study, it can therefore be concluded that for such applications EVAPVC should rather be avoided. However, from other considerations like flow during processing, if it becomes absolutely essential, the quantity of EVAPVC should be kept to a minimum.

TABLE 4.2.3 Extension at different times on Application of Fixed Stress

Sample	Extension at different times, %						
	5 Min.	15 Min.	30 Min.	1 Hr.	3 Hr.	6 Hr.	24 Hr.
PPVC	18.2	20.8	22.0	23.6	25.8	27.0	31.0
EVAPVC	70.2	89.4	104.0	115.8	134.0		
NBR1	22.4	28.8	35.2	58.6			
BB2 91	30.4	33.2	36.0				
BB2 37	45.2	50.0	53.4				
TB111	35.4	39.4	43.0	46.6	50.2	55.0	
TB311	26.6	29.4	30.0				
TB811	14.0	15.2	16.0	17.2	19.8	22.0	
TB131	45.0	52.4	53.6	59.6	70.4		
TB181	43.8	52.6	57.6	65.0	78.2	92.2	119.4
TB113	38.6	46.6	49.4	53.4	57.6		

TABLE 4.2.4 Extension at different times on Release of Stress

Sample	Extension on release of load, %									
	A	B	C	D	E	F	G	H	I	J
PPVC	6.8	5.2	4.0	3.2	2.6	2.0		0.0		
EVAPVC	29.8	23.8	18.8	13.6	10.8	9.2		8.2		0.6
NBR1	10.2	5.8	4.2	3.2	1.8	1.0		0.0		
BB2 91	3.2	1.4	1.0					0.0		
BB2 37								0.0		
TB111								1.2		
TB311		1.8						0.6		
TB811	7.0	1.0						0.0		
TB131				10			3.4	1.6		1.2
TB181				22				7.2	6.0	3.8
TB113								1.2		1.0

A: 5 Min., B: 15 Min., C: 30 Min., D: 1 Hr., E: 3 Hr., F: 6 Hr., G: — 12 Hr., H: 1 Day, I: 2 Days and J: 7 Days

4.2.8 Hardness

In industry, hardness of PVC is taken as a crude measure of flexibility and hardness value of medical tubings is one of the important specifications used in trade. From Fig. 4.2.14 it is seen that shore (A) hardness of plasticized PVC increases form 80 to 95 as the content of plasticizer is decreased from 40% to 25%. Polyester blends have hardness values which are similar and all values are within 70-80 °A. The behaviour observed in both the above cases are expected.

Fig. 4.2.15 and Fig. 4.2.16 indicate that the blends have intermediate hardness values. Also the values are generally additive in nature. The interactions like hydrogen bonding are too small to change a gross surface property like hardness. An intermediate hardness value and absence of large variation of hardness values from one point to another on the same sample would also indicate that the mixing and hence miscibility of the components are reasonably good, at least in macroscopic level.

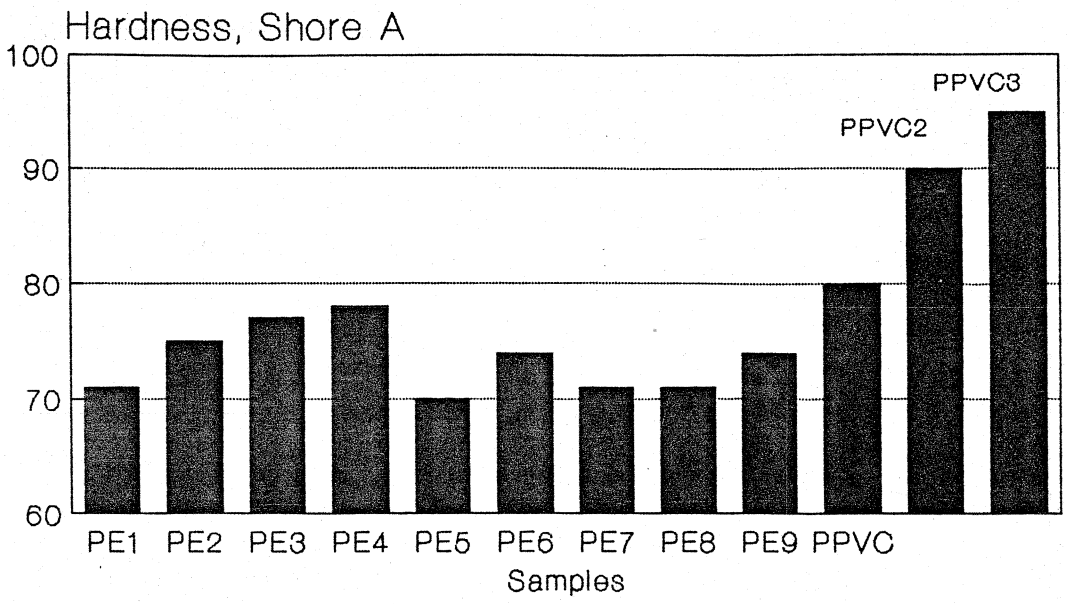


Fig. 4.2.14 Hardness values of plasticized PVC and polyester blends

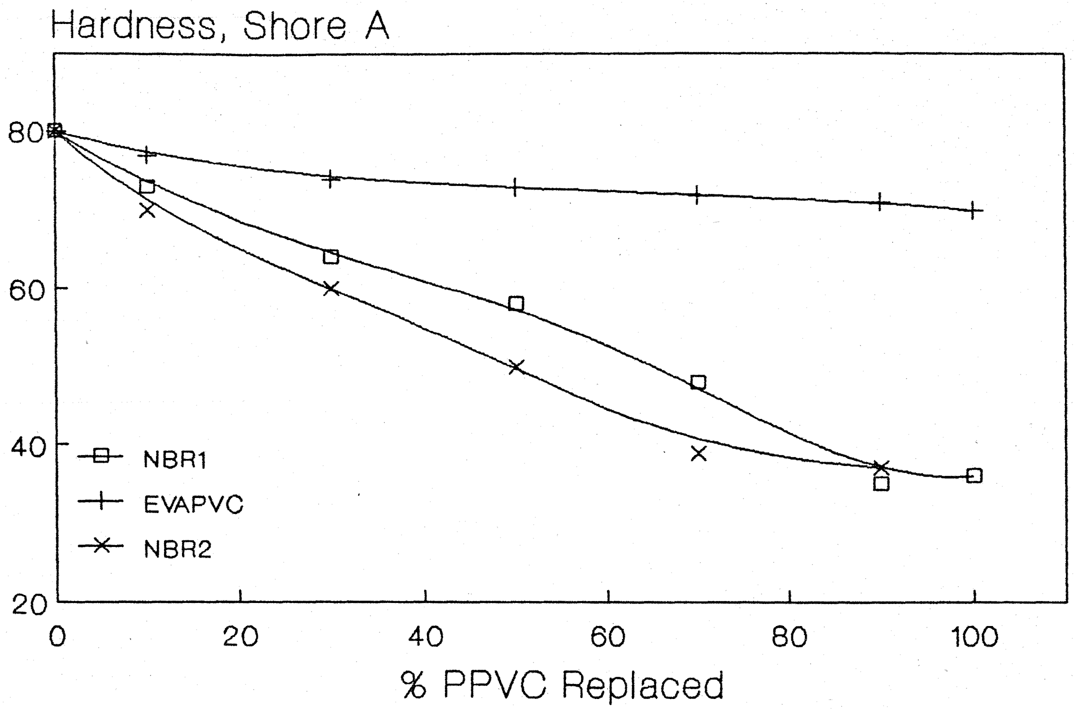


Fig. 4.2.15 Hardness for binary blends of PPVC with EVAPVC, NBR1 and NBR2

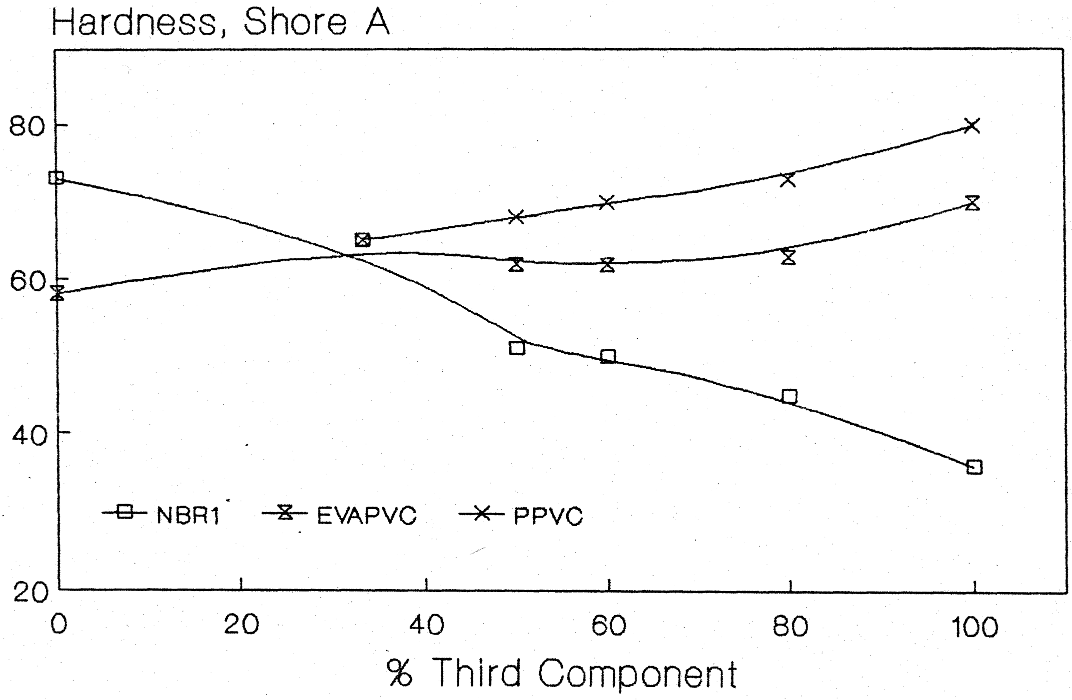


Fig. 4.2.16 Hardness for ternary blends with equal fractions of two components

DYNAMIC MECHANICAL ANALYSIS AND BRITTLENESS TEMPERATURE

SECTION - 3

4.3 DYNAMIC MECHANICAL ANALYSIS AND BRITTLENESS TEMPERATURE STUDIES

Dynamic mechanical properties measure the response of polymers to cyclic deformation and these are extremely sensitive to all types of transitions, relaxation processes, structural heterogeneities and morphology of multiphase systems like polyblends. Many authors have discussed about the usefulness of the study of dynamic mechanical properties in understanding material behaviour (Aklonis, 1983; Marayama, 1978; Heijboer, 1982; Ma, 1989). Study of brittleness temperature gives important information regarding the usefulness of a material at lower temperatures.

In this section, the results of dynamic mechanical properties and brittleness temperature are presented.

4.3.1 Dynamic Mechanical Properties

4.3.1.1 Plasticized PVC

The loss tangent, storage modulus and loss modulus versus temperature plots for plasticized PVC samples are shown in Figs. 4.3.1 to 4.3.3. From Fig. 4.3.1 it is observed that tan δ is having peak values at around 17°C and 41°C for PPVC and PPVC2 respectively indicating the glass transition temperatures. The peaks are relatively narrow and peak value for PPVC is more than that of PPVC2.

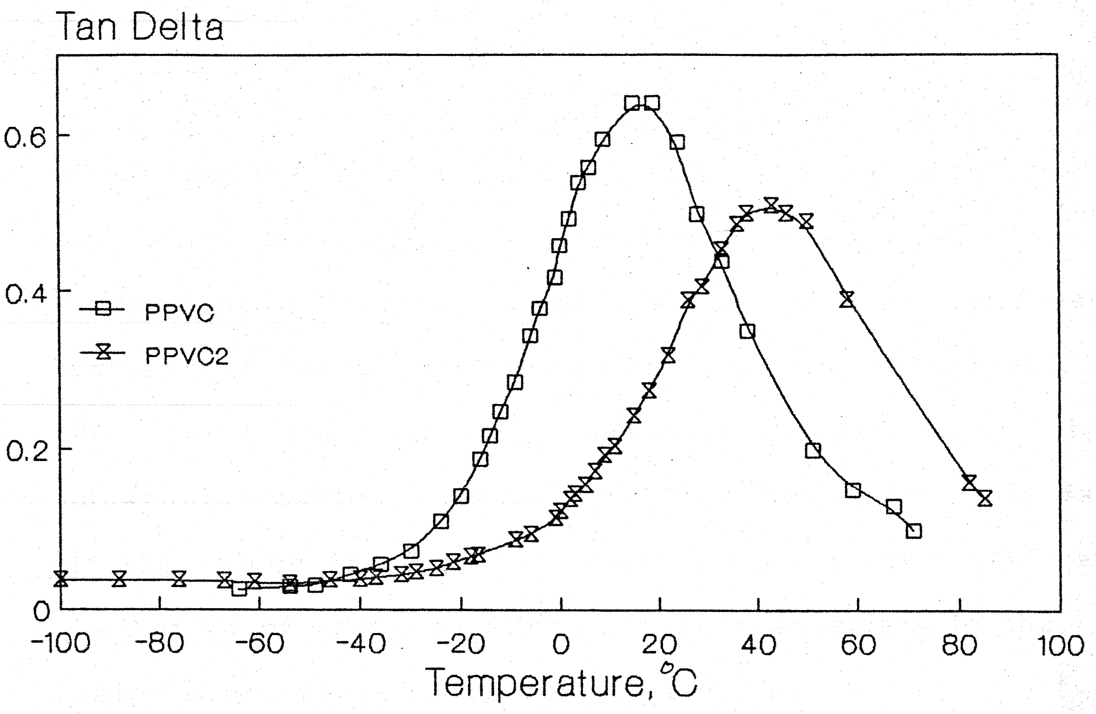


Fig. 4.3.1 Tan delta vs. temperature plots for plasticized PVC samples

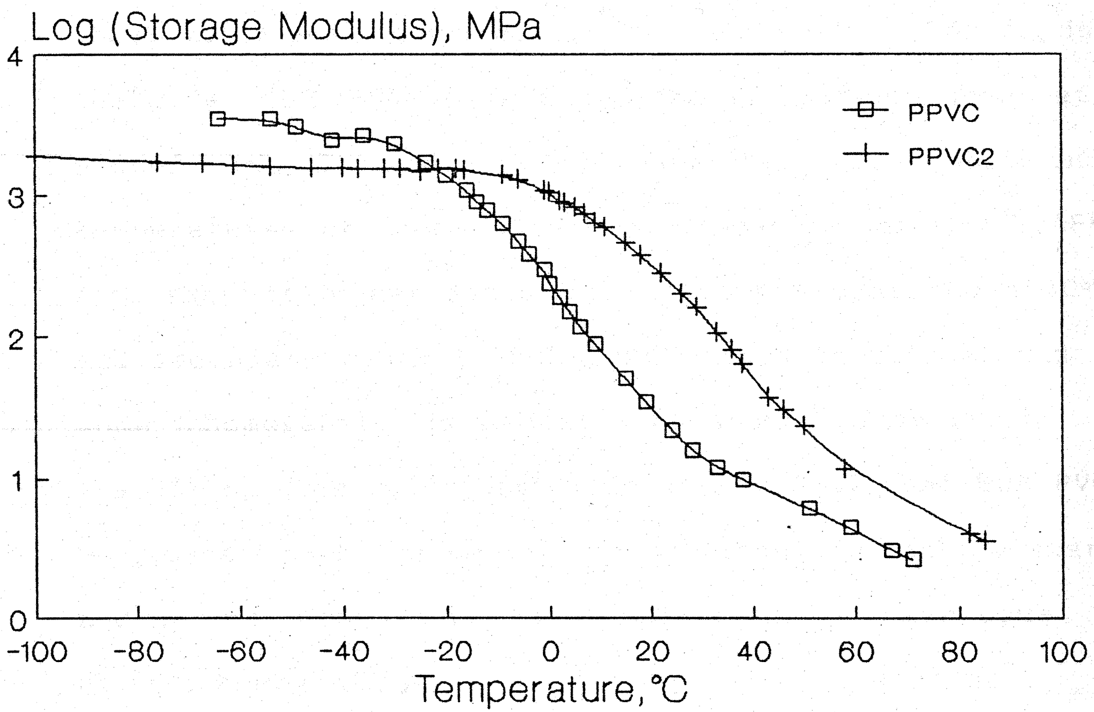


Fig. 4.3.2 Plots of storage modulus vs. temperature for plasticized PVC samples

The sharpness of peaks and absence of second peak are indicative of homogeneous single component system. The difference in temperature for the transition and the peak values are due to the difference in plasticizer content. PPVC has better dampening characteristics due to the higher plasticizer content. One distinct peak for E'' and sharp fall in the values for E' and E'' also (Figs. 4.3.2 and 4.3.3) are indicative of one transition for these materials in the temperature range noted for tan δ values.

4.3.1.2 'Pure' Components

From Fig. 4.3.4 it is observed that NBR1 has a very sharp tan δ peak compared to PPVC and EVAPVC. Tan δ_{max} is in the order NBR1>PPVC>EVAPVC and the transitions occur at around -9°C, 17°C and -1°C indicating the glass transition temperatures of these materials. Characteristically EVAPVC also exhibits higher dampening at temperatures above 40°C and secondary peak at 78°C. EVAPVC is a terpolymer and some inhomogeneity is indicated by second minor glass transition. This is probably due to the fact that 50% PVC is grafted on to co-polymer of ethylene and vinyl acetate and the resultant terpolymer still seems to have some micro inhomogeneity.

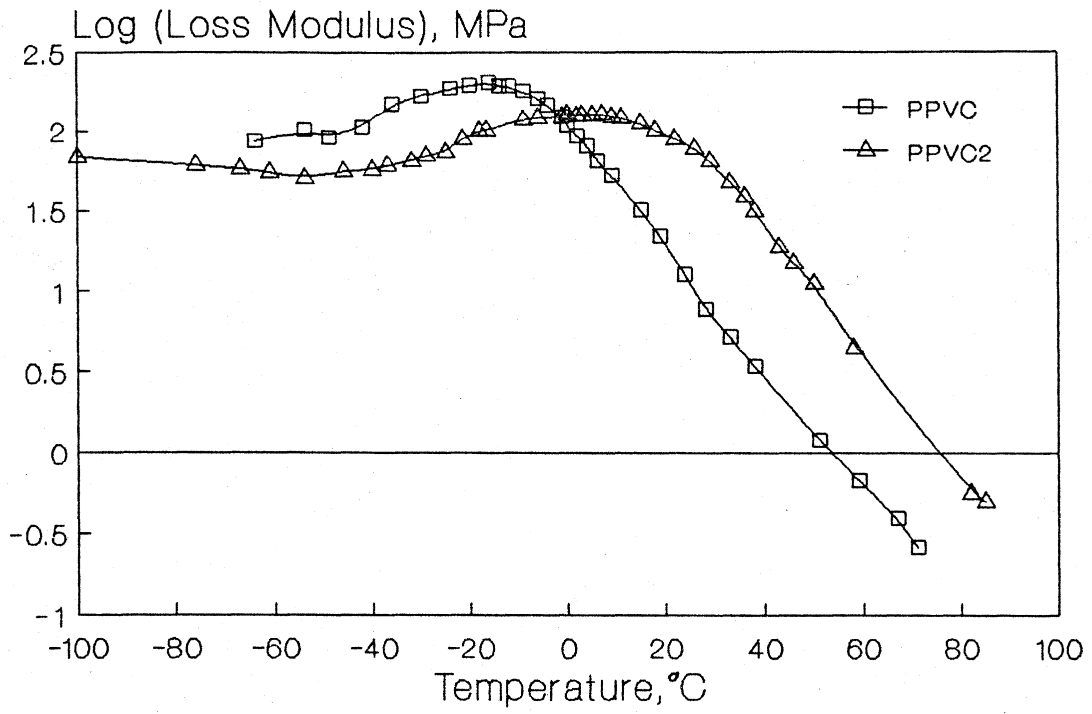


Fig. 4.3.3 Plots of loss modulus vs. temperature for plasticized PVC samples

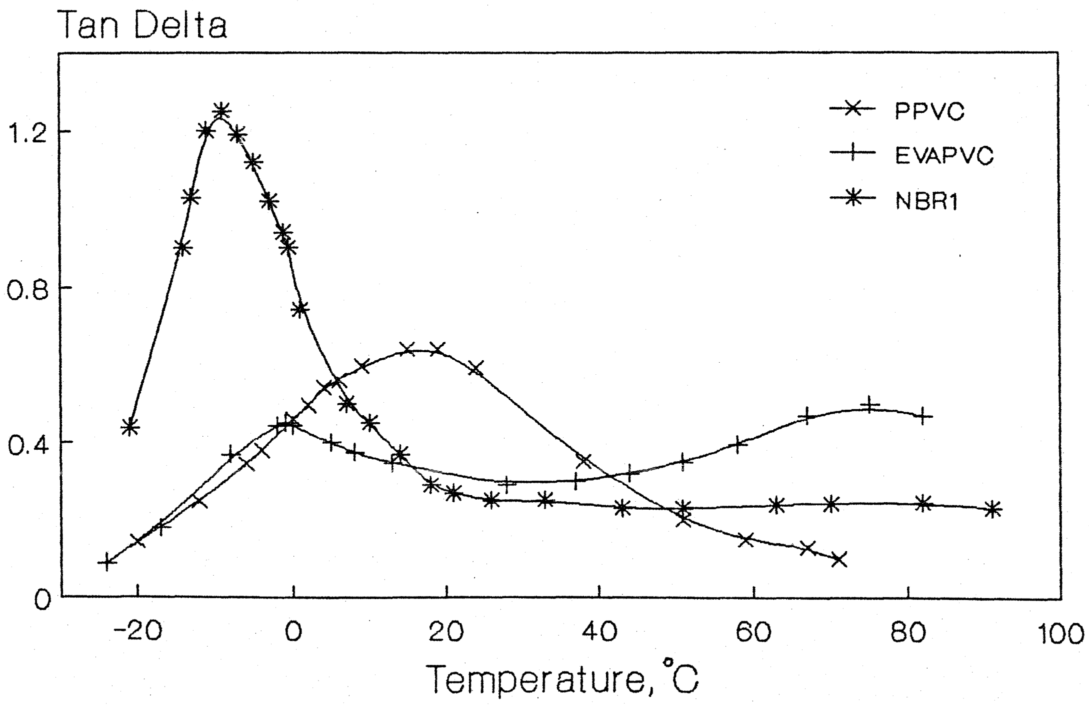


Fig. 4.3.4 Tan delta vs. temperature plots for three 'pure' components

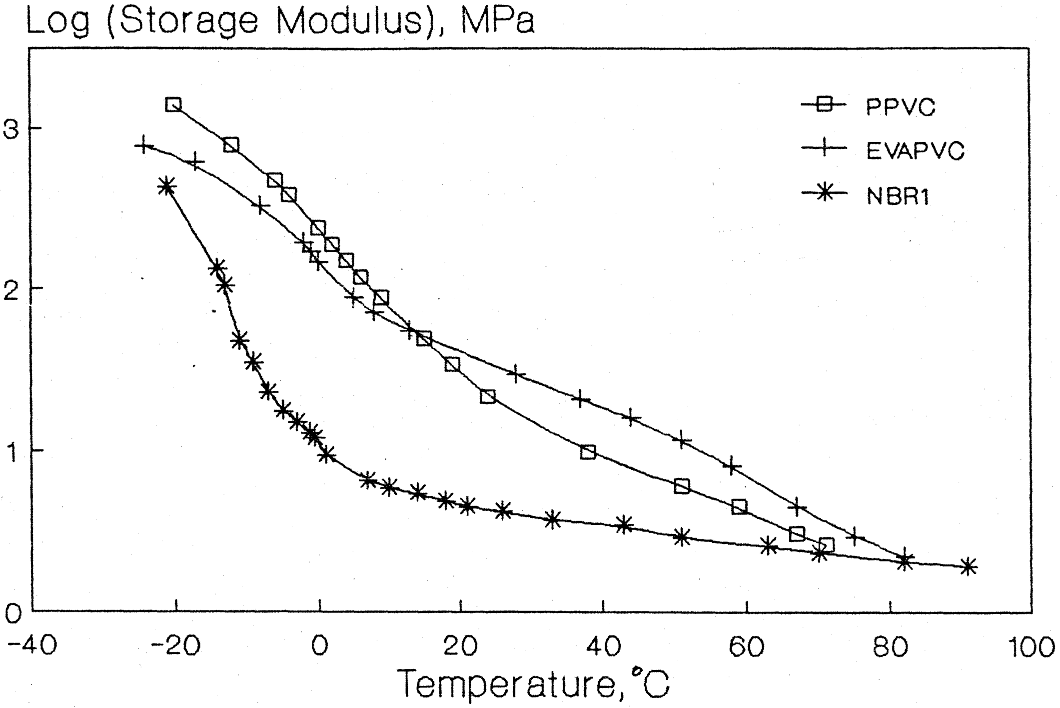


Fig. 4.3.5 Plots of storage modulus vs. temperature for 'pure' components

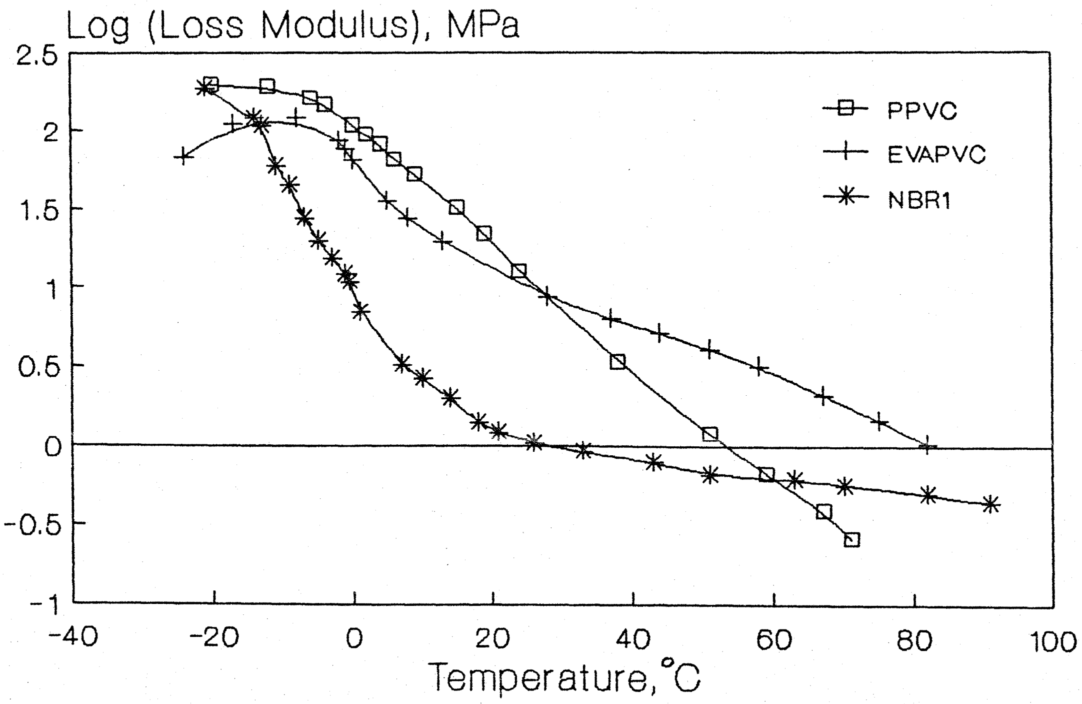


Fig. 4.3.6 Plots of loss modulus vs. temperature for 'pure' components

Storage and loss modulus plots shown in Figs. 4.3.5 and 4.3.6 generally confirm the observations made from tan δ plots. A rapid decrease in modulus is seen for all samples as temperature is increased through the glass transition region. Like a typical rubber, the modulus of NBR1 remains fairly constant for temperatures 30°C above the T_g. The minor transition for EVAPVC at 78°C noted in tan δ plots is missing in these plots.

4.3.1.3 Binary Blends

Tan δ plots for binary blends are shown in Figs. 4.3.7 and 4.3.8. PVC-NBR1 blends have one distinct transition as in 'pure' components indicating phase mixing between NBR1 and amorphous PVC segments. The peaks are broader for the blends compared to 'pure' components and this indicates certain degree of heterogeneity for these seemingly compatible blends. Due to presence of equal amount of both the components BB2 55 exhibits broader peak than BB2 91. Being a 9:1 PPVC-NBR1 blend, BB2 91 shows T_g which is almost similar to that of PPVC. As expected, BB2 55 on the other hand shows intermediate T_g. The observations made by Wang et al. (1983) agree well with the present study.

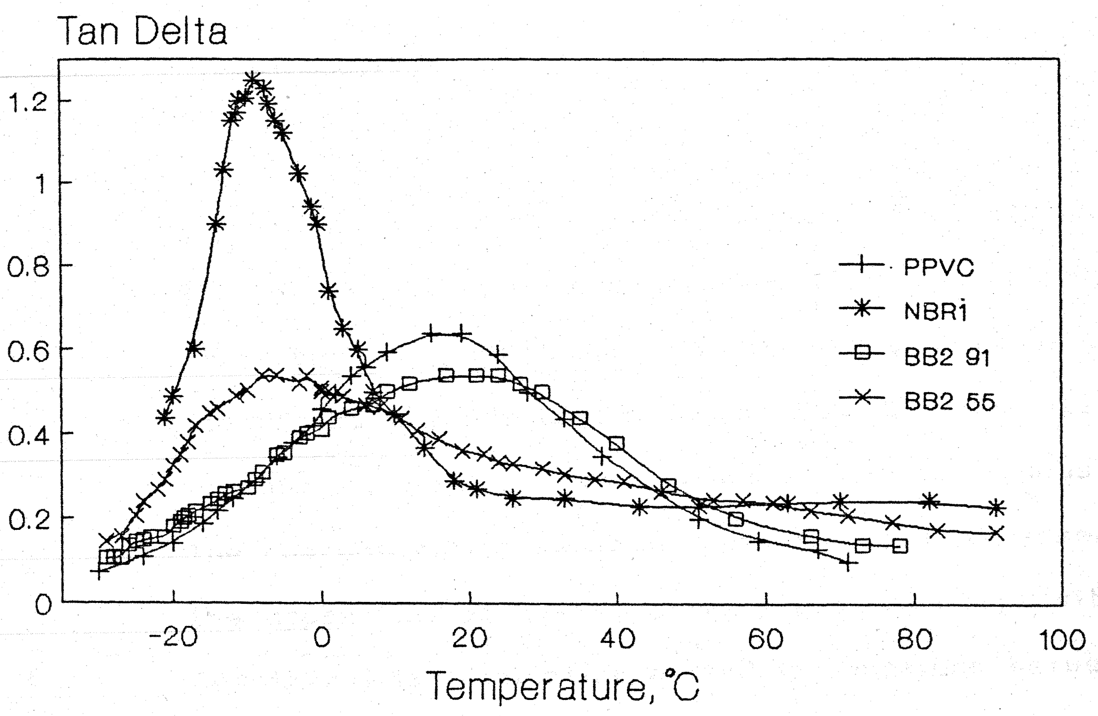


Fig. 4.3.7 Tan delta vs. temperature plots for binary blends, PPVC-NBR1

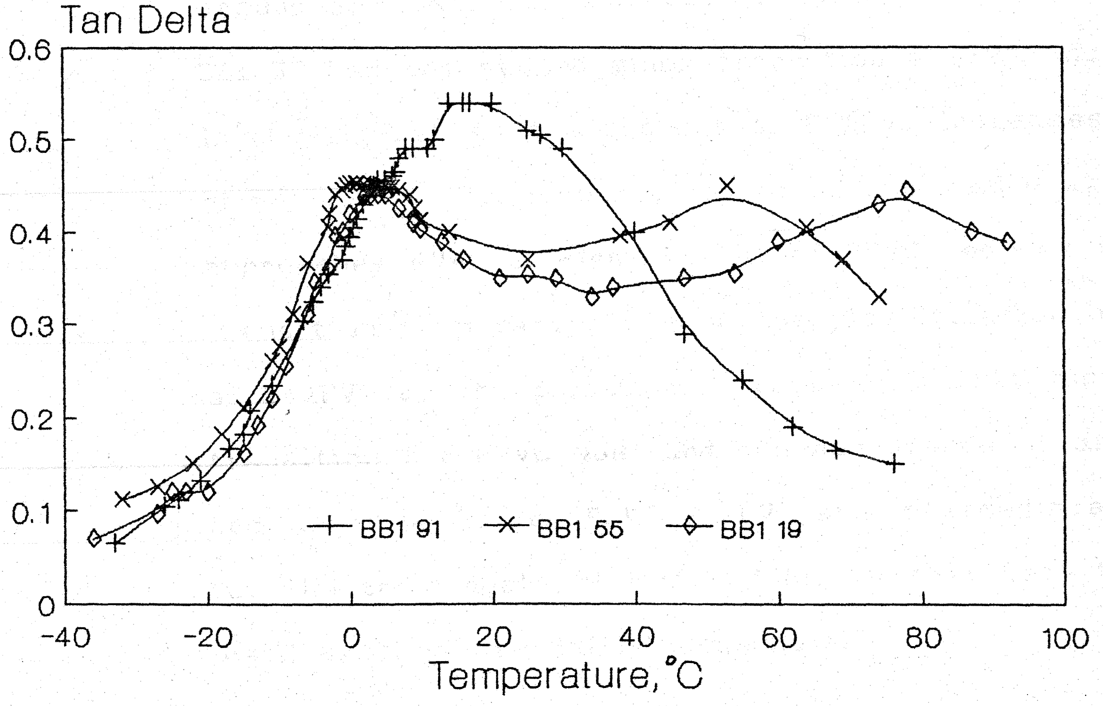


Fig. 4.3.8 Tan delta vs. temperature plots for binary blends, PPVC-EVAPVC

PPVC-EVAPVC binary blends, shown in Fig. 4.3.8, indicate the presence of only one transition for BB1 91 and two transitions for BB1 55 and BB1 19. Tan δ_{max} also is lesser for BB1 55 and BB1 19. BB1 91 has 90% PPVC and its property is more influenced by PPVC which is the continuous phase. The characteristic separate peak for PPVC is absent and the upper tail of EVAPVC primary peak overlaps with the PVC transition indicating marked interactions between the two polymers. EVAPVC influences the characteristics of both BB1 55 and BB1 19 and thus second minor transition appears. It can be noted that the second minor transition is at around 53°C, and 75°C for BB1 55 and BB1 19 respectively. BB1 37 had the second minor transition at 62°C (not shown in the figure). As the content of EVAPVC increases in the binary blend, the second minor transition temperature approaches EVAPVC. High content of PPVC reduces this transition temperature due to the plasticization of the PVC of EVAPVC by the plasticizers present in PPVC. Only one transition for PPVC-NBR1 and non-appearance of any additional peaks for PPVC-EVAPVC and intermediate behaviour for the tan δ peaks of blends indicate that both the binary blend systems are fairly compatible.

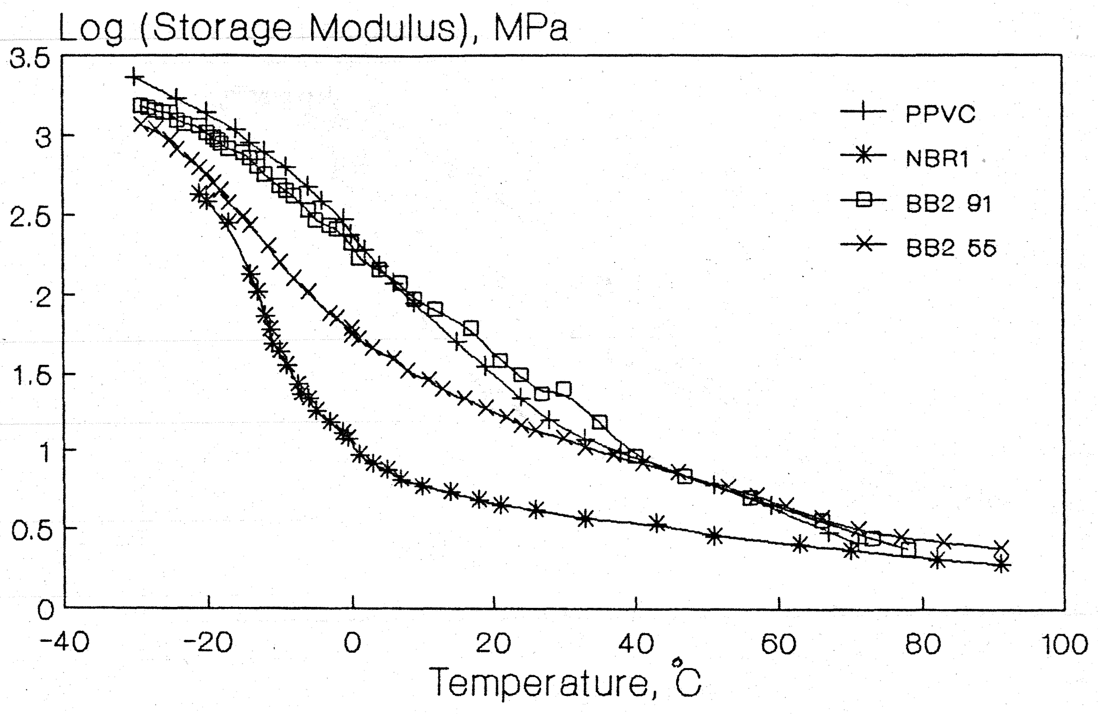


Fig.4.3.9 Storage Modulus as a function of temperature for PPVC-NBR1 blends

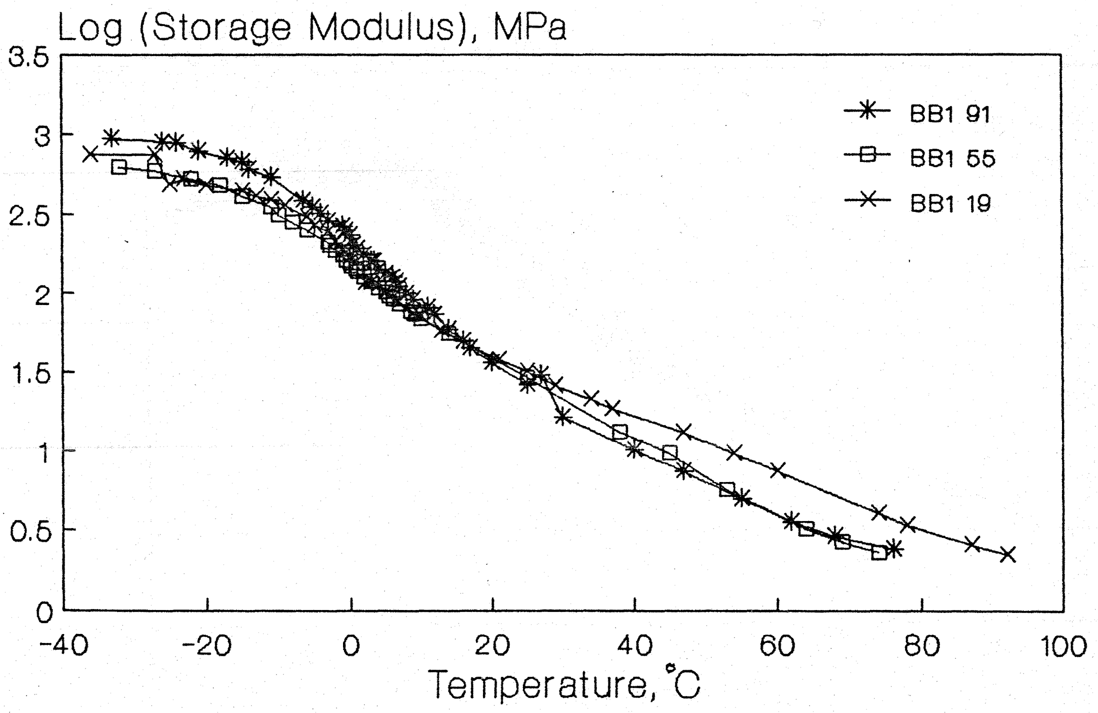


Fig. 4.3.10 Storage modulus of blends of PPVC-EVAPVC as a function of temperature

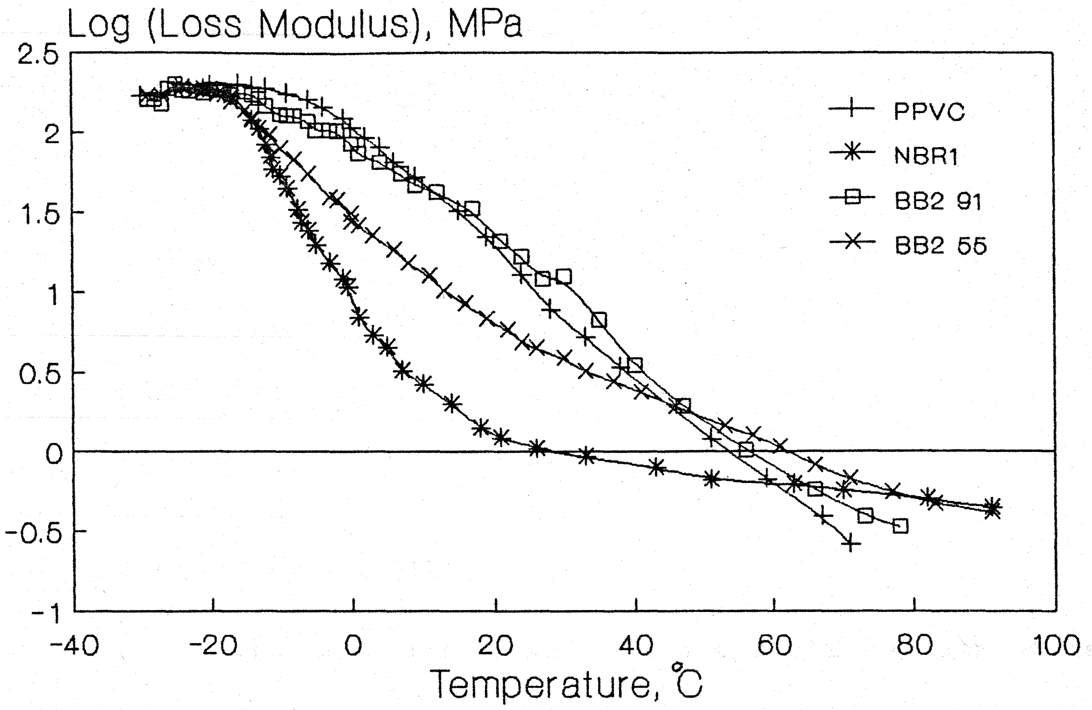


Fig. 4.3.11 Loss modulus as a function of temperature for PPVC-NBR1 blends

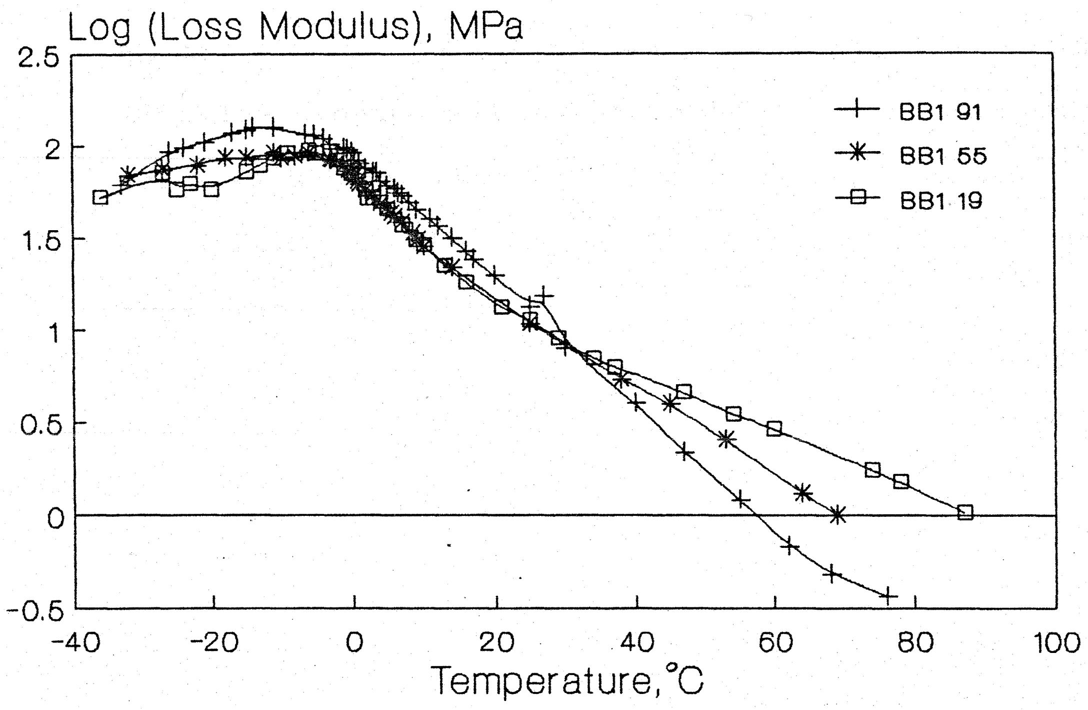


Fig. 4.3.12 Loss modulus as a function of temperature for PPVC-EVAPVC blends

Storage and loss modulus plots for the two binary blend systems shown in Figs. 4.3.9 to 4.3.12 confirm the observations and conclusions made from the results of tan δ plots. Comparison of these plots with the 'pure' components also indicate intermediate nature of the blends.

4.3.1.4 Ternary Blends

Data on tan δ versus temperature behaviour of ternary blends are presented in Fig. 4.3.13. The plots are characterized by single transition with broader peaks. The transition temperature is influenced by the relative amount of each 'pure' component. Tan δ_{max} is within 0.45 to 0.80 for all the blends, the maximum being for TB112 which has 50% NBR1. The storage and loss modulus plots for these blends are also indicative of fairly good interactions and compatibility of the components as is evident from the Figs. 4.3.14 and 4.3.15.

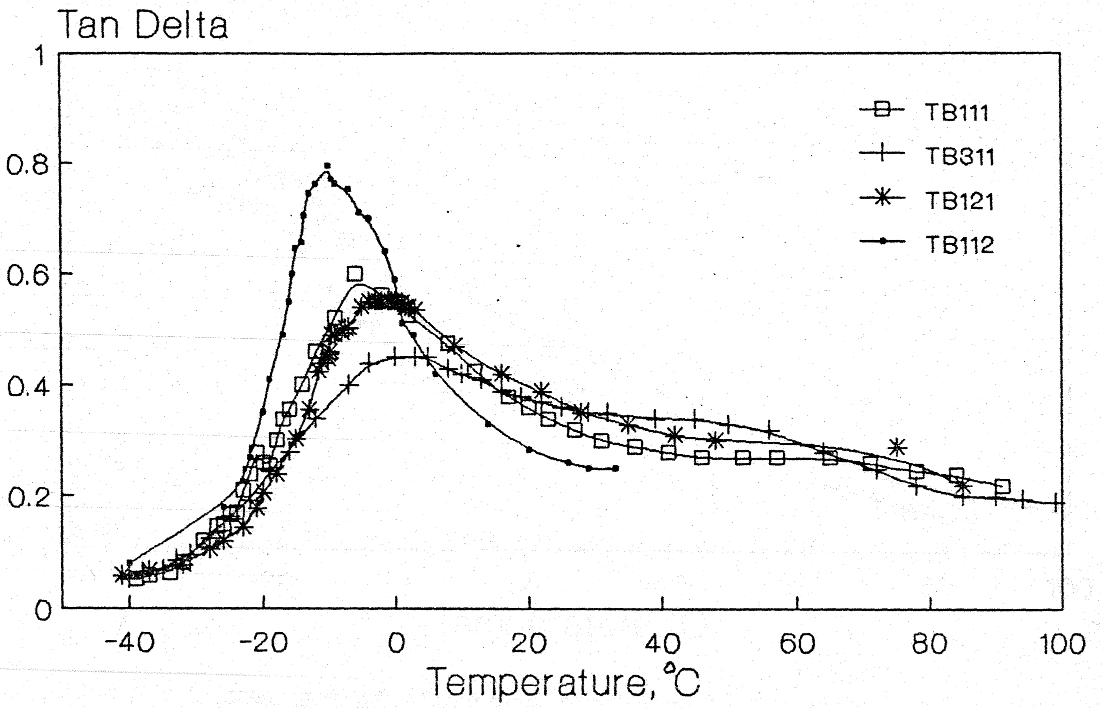


Fig. 4.3.13 Tan delta vs. temperature plots for ternary blends

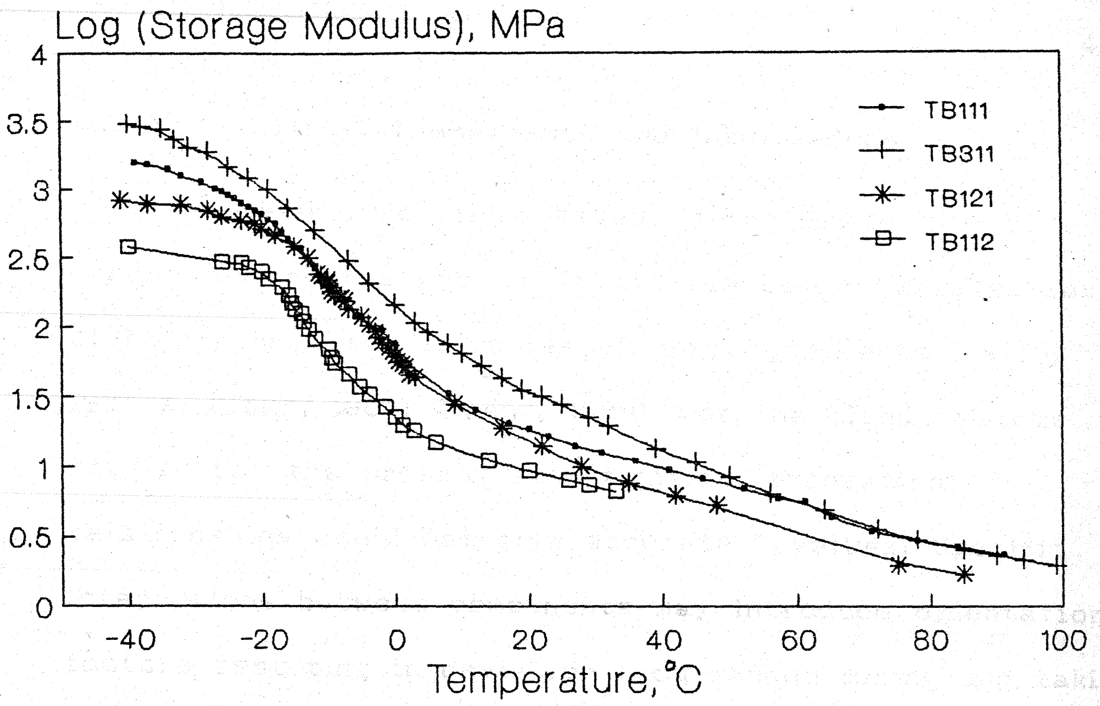


Fig. 4.3.14 Storage modulus of ternary blends as a function of temperature

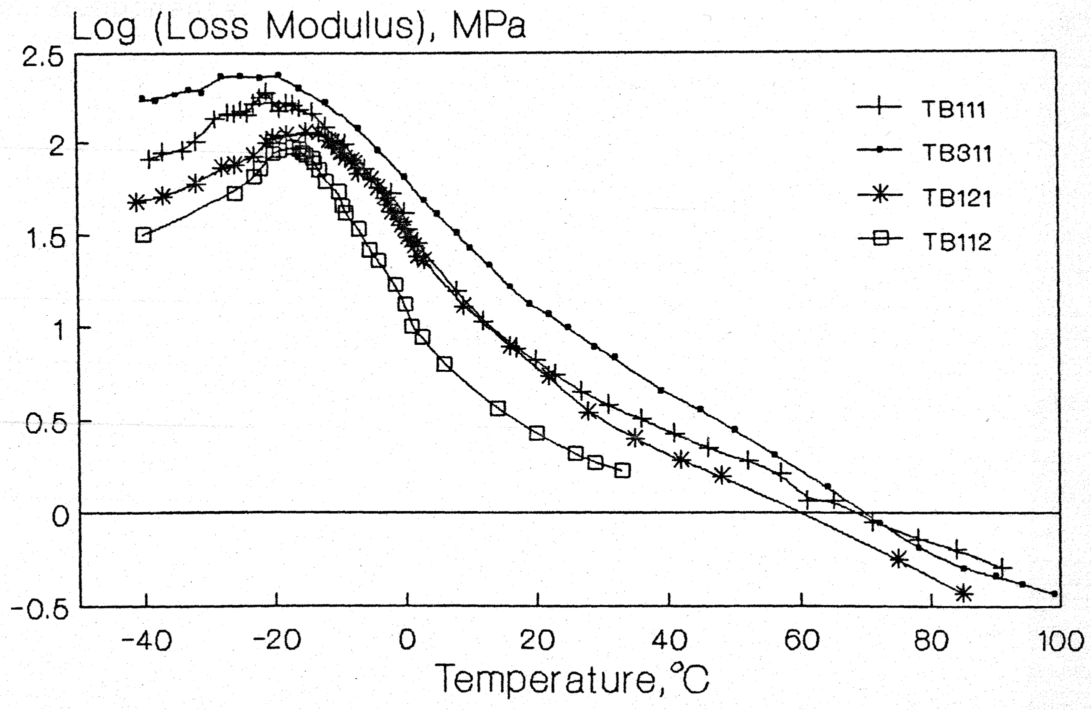


Fig. 4.3.15 Loss modulus as a function of temperature for ternary blends

4.3.1.5 Transition Temperature and Interactions

Theoretical relations based on the assumption of random mixing at segmental level have been suggested for T_g of blends from the T_g values of pure components (Walsh, 1984 a; Plans, 1984; Qipeng, 1990). For the blend systems studied for the present investigation, theoretical relationships could not give accurate T_g values. Specific interactions between components may introduce orientation factors resulting in deviation from random mixing and taking the arguments of Plans et al. (Plans, 1984) one can further conclude that deviation of experimental from theoretical T_g values gives indication of presence of interactions between components.

4.3.2 Brittleness Temperature

Brittleness temperature of the samples studied are shown in Figs. 4.3.16 to 4.3.18. From Fig. 4.3.16, it is seen that the brittleness temperature of polyester blends are higher than PPVC. This is expected due to the lesser quantity of plasticizer in PE3 and PE6. PE6 has the brittleness temperature marginally higher than PE3. This is also expected because molecular weight of PE3 is lower than that of PE6.

As expected, the binary blends have intermediate brittleness temperature (Fig. 4.3.17). The ternary blends also generally show similar behaviour excepting TB311 (60% PPVC) and TB811 (80% PPVC) which for unknown reasons have brittleness temperature higher than any other blends or 'pure' components.

One interesting point to note is that though PPVC has T_g (around 17°C) higher than both EVAPVC (around -1°C) and NBR1 (around -9°C), it gives the lowest brittleness temperature. Brittleness temperature of all the 'pure' components are in the glassy region and PPVC seems to be able to dissipate more energy at temperatures below T_g due to the presence of large quantity of plasticizer.

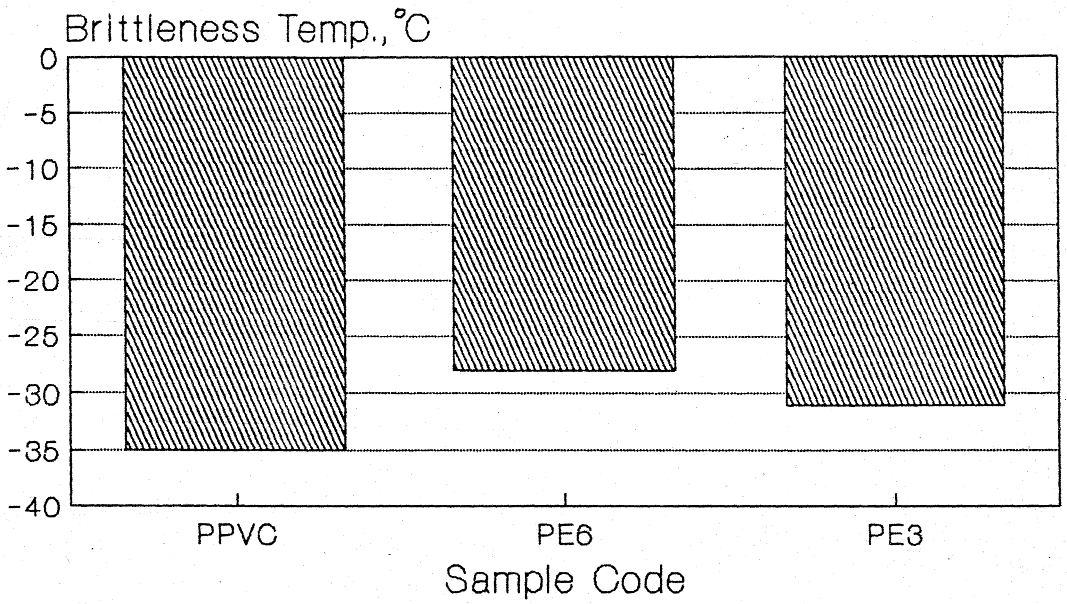


Fig. 4.3.16 Brittleness temperature of PPVC and polyester blends

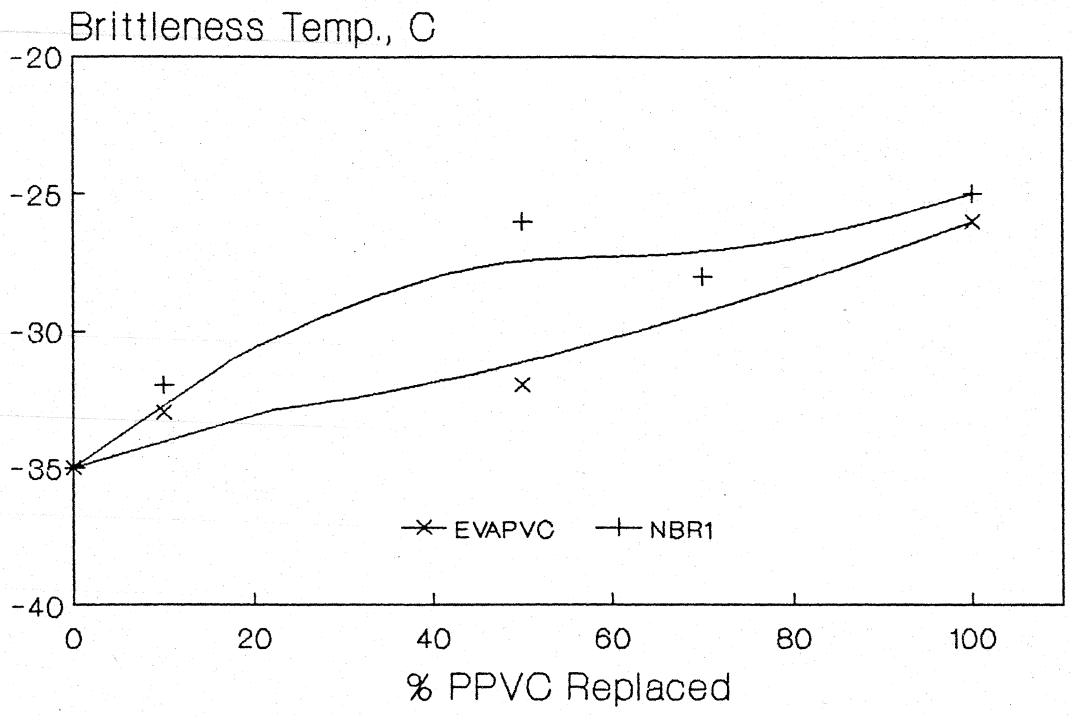


Fig. 4.3.17 Brittleness temperature of PPVC-EVAPVC and PPVC-NBR1 binary blends

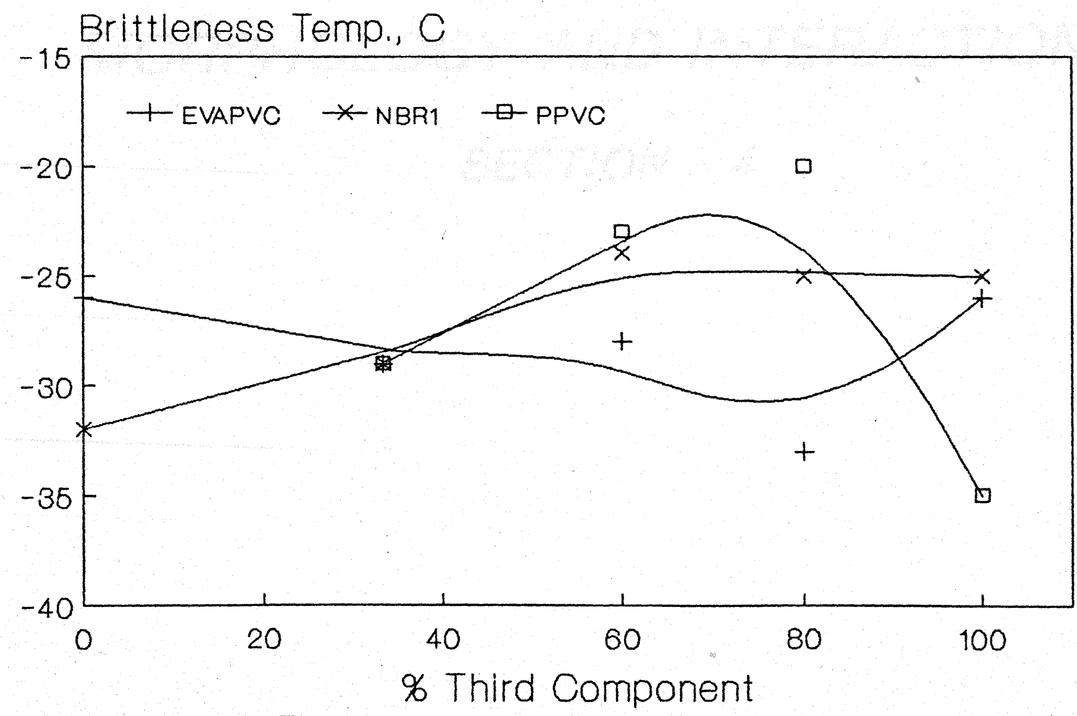


Fig. 4.3.18 Brittleness temperature of ternary blends with equal fractions of two components

MORPHOLOGY AND INTERACTIONS

SECTION - 4

4.4 MORPHOLOGY AND INTERACTIONS

Knowledge of morphology and presence or absence of interactions in polyblends help in understanding the behaviour of polyblends. The technique of scanning electron microscopy is one of the important methods to probe into the morphology of polyblends (Matsuo, 1968; Kruse, 1973; Ma, 1989). FTIR technique has been used to study the mechanisms of interactions between polymers by a number of workers in the area (Coleman, 1979; Coleman, 1984; Ting, 1980).

In this section, results of the studies with scanning electron microscope and FTIR are reported with discussions for the observed behaviour.

4.4.1 Scanning Electron Microscope

4.4.1.1 Effect of Method of Sample Preparation

Sample preparation for the SEM studies was done by casting and two roll mill technique. Fig. 4.4.1 shows SEM pictures of cast film of one 'pure' component PPVC. Scanning electron photomicrograph of the sample made by two roll mill is shown in Fig. 4.4.2. As can be seen, the cast film is totally featureless, indicating single phase behaviour. The sample prepared by two roll mill at 160°C shows uniformly distributed globular morphology even at lower magnification. The 'globule' like characteristics with a size of 2-3 microns is due to the presence of incompletely melted PVC particles. Probably, blending in two roll mill at higher temperature and for longer durations may give featureless morphology as in cast film. The early studies by Walters and Keyte (1965) for different system also support this speculation. In fact, the rolled sample of EVAPVC has the same morphology as the cast film of PPVC as shown in Fig. 4.4.3. This is because, EVAPVC is lower melting than PPVC and all the solid particles get completely melted.

SEM picture of the cast film of binary blends BB1 55 and BB1 37 are shown in Figs. 4.4.4 and 4.4.5 and both are characterized by absence of any contrasting phases. The wavy appearance is the pattern that developed during solvent evaporation. Samples prepared by two roll mill for BB1 55 (Fig. 4.4.6) and BB1 37 (Fig. 4.4.7) have altogether different morphology. From both of these pictures presence of two phases are apparent.

It can be concluded from the observations made that the method of sample preparation affects the morphology of the blends. This phenomenon has been observed by many other researchers for other systems (Kresge, 1978; Beecher, 1969).

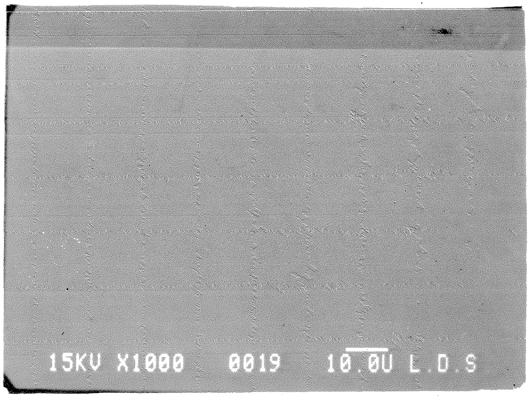


Fig. 4.4.1 High magnification (X 1000) photomicrograph of cast film of PPVC

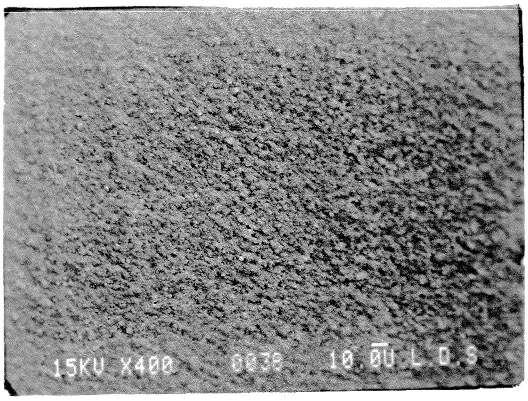


Fig. 4.4.2 High magnification (X 400) photomicrograph of PPVC, sample prepared by two roll mill

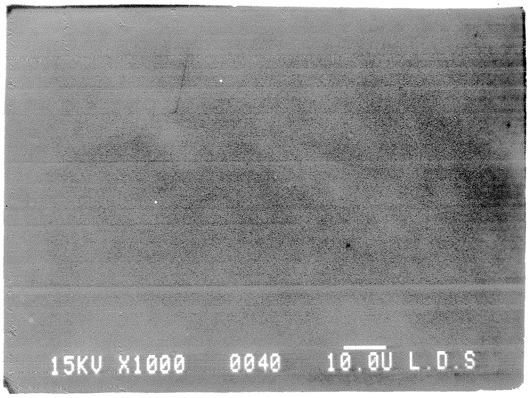


Fig. 4.4.3 Photomicrograph (X 1000) of EVAPVC, sample prepared by two roll mill

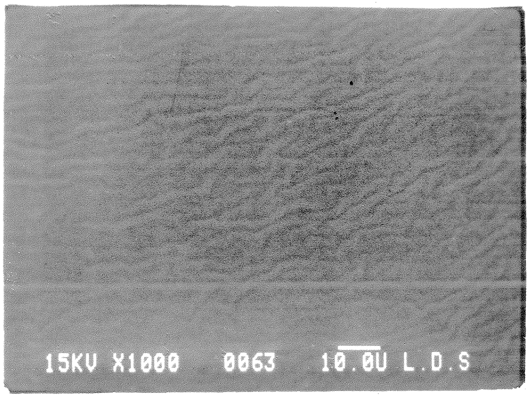


Fig. 4.4.4 High magnification (X 1000) photomicrograph of cast film of BB1 55

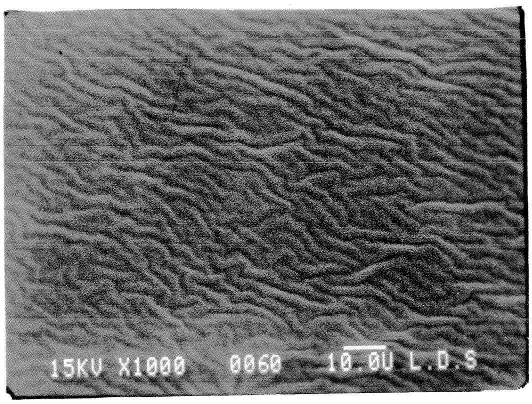


Fig. 4.4.5 High magnification (X 1000) photomicrograph of cast film of BB1 37

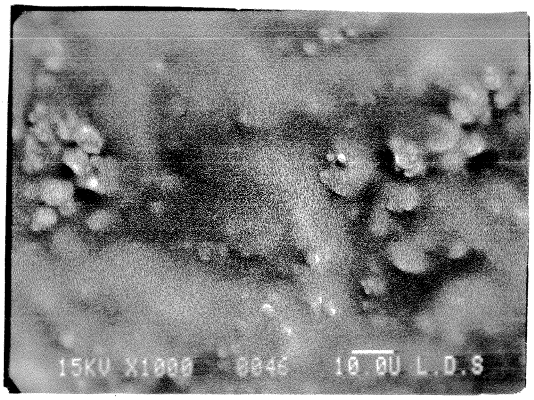


Fig. 4.4.6 Scanning electron micrograph (X 1000) of BB1 55, sample prepared by two roll mill

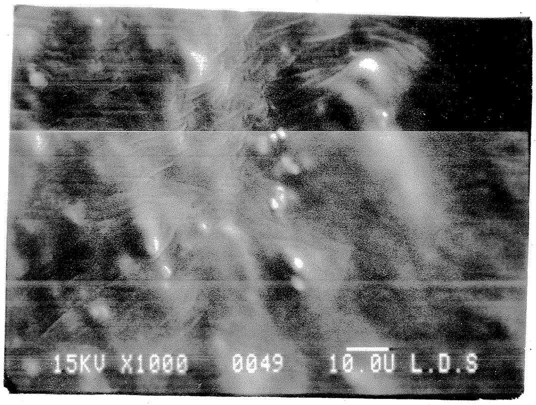


Fig. 4.4.7 SEM micrograph (X 1000) of BB1 37, sample prepared by two roll mill

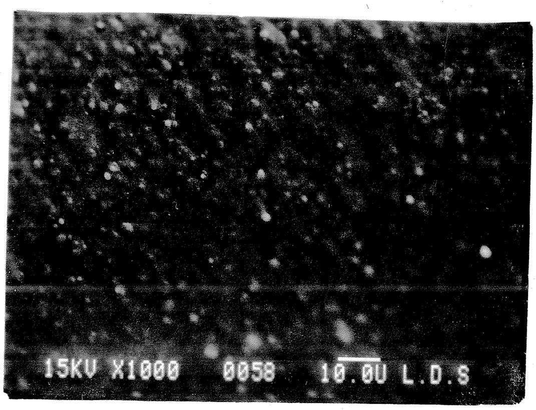


Fig. 4.4.8 Photomicrograph (X 1000) of BB2 91, sample prepared by two roll mill

4.4.1.2 Binary Blends

Figs. 4.4.8 to 4.4.10 show the SEM pictures of milled samples of BB2 91, BB2 55 and BB2 37 respectively and these are binary blends of PPVC-NBR1. Presence of uniformly distributed dispersed phase is evident in all the pictures as has been reported by other workers (Rovatti, 1963; Matsuo 1969 b). By comparing the area occupied by the continuous and dispersed phases in Fig. 4.4.8, it becomes clear that PPVC is the continuous phase. In case of BB2 55 (Fig. 4.4.9) the uniformly distributed dispersed phase is present more prominently and it becomes difficult to predict which component is matrix. In Fig. 4.4.10, it is observed that the amount of dispersed phase is lesser than the previous two figures and since BB2 37 has 70% NBR1, this must be the continuous phase.

SEM pictures of binary blends of PPVC-EVAPVC, BB1 55 and BB1 37 are shown in Figs. 4.4.6 and 4.4.7. From both of these photomicrographs presence of two phases are apparent. The dispersed phase is PPVC and in BB1 55 some occasional agglomerated PPVC with globule size of about 2 microns are seen. In BB1 37 the relative presence of these globules are reduced confirming that EVAPVC is the matrix phase and PPVC is the dispersed phase.

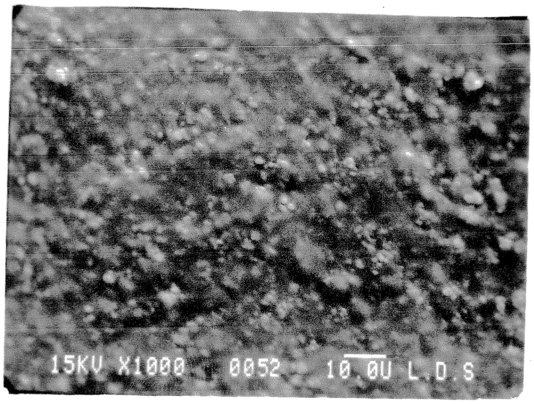


Fig. 4.4.9 SEM micrograph (X 1000) of BB2 55, sample prepared by two roll mill

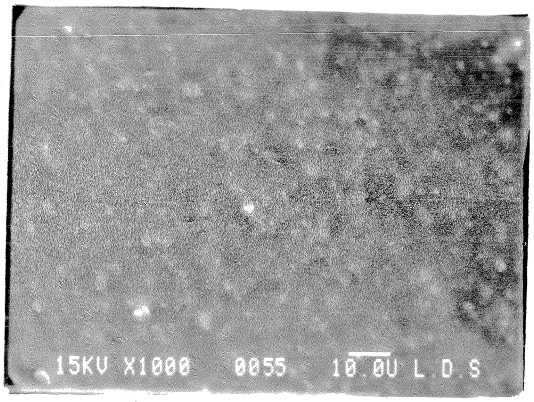


Fig. 4.4.10 Photomicrograph (X 1000) of BB2 37, sample prepared by two roll mill

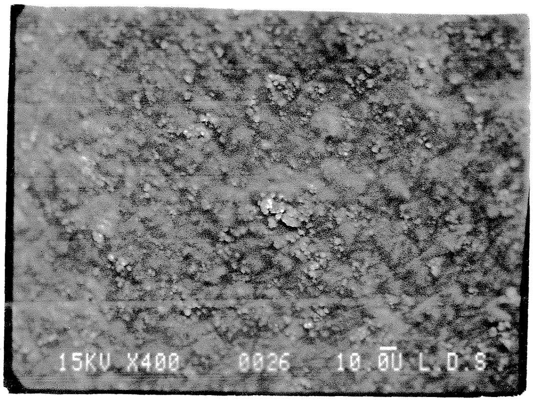


Fig. 4.4.11 Photomicrograph (X 400) of TB111, sample prepared by two roll mill

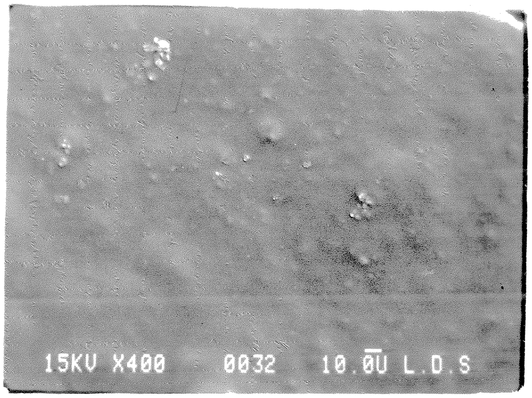


Fig. 4.4.12 Scanning electron photomicrograph (X 400) of TB131, sample prepared by two roll mill

4.4.1.4 Homogeneity

Homogeneity is a relative term. If one goes into molecular level, even a single pure polymer like polyethylene is not homogeneous due to the difference in molecular weight and the distribution. But for all practical purposes, polyethylene is never considered inhomogeneous. For a polyblend to be used in an application, other properties of the blend, like mechanical, optical, processing etc., are to be considered. If a polyblend is not so homogeneous in molecular level and yet it has properties good enough for an application, a practical scientist would consider it acceptable (Deanin, 1974). However, if homogeneity is so poor that polyblending results in delamination, agglomeration, and uneven distribution of one in the other, the polyblend is not likely to be useful.

Figs. 4.4.6 to 4.4.13 show clearly the presence of dispersed phase in the blends. DMA studies (Section 4.3.1) indicate single phase behaviour for all the blends. This discrepancy in DMA and SEM results are, as suggested by Swinyard et al. (1990), due to the fact that T_g analysis cannot detect minor phase separation.

Films of TB111 (Fig. 4.4.11), BB2 55 (Fig. 4.4.9), and BB1 55 (Fig. 4.4.6) which are characterized by prominent presence of two phases at high magnification are practically

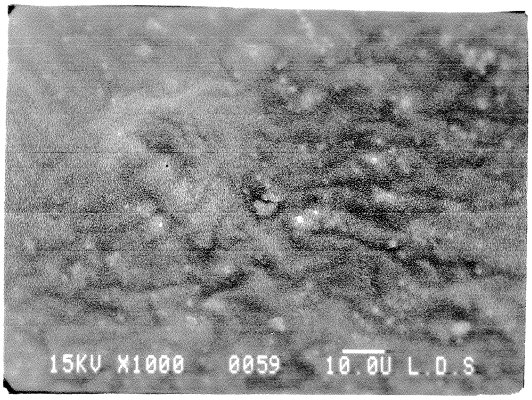


Fig. 4.4.13 High magnification (X 1000) photomicrograph of TB118, sample prepared by two roll mill

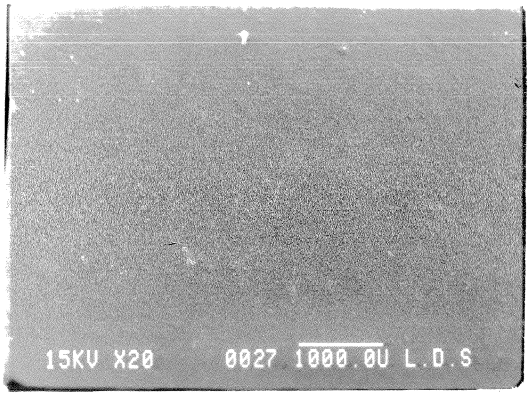


Fig. 4.4.14 Scanning electron micrograph (X 20) of TB111, sample prepared by two roll mill

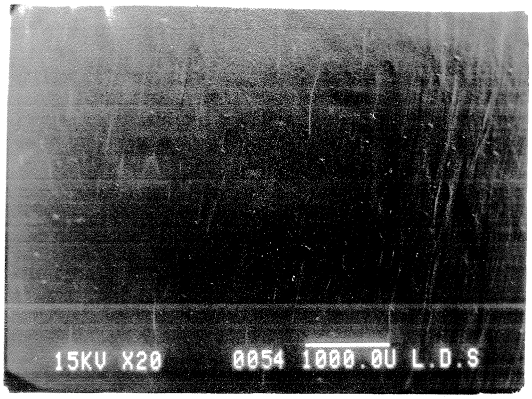


Fig. 4.4.15 SEM micrograph (X 20) of BB2 55, sample prepared by two roll mill

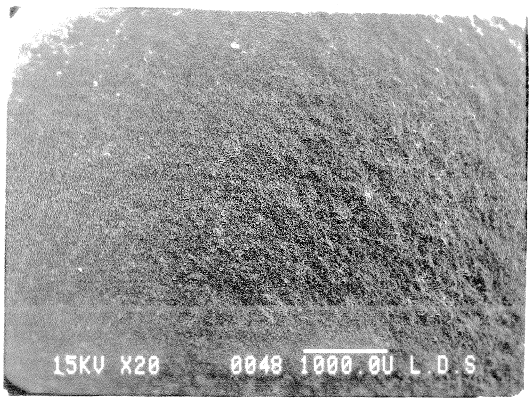


Fig. 4.4.16 Photomicrograph (X 20) of BB1 55, sample prepared by two roll mill

4.4.2 *FTIR Studies*

Some level of thermodynamic compatibility is necessary between components of polyblend to prevent phase separation during processing and use. Specific interactions like dipole-dipole, van der Waals and hydrogen bonding among the components of a polyblend help in having better miscibility. FTIR technique gives evidence of the existence of such interactions. Frequency shifts and band broadening for blends have been ascribed to intermolecular chemical interactions and changes in polymer chain conformations (Macknight, 1989). The technique of comparing difference spectra with that of 'pure' components is an important method in studying intermolecular interactions. Coleman et al. (1979; 1984) have used this technique extensively.

4.4.2.1 'Pure' Components

The spectra of 'pure' components PPVC, EVAPVC and NBR1 are shown in Figs. 4.4.17 to 4.4.25. The characteristic peaks for these components are tabulated in Tables 4.4.1 to 4.4.3.

TABLE 4.4.1 Peaks of IR Spectra of PPVC

Wave Number, cm^{-1}	Peak Characteristics
1723.4	-C=O stretching of ester of plasticizer
1426.4	-C-H bending deformation of $-CH_2-$ saturated
1332.8	=C-H in plane bending in CHCl
1274	=C-H in plane bending in CHCl
1254.7 (shoulder)	=C-H in plane bending in CHCl
1072.4	-C-C- stretching
957.7	-C-H rocking (bending) of $-CH_2-$ saturated

TABLE 4.4.2 Peaks of IR Spectra of NBR1

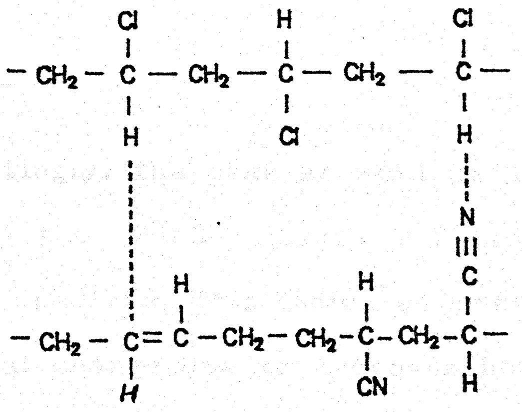
Wave Number, cm^{-1}	Peak Characteristics
1447.6	-C-H deformation of saturated $-CH_2$ of butadiene
974	trans -C-H stretching of unsaturated -CH=CH-
963.4	trans -C-H stretching of unsaturated -CH=CH-
918.1	cis -C-H stretching of -CH=CH-

TABLE 4.4.3 Peaks of IR Spectra of EVAPVC

Wave Number, cm^{-1}	Peak Characteristics
1745.8	-C=O stretching of vinyl acetate
1719.5	-C=O stretching of vinyl acetate
1462	-CH deformation bending of saturated $-CH_2$ in ethylene unit
1434.1	-CH deformation of saturated $-CH_2$ in vinyl chloride unit
1371.4	-C-H deformation of saturated $-CH_2$ in ethylene unit
1220	-C-O stretching of vinyl acetate unit
1119.7	-C-O stretching of vinyl acetate unit
1022.3	-C-O stretching of vinyl acetate unit
958.6	-C-H rocking (bending) of saturated $-CH_2$ in vinyl chloride unit

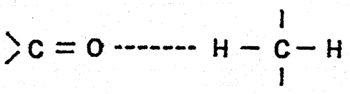
4.4.2.2 PPVC-NBR1 Binary Blends

The interactions through hydrogen bonding for this blend system is expected to take place as shown here.



—— (A)

BB2 91-PPVC difference spectrum (Fig. 4.4.17) indicates shifting of the peak for trans-CH stretching of unsaturated -CH=CH- group of butadiene from 974 cm^{-1} to 967.3 cm^{-1}. The peak at 1447.6 cm^{-1} present in pure NBR1 is shifted to 1435 cm^{-1}. Such a shift is expected in the blend due to the hydrogen bonding through the -CH of saturated $-CH_2$ group of butadiene with free plasticizer present in PPVC. The plasticizer ester peak originally appears at 1723.4 cm^{-1} in PPVC. But, in the subtracted spectrum two peaks are observed. The peak at 1733 cm^{-1} is due to the free plasticizer and the one at 1718.6 cm^{-1} reflects shift due to hydrogen bonding as shown in the next page.



$$>C=O\cdots\cdots H-\overset{|}{\underset{|}{C}}-H \qquad \text{——— (B)}$$

Interestingly, the peak at 918.1 cm^{-1} for cis -CH stretching of the -CH=CH- group of butadiene disappears in BB2 91-PPVC spectrum. This indicates possibilities of conformational change due to hydrogen bonding. In BB2 55-PPVC and BB2 19-PPVC spectra (Figs. 4.4.18 and 4.4.19), peaks responsible for the cis-CH stretching of the -CH=CH- group appears indicating moderate degree of hydrogen bonding. The peak at around 1446 cm^{-1} for the pure NBR1 also appears for these blends. The original plasticizer (in PPVC) ester peak also appears at around 1723 cm^{-1}. This indicates very little hydrogen bond formation through -CH of the saturated -CH_2 group of butadiene in these two blends.

Interaction is very good for BB2 91 where 10% PPVC is replaced with NBR1. This inference is also in conformity with the observation made for synergis~~i~~tic behaviour in ultimate tensile stress (Section 4.2.3) for BB2 91.

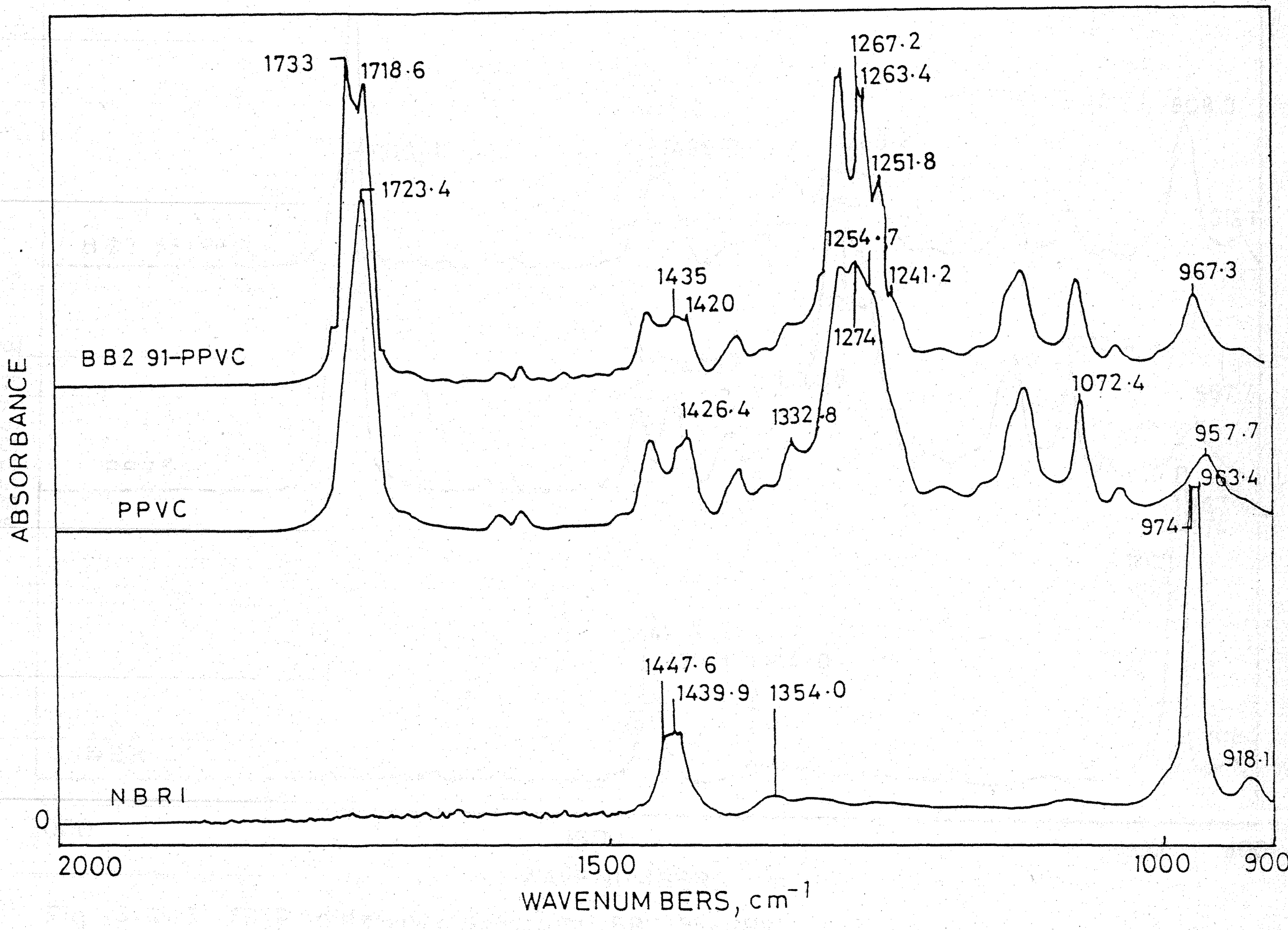


Fig. 4.4.17. FTIR difference spectrum, BB2 91–PPVC

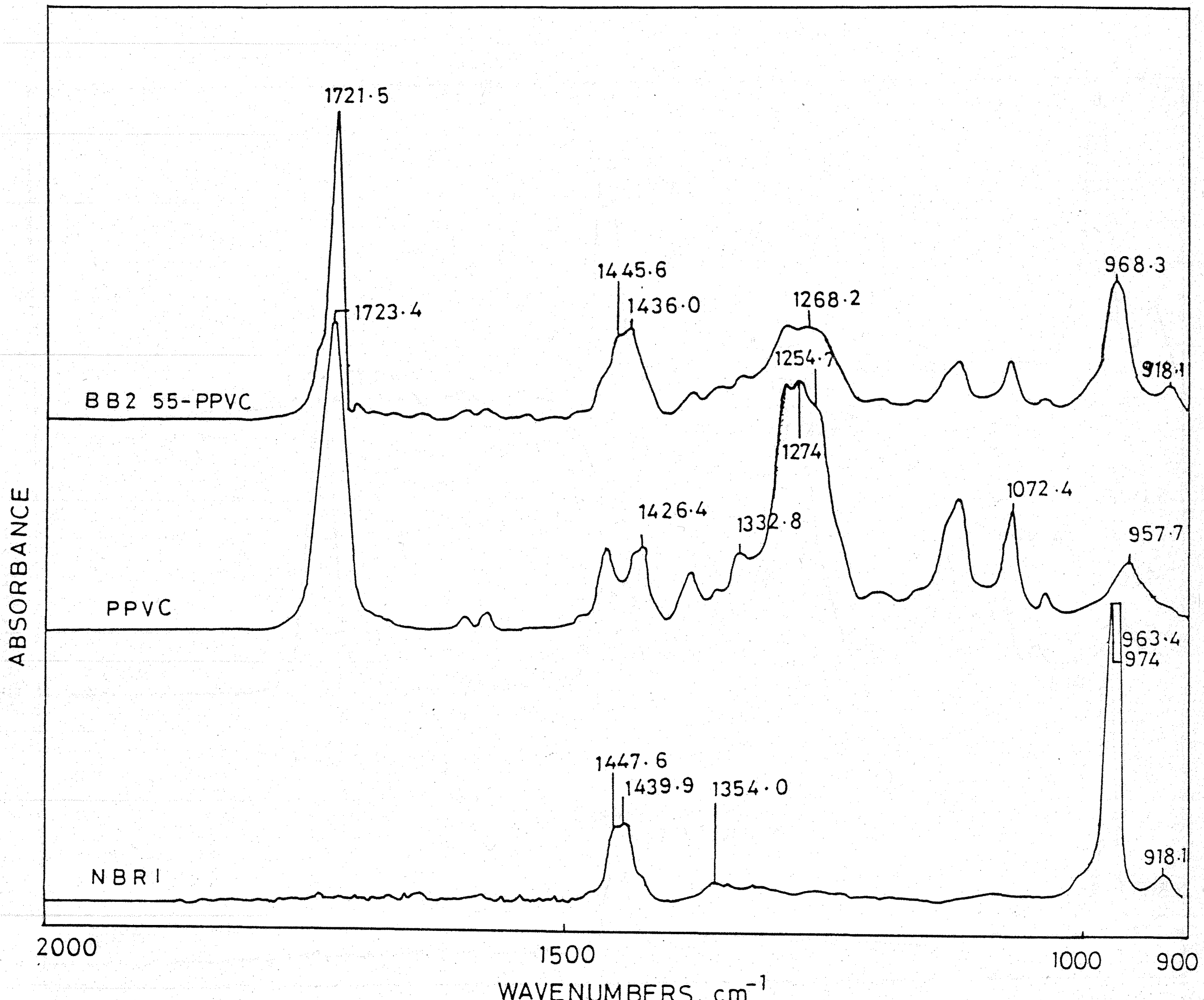


Fig ·4·4·18· FTIR difference spectrum, BB2 55-PPVC

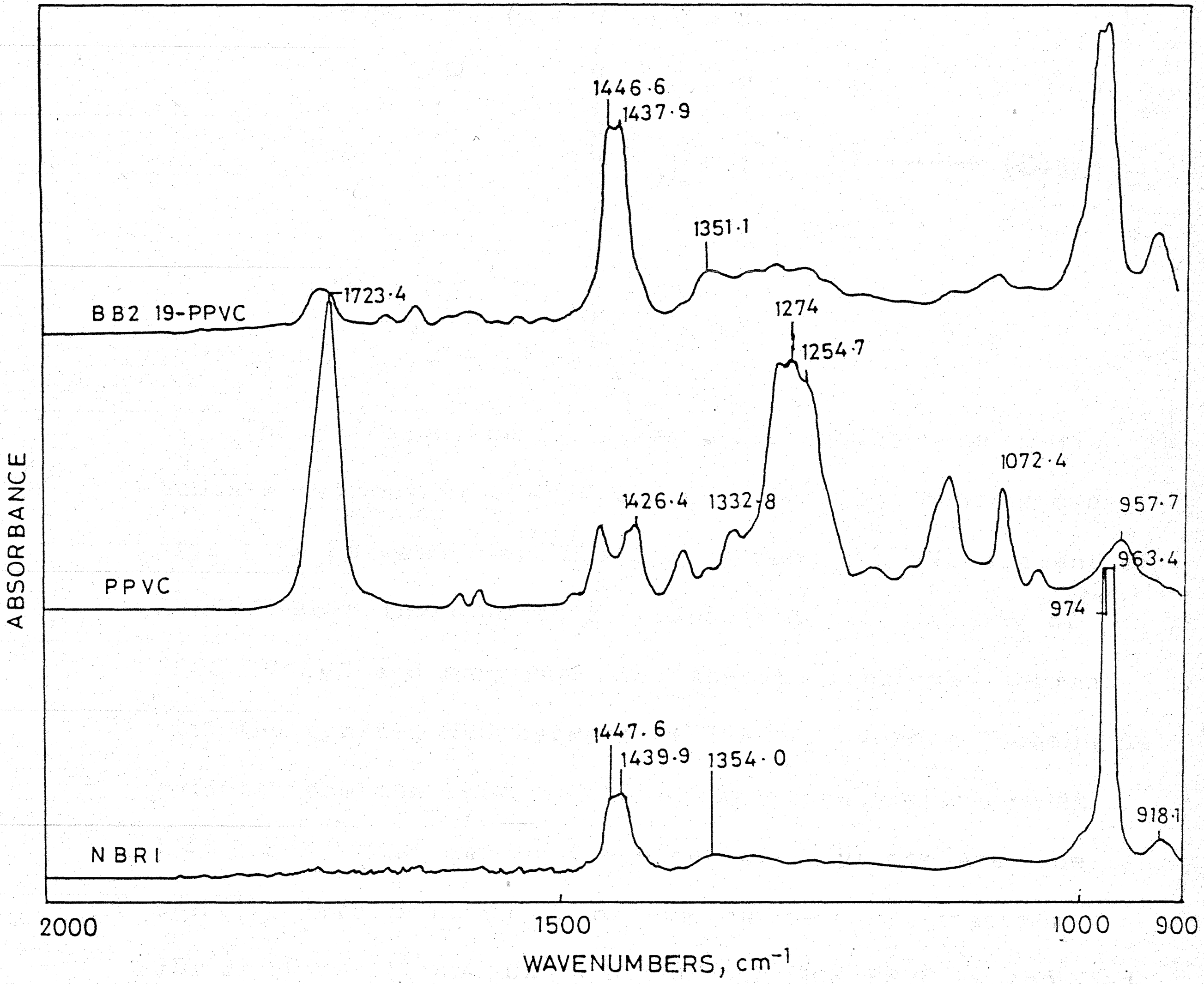
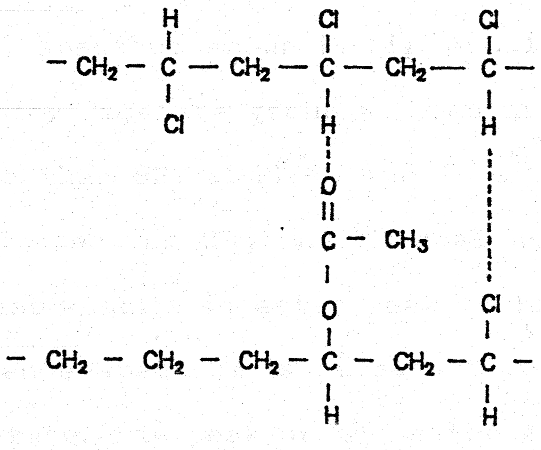


Fig. 4.4.19. FTIR difference spectrum, BB2 19-PPVC

4.4.2.3 PPVC-EVAPVC Binary Blends

PPVC-EVAPVC binary blends elicit hydrogen bonding through the oxygen of the ester group in vinyl acetate as shown below:



— (C)

The hydrogen bonding takes place between the vinyl acetate segment of EVAPVC and PVC. Hydrogen bonding can also form between vinyl acetate segment and PVC segment of EVAPVC. Both these effects enhance the compatibility of PPVC-EVAPVC and ethylene-vinyl acetate copolymer segment with the grafted PVC segment of EVAPVC. Hydrogen bonding is evident from the shift in the infrared spectral peaks at 1745.8 and 1719.5 cm^{-1} for the ester of vinyl acetate. The shift is very pronounced for the subtraction spectrum, BB1 91-PPVC (Fig 4.4.20). In BB1 91 only 10% PPVC is replaced with EVAPVC and vinyl acetate ester peak for this appears at 1737.9 and 1716.6 cm^{-1}. The shifting of the -CH bending peak in -CHCl from 1274 cm^{-1} (PVC) to 1244.1 cm^{-1} is due to the formation of hydrogen bonding through vinyl acetate group. Interestingly, two new peaks at 1294.2 and 1134.1 cm^{-1} appear in the blend. As reported by Allara (1979), this could arise from the optical phenomena due to the difference in the refractive indices of the polymers present in the blend. BB1 55-PPVC spectrum shown in Fig. 4.4.21, indicates multiple peaks for vinyl acetate group with an appreciable shift (though less than BB1 91-PPVC) due to interactions.

BB1 19-PPVC spectrum (Fig. 4.4.22) does not however, reveal any appreciable shift in ester peak to lower wave number. This difference spectrum is comparable to that of the polymer mixture. The peak of the ester group of plasticizer is either merged with ester band of the blend or it appears as a small peak at around 1723 cm^{-1}. From the amount of shift in the spectral appearance, it can, therefore, be concluded that interaction between PPVC and EVAPVC is in the order BB1 91> BB1 55> BB1 19 and generally the shifts are more for PPVC-EVAPVC system compared to PPVC-NBR1 system.

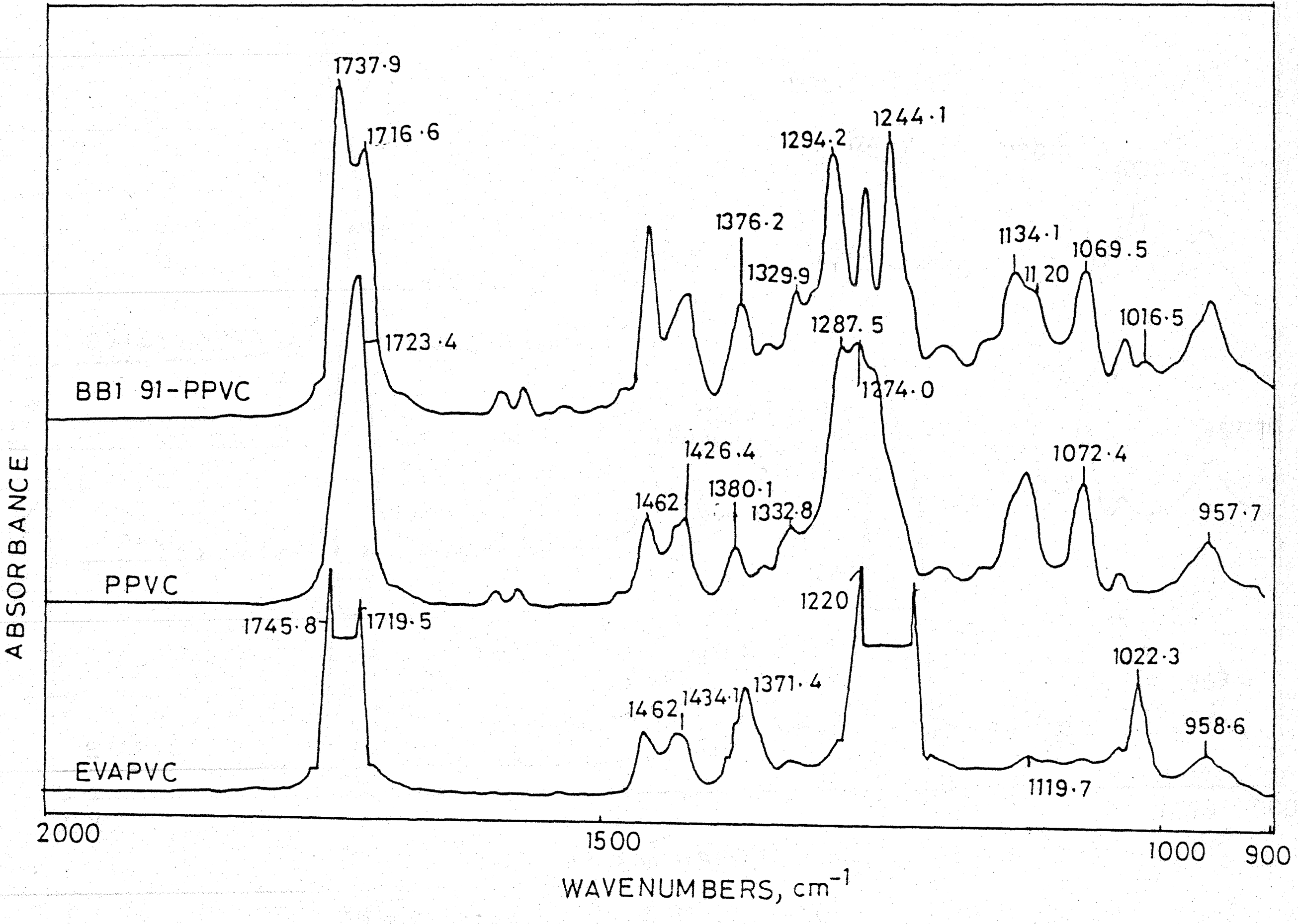


Fig · 4·4·20· FTIR difference spectrum, BB1 91-PPVC

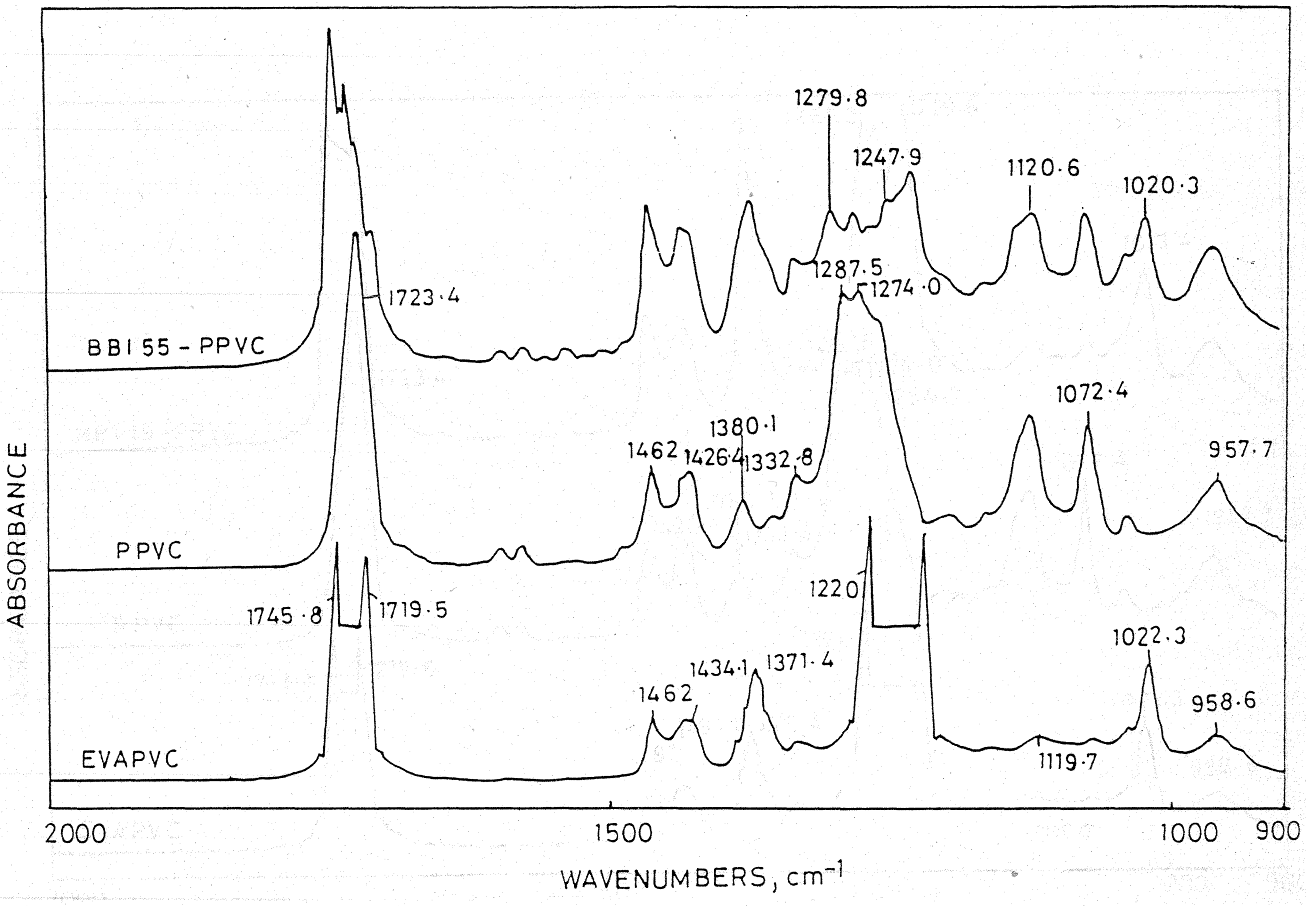
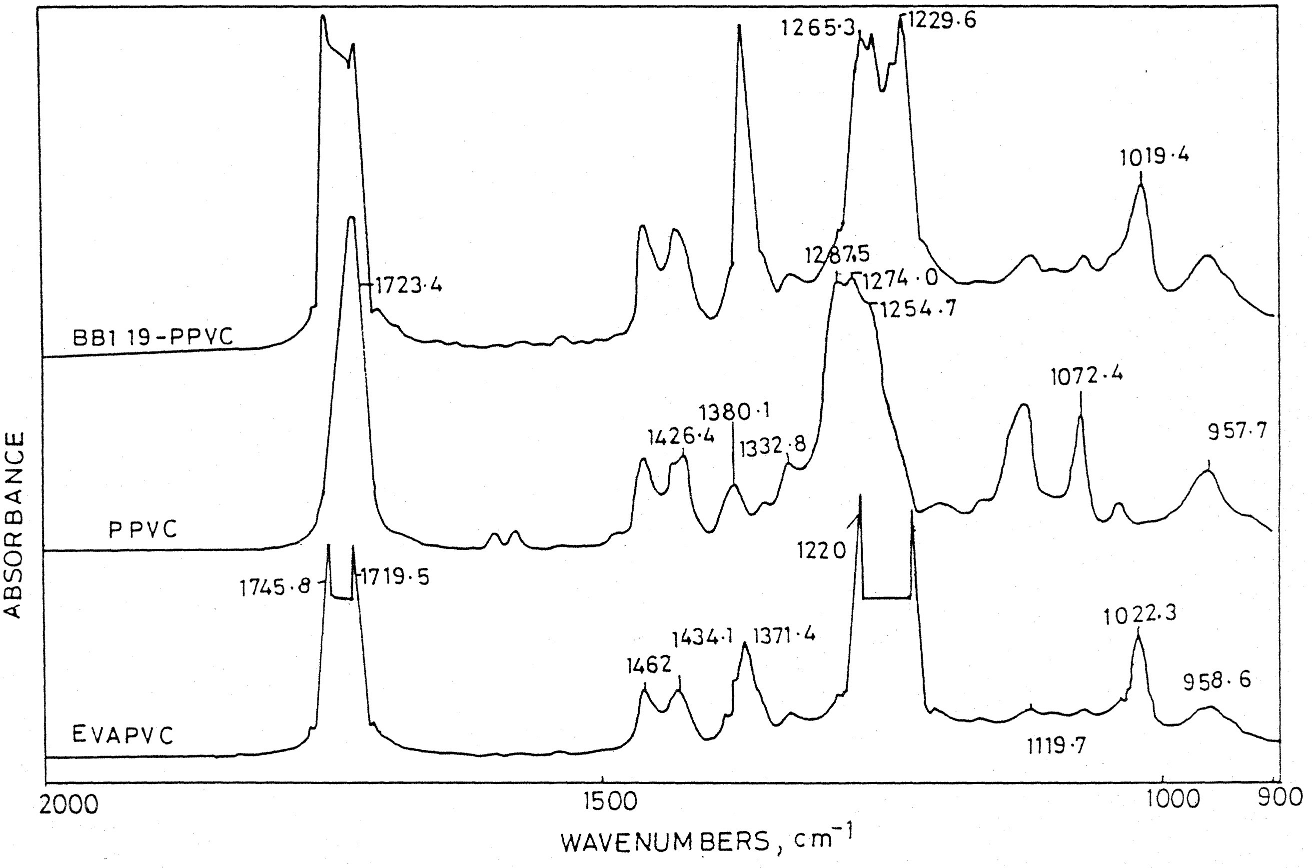


Fig ·4·4·21. FTIR difference spectrum, B B1 55-PPVC



Fig·4·4·22. FTIR difference spectrum, BB1 19-PPVC

4.4.2.4 Ternary Blends

Figs. 4.4.23 to 4.4.25 show the subtraction spectra TB811-PPVC, TB181-PPVC and TB118-PPVC. Fairly good interactions between polymer components are reflected in shift in ester peak to lower wave number in these spectra. The shift is due to the hydrogen bonding between vinyl acetate and vinyl chloride as discussed for PPVC-EVAPVC blend system. For TB811-PPVC, ester peak gets shifted from 1745.8 to 1738.8 cm^{-1} and the peak at 1723.4 cm^{-1} is attributed to the plasticizer DEHP. It also exhibits shift in the peak for -CH bending in CHCl of PVC from 1274 to 1247.9 cm^{-1}. The difference spectrum shows a broad band from 1288.4 to 1247.9 cm^{-1}. 1288.4 cm^{-1} plasticizer peak merges with -CH bending peak of PVC indicating intense hydrogen bonding interactions. The blends TB181 and TB118 exhibit more or less similar kind of interactions as is evident from the subtraction spectra of these blends.

The ternary blends also possess hydrogen bonding with butadiene units of NBR1 and vinyl chloride units of PPVC as well as acrylonitrile units of NBR1 and vinyl chloride units of PVC. For TB811, shift due to hydrogen bonding in the peak for trans -CH stretching of unsaturated -CH=CH- group of butadiene from 974 to 966.3 cm^{-1} is also seen. The peak for cis -CH stretching of the unsaturated group of butadiene at 918.1 disappears. This indicates conformational change due to hydrogen bonding. A similar kind of spectral response was noted for TB181. However, such a behaviour was not observed in case of TB118, though, a strong peak was observed at 967.3 cm^{-1}. The presence of a shoulder at 976.9 cm^{-1} indicates free butadiene and lesser degree of hydrogen bonding. In this blend, the hydrogen bonding between PVC and EVAPVC is more intense compared to that between PVC and NBR1 units.

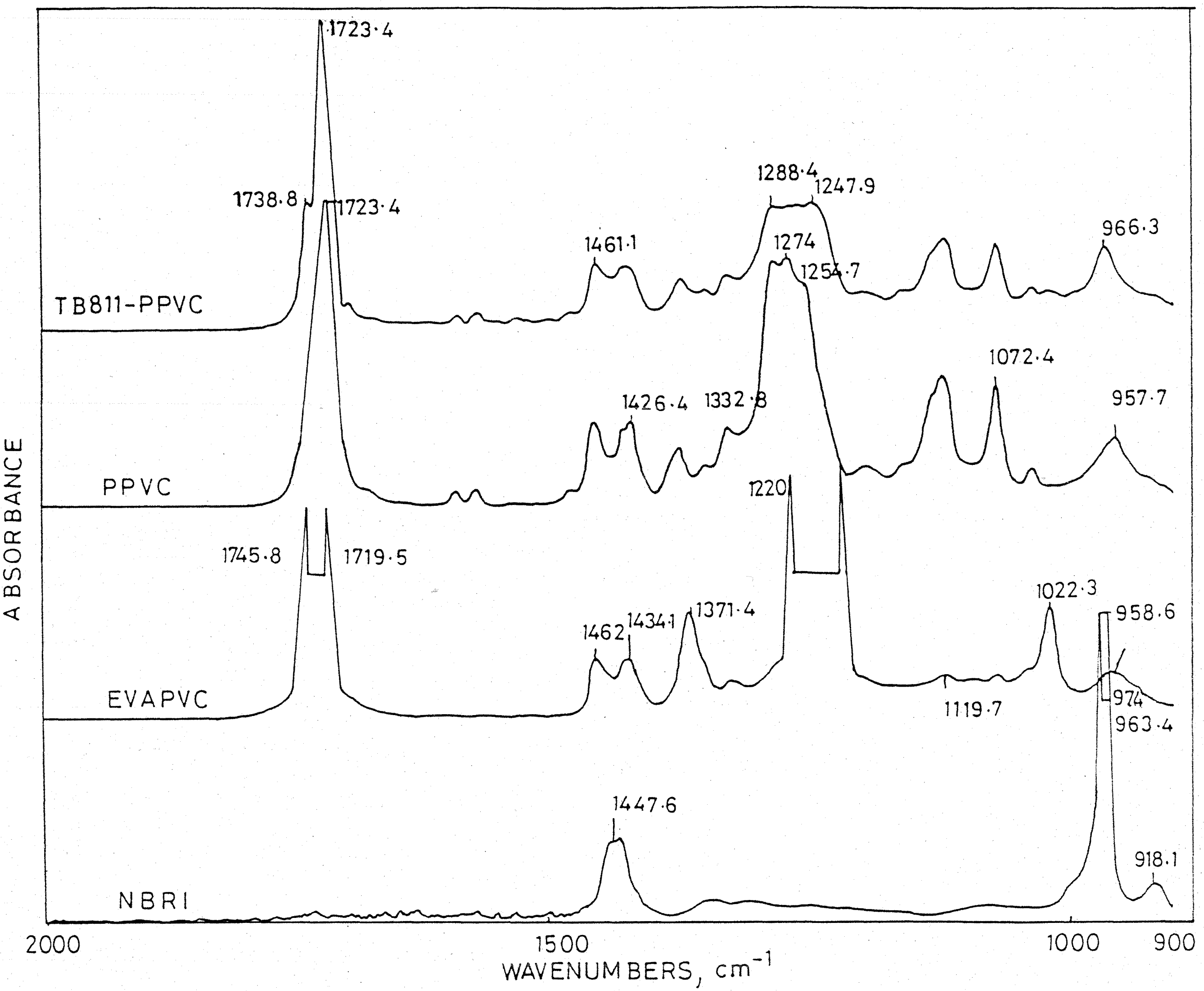


Fig .4.4.23 FTIR difference spectrum, TB811-PPVC

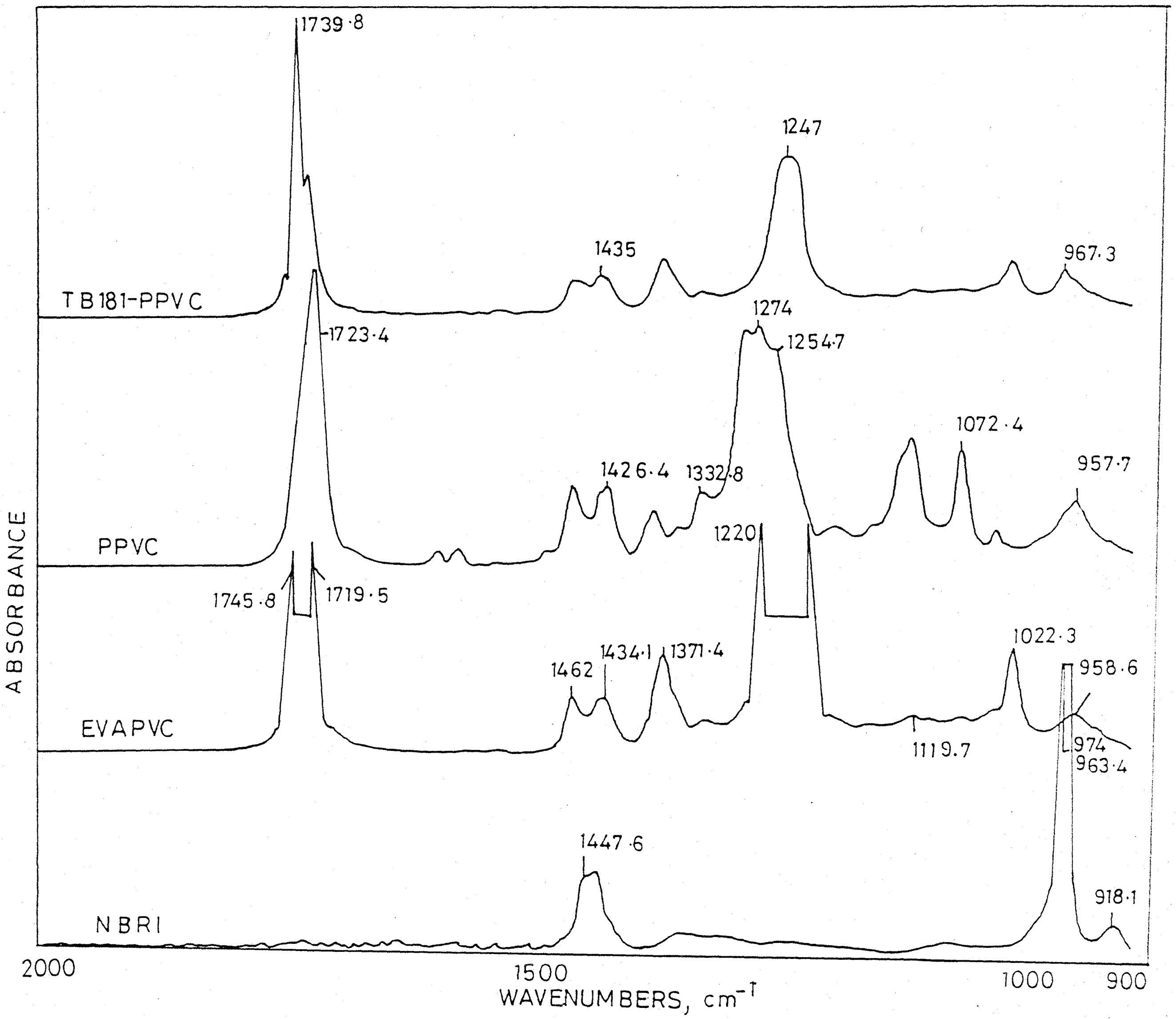


Fig. 4.4.24. FTIR difference spectrum, TB181-PPVC

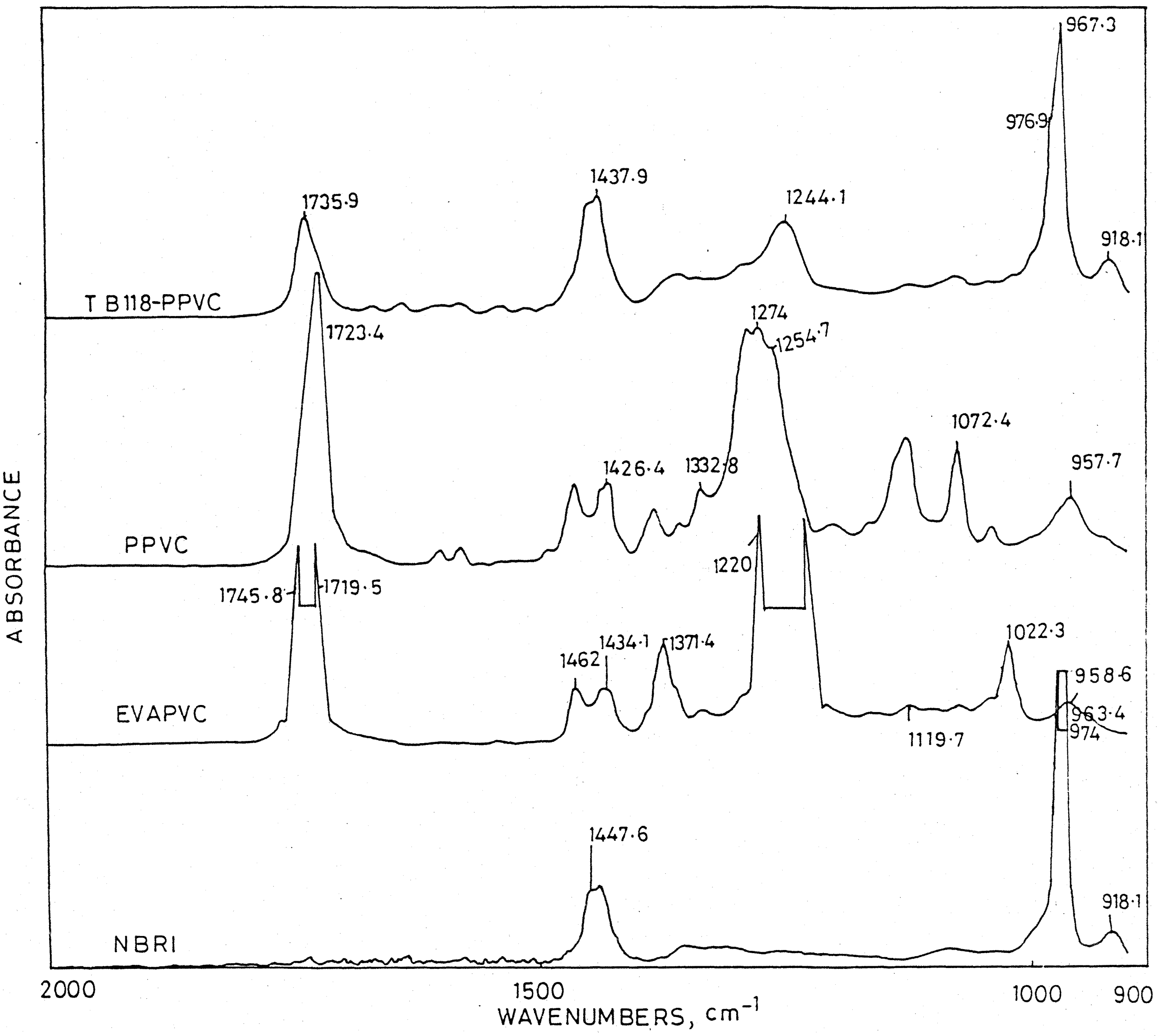


Fig · 4·4·25· FTIR difference spectrum, T B118–PPVC

MIGRATION AND PERMANENCE

SECTION - 5

4.5 MIGRATION AND PERMANENCE

The most important drawback of currently available plasticized PVC used in medical applications is that the low molecular weight additives like plasticizers migrate into the media in contact (Vergnaud, 1983). This leads to change in properties and may cause toxic problems to the patients. It is therefore, necessary to study the extractability of PVC based formulations intended for medical applications. It is also important that the permanence i.e., the relative changes in properties due to extraction should be assessed.

In this section, results of the study of extractability in physiologically simulated media like vegetable oil and synthetic gastric juice are reported and discussed. Extraction/absorption in water and change in properties due to extraction are also discussed.

4.5.1 Extraction in Vegetable Oil

Vegetable oil was chosen as a medium because it simulates the lipid component of blood. Since there are practical difficulties in carrying out the experiment for very long durations, accelerated testing at 70°C was adopted. Absorption of oil by PVC, and NBR in small quantities (<1%) can not be ruled out. But since, oil absorption is very small compared to the loss of non-resinous matters, and the purpose is to have comparative results of different blend samples, oil absorption, if any, can be neglected. Kampouris et al. (1976) used olive oil to study migration of plasticized PVC samples. USP also recommends accelerated extraction at 70°C in vegetable oil for acute systemic toxicity test (USP, 1985 b).

4.5.1.1 Plasticizer Content vs. Extraction

Results of the extraction study of plasticized PVC samples in vegetable oil are shown in Figs. 4.5.1 and 4.5.2. PVC samples having different levels of plasticizers were used in this study to understand whether correlation exists between the amount of migration from the test material and its content of non-resinous matter. Since in plasticized PVC, plasticizer constitutes the major part of non-resinous matter, the term plasticizer migration/extraction is generally used to mean loss of all non-resinous matter.

From Figs. 4.5.1 and 4.5.2, it is seen that the amount of extraction increases with time and this is expected. Amount of extraction for PPVC3 is quite low compared to PPVC and PPVC2 has intermediate behaviour. The important point to note from the three plots of Fig. 4.5.1 is the difference in rates of extraction.

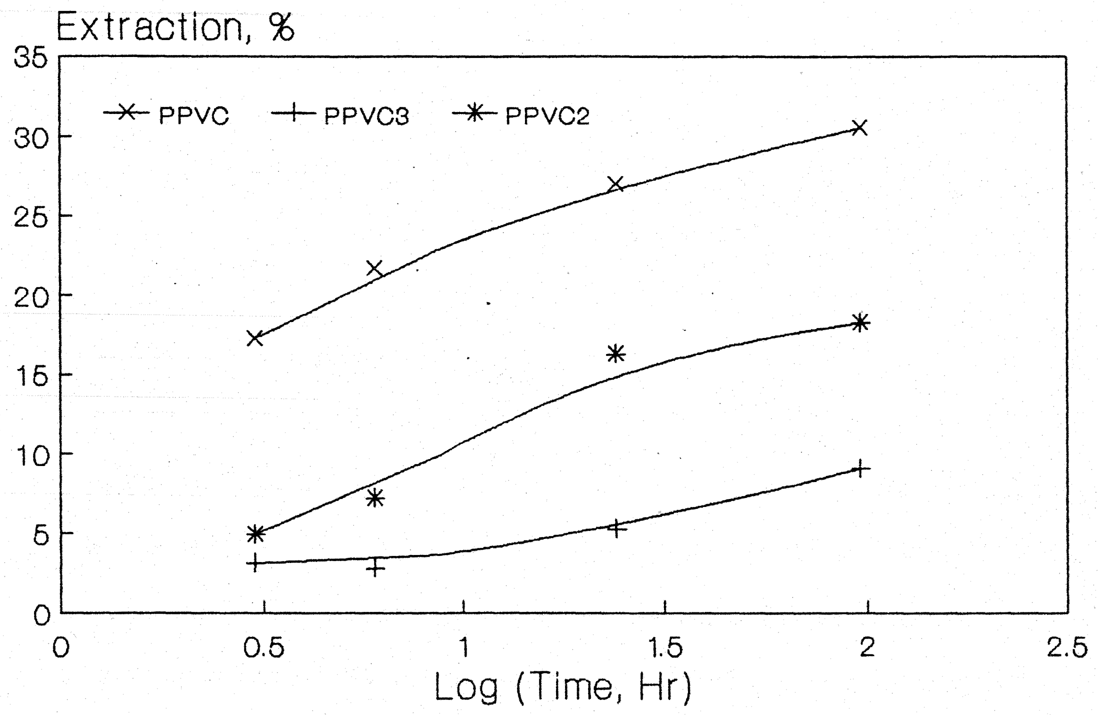


Fig. 4.5.1 Extraction in vegetable oil at 70°C for plasticized PVC samples

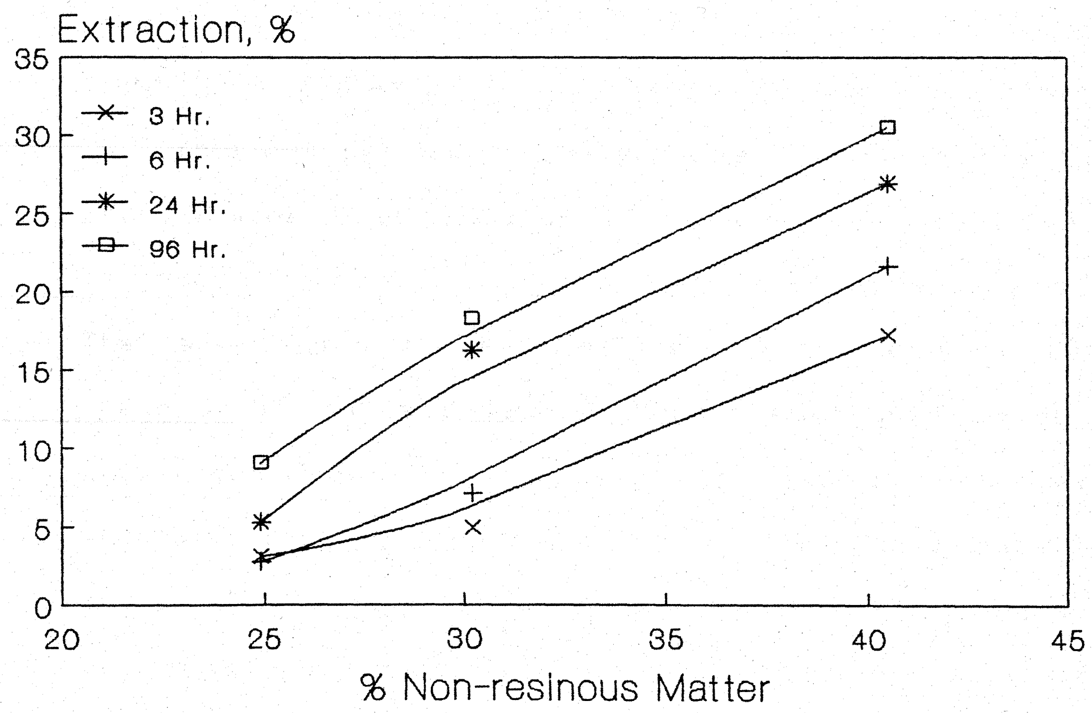


Fig. 4.5.2 Extraction in vegetable oil at 70°C for plasticized PVC as a function of content of non-resinous matter

Content of non-resinous matter in PPVC, PPVC2 and PPVC3 are 40.5%, 30% and 25% respectively (Fig. 4.5.2). This means that PPVC3 has 15.5% less non-resinous matter compared to PPVC. However, the amount of extraction in 96 hours is more than 3 times for PPVC compared to PPVC3. In case of PPVC2, though the reduction is not as dramatic, yet a reduction in 10.5% of non-resinous matter resulted in substantial reduction (40%) in amount of extraction (compared to PPVC). In fact, PPVC2 has double the amount of loss of non-resinous matter in 96 hours compared to PPVC3, though the increase in content of non-resinous matter is only from 25% to 30%. These findings would suggest that plasticized PVC becomes much more susceptible to loss of plasticizer if plasticizer content goes higher than 25%.

This observation can be explained by considering the mechanism of plasticization. Plasticizers swell the polymers by entering into the spaces between the polymer chains. They also form some weak linkages with the active sites of the PVC chains (Sears, 1982 a). When smaller quantity of plasticizer is present in PVC, the swelling of PVC is partial and therefore, physically migration of the plasticizers from PVC is not as easy as for a more swollen PVC having more plasticizer. In highly plasticized PVC, there are more free plasticizer molecules that do not have any linkages with

PVC chains and also the gel structure is more swollen and open (Sears, 1982 b) and these make plasticizer molecules more mobile to migrate out.

From these results, it emerges that if substantial reduction in migration is to be achieved, formulations must have plasticizer content below a level of 25%. Unfortunately, PVC containing 25% or lower amount of plasticizer does not possess adequate flexibility for most of the medical applications and typically, these formulations contain 40% or higher plasticizer (Vergnaud, 1983). Therefore, it becomes apparent that by use of conventional plasticizers like DEHP, one cannot expect to have both the required flexibility and plasticizer migration within desirable limits. Polyblends, where plasticized PVC is replaced with an elastomeric component seems to be a rational way of getting over these problems. Reduced amount of plasticizer in polyblend is expected to reduce the amount of plasticizer migration and elastomeric component is expected to impart the flexibility. Complete elimination of plasticizer may be ideal from plasticizer migration point of view, but, there are processing problems in such a system (Section 4.1.1.2).

4.5.1.2 Extraction Study for PE Blends

Amount of extraction for plasticized PVC - polyester blends are shown in Figs. 4.5.3 and 4.5.4. It can be seen that PE1 and PE3 have similar extraction characteristics as that of PPVC. PE4, PE6, PE7 and PE9 have almost similar extraction, though the values are somewhat lower than those of PE1 and PE3. In all the polyester blends both the quantities of polyester and DEHP were varied so as to have moulded materials with similar hardness (and possibly flexibility). Though, individually quantities of DEHP and polyester were varied in the blend pairs PE1 and PE3, PE4 and PE6, and PE7 and PE9, the total amount of DEHP and polyester in the blends were maintained at similar level. Similar levels of (DEHP + polyester) and no significant improvement in extraction over PPVC suggest that either these liquid polyesters also migrated out of PVC or presence of polyesters in the blends enhanced migration of DEHP from PVC to the oil. PE1 and PE3 have polyester with lowest molecular weight and this explains the observation of having more extraction for these blends compared to other polyester blends.

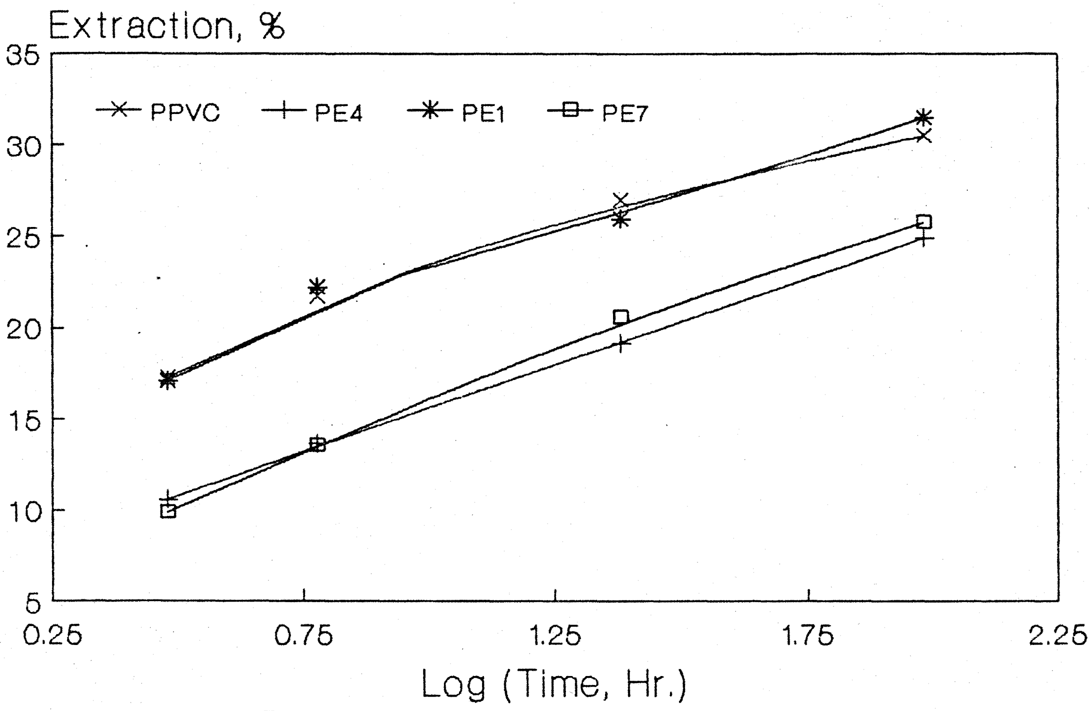


Fig. 4.5.3 Extraction in vegetable oil at 70°C for PPVC and polyester blends as a function of time

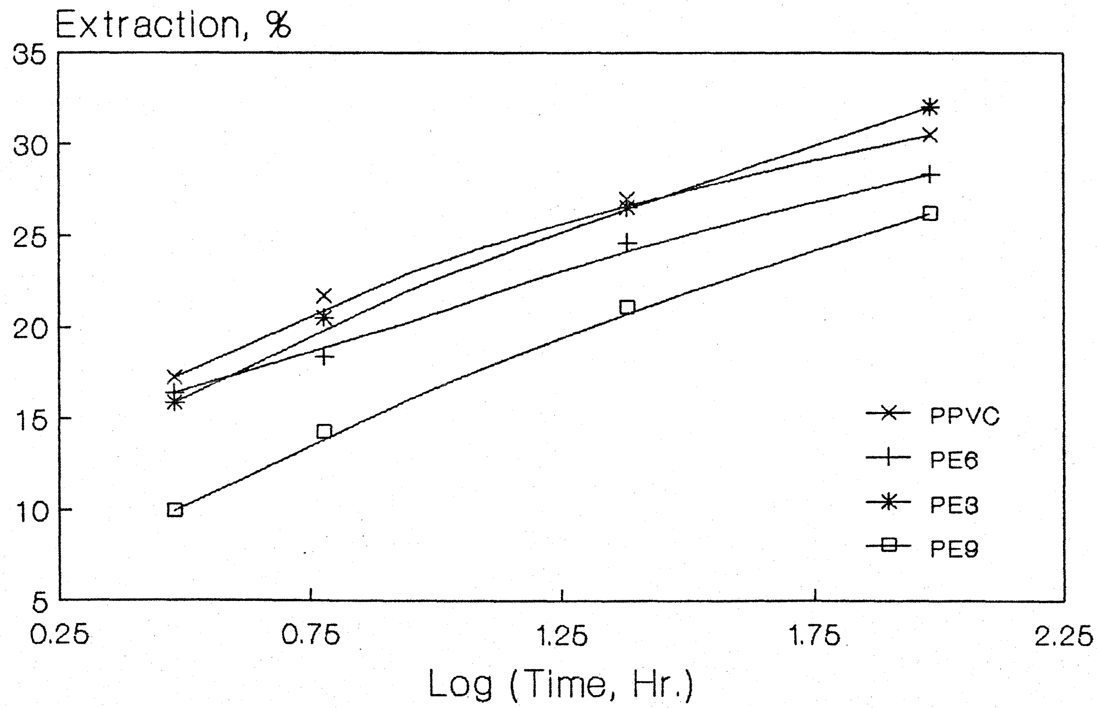


Fig. 4.5.4 Extraction in vegetable oil at 70°C for PPVC and polyester blends as a function of time

4.5.1.3 Extraction for NBR1 Blends

Results of accelerated extraction in vegetable oil for PPVC-NBR1 blends are given in Figs. 4.5.5 to 4.5.7. From all these figures it is seen that, as expected, the amount of extraction increases with time. From Fig. 4.5.5 it is observed that for all durations, the blends with content of non-resinous matter upto 20% have similar extraction. However, for a non-resinous matter content of 25%, which corresponds to 40% replacement of PPVC by NBR1 (Fig. 4.5.6), the migration is quite different for different durations.

Accelerated extraction for 96 hours can be taken as the long term effect in service. Looking at 96 hours extraction values from these figures, it also becomes apparent that replacement of PPVC below 10% does not minimise extraction. A replacement of around 20% and preferably 30%, with the resultant non-resinous matter content of 28.5% can only reduce extraction by oil to a significant level.

It is interesting to observe that reduction in non-resinous content by 15% from PPVC results in 40% reduction in extraction. This is indeed good but, this reduction is significantly lower than plasticized PVC having 15% less non-resinous matter compared to PPVC (Section 4.5.1.1). In other words, amount of non-resinous matter extracted in vegetable oil is higher for PPVC-NBR1 blends compared to plasticized PVC containing the same amount of plasticizer. This has also been reported earlier (Pal, 1988 b). Observations are also made (Section 4.5.1.2) that presence of polyester did not significantly improve resistance to extraction in vegetable oil.

Polyblends, having two polymers have somewhat inhomogeneous morphology and the packing of the individual polymer chains gets hindered due to the presence of the other. This leads to voids in the blends and the plasticizer molecules can have better mobility. In miscible polyblends (like PVC-NBR and PVC-PE) the polymers interact with each other due to hydrogen bonding. This interaction reduces the active sites available for the plasticizer and plasticizer molecules become free and can migrate out in the oil more easily. Also, the oil itself can probably permeate in and out of polymer (NBR1 showed about 1% increase in weight in oil) and easier permeation of the oil due to the voids in the polyblends and better solubility of the plasticizer in the vegetable oil make extraction of the plasticizer easier.

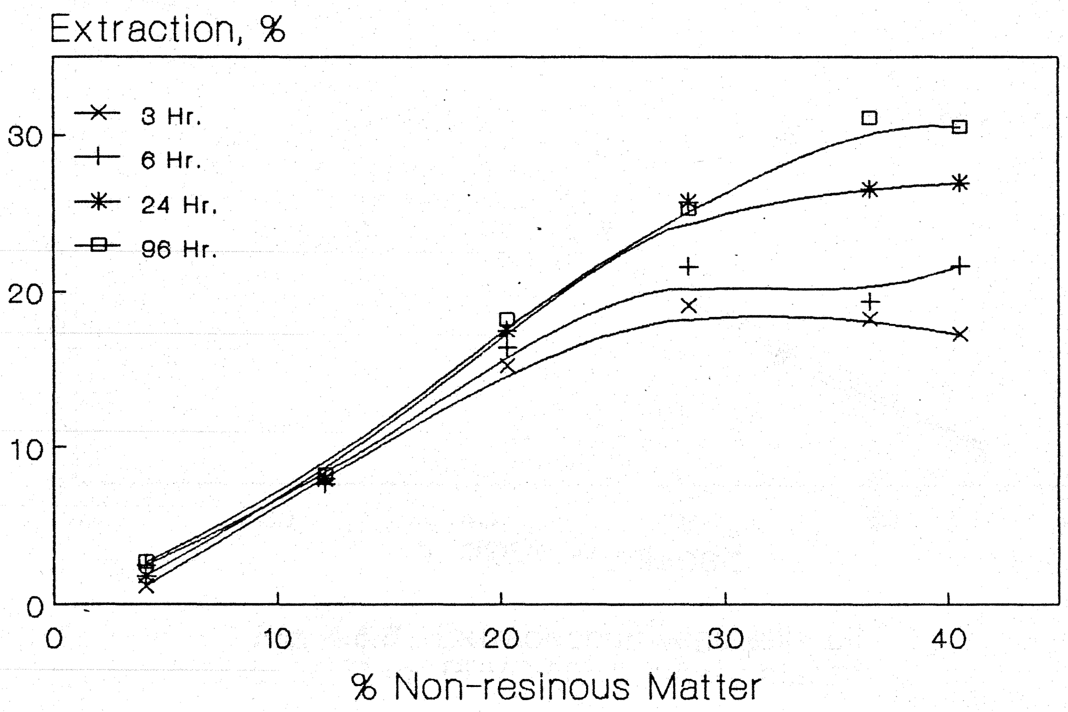


Fig. 4.5.5 Extraction in vegetable oil at 70°C for PPVC-NBR1 binary blends as a function of non-resinous matter content

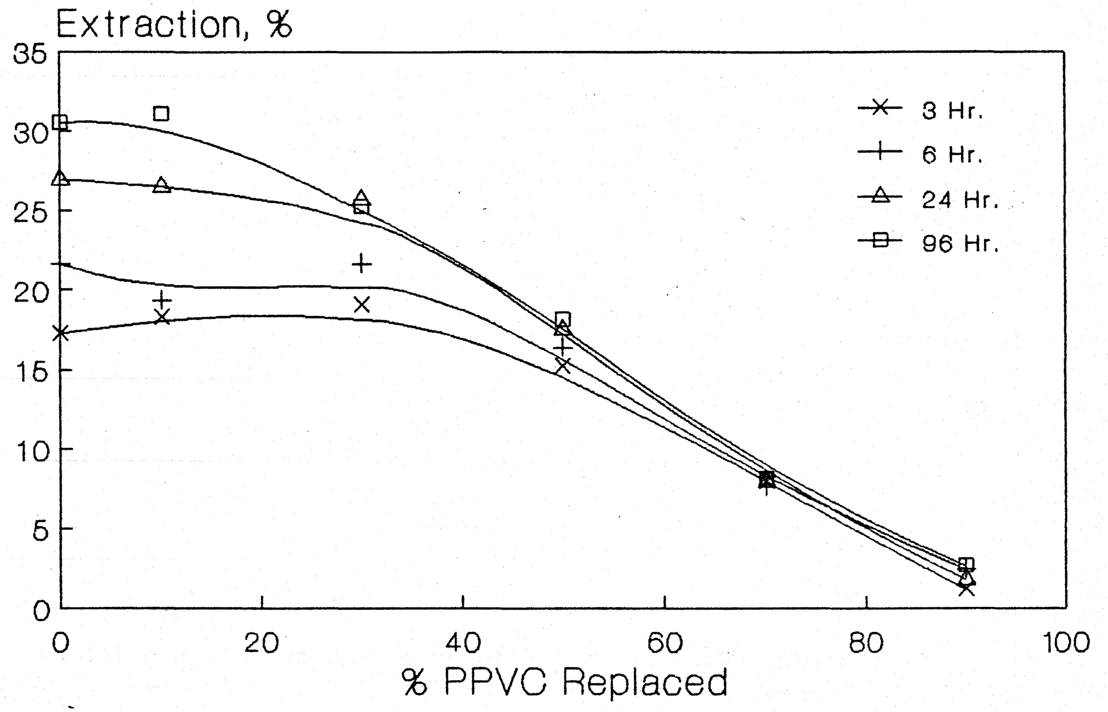


Fig. 4.5.6 Extraction in vegetable oil at 70°C for PPVC-NBR1 binary blends

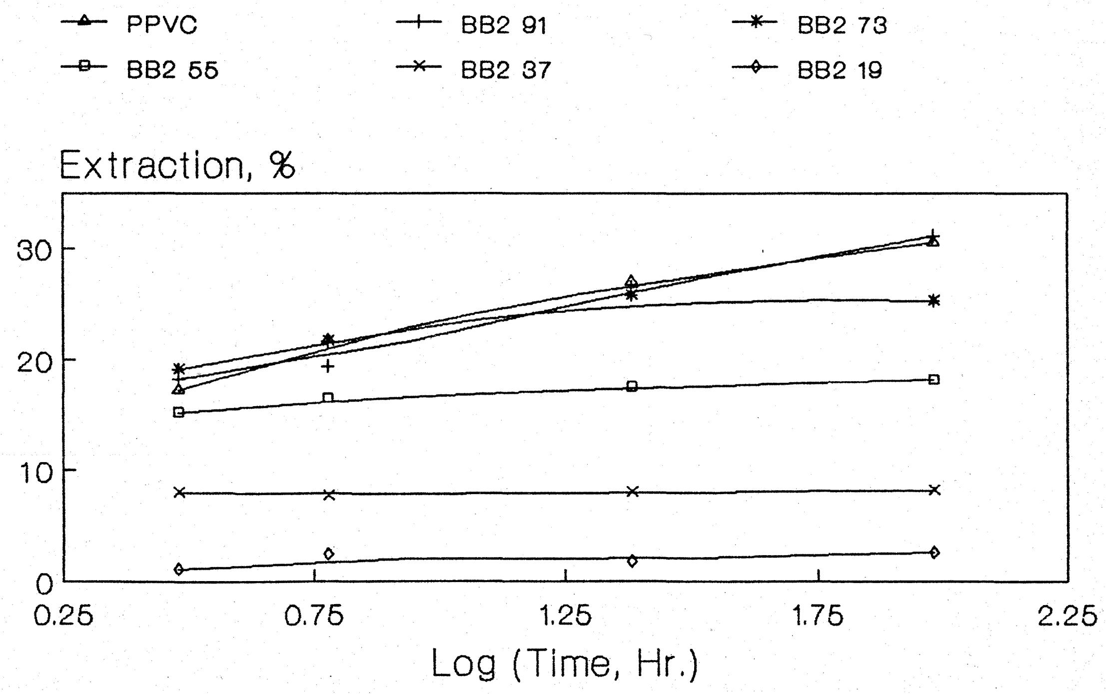


Fig. 4.5.7 Extraction vs. time for binary blends at 70°C in vegetable oil

4.5.1.4 Extraction for EVAPVC blends

EVAPVC and all PPVC-EVAPVC blends having 30% or more EVAPVC showed high oil absorption and swelling in vegetable oil at 70°C. The results of weight loss in vegetable oil were very erratic and therefore the experiments were discontinued for this blend system. This does, however, indicate that EVAPVC or blends containing substantial quantities of EVAPVC are likely to be affected by the lipid components of blood and one must consider this while selecting EVAPVC for blood contacting applications and particularly for those applications where the contact is not transient in nature.

4.5.1.5 Effect of Extraction on Mechanical Properties

When plasticizers migrate out from plasticized PVC, the mechanical properties are affected. It is known that loss of plasticizer leads to reduced flexibility and ultimate elongation and increased ultimate tensile stress. These changes should be less for a material that exhibits lesser loss of plasticizer when in contact with a medium and thus the material concerned should be more 'permanent' in mechanical properties.

The ultimate elongation of PPVC-NBR1 and plasticized PVC-PE blends are shown in Figs. 4.5.8 and 4.5.9. As expected from the results of extraction studies

(Section 4.5.1.2), PPVC and polyester blends exhibit drastic fall in UE with increase in period of extraction. Increase in period of extraction is associated with increased loss of plasticizer and therefore the fall in UE takes place indicating poor 'permanence' for both PPVC and PE blends. Results of PPVC-NBR1 blends indicate that even 10% replacement of PPVC (BB2 91) helps to retain good amount of its pre-extraction UE. Very little loss in UE is observed for blends having higher amount of NBR1. NBR1 shows slightly more UE after extraction. This is due to oil absorption (about 1%) and plasticization by the oil.

The effect of extraction on UTS is apparent from Figs. 4.5.10 and 4.5.11. The UTS goes up in all cases for both PPVC-NBR1 and PE blends with increase in period of extraction (and hence increase in the amount of extraction). The change becomes less significant with increase in the content of NBR1. This supports the inference made from the results of UE that replacement of PPVC with NBR1 improves permanence in mechanical properties and polyester blends do not have the permanence in mechanical properties when in contact with vegetable oil.

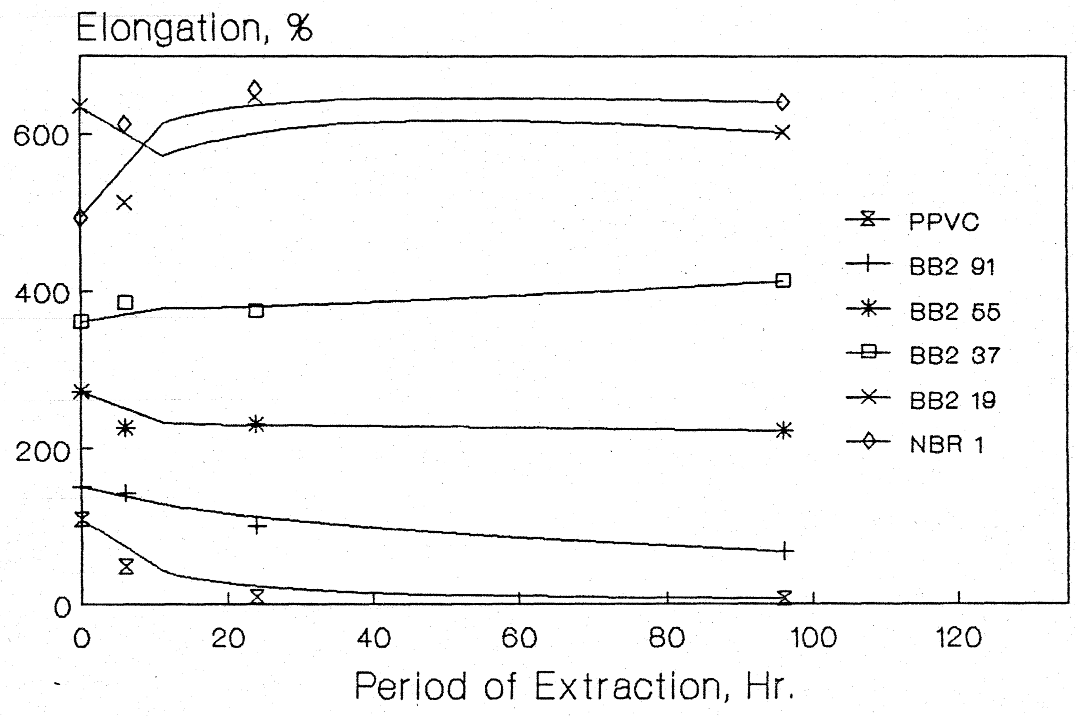


Fig. 4.5.8 Effect of extraction at 70°C in vegetable oil on ultimate elongation

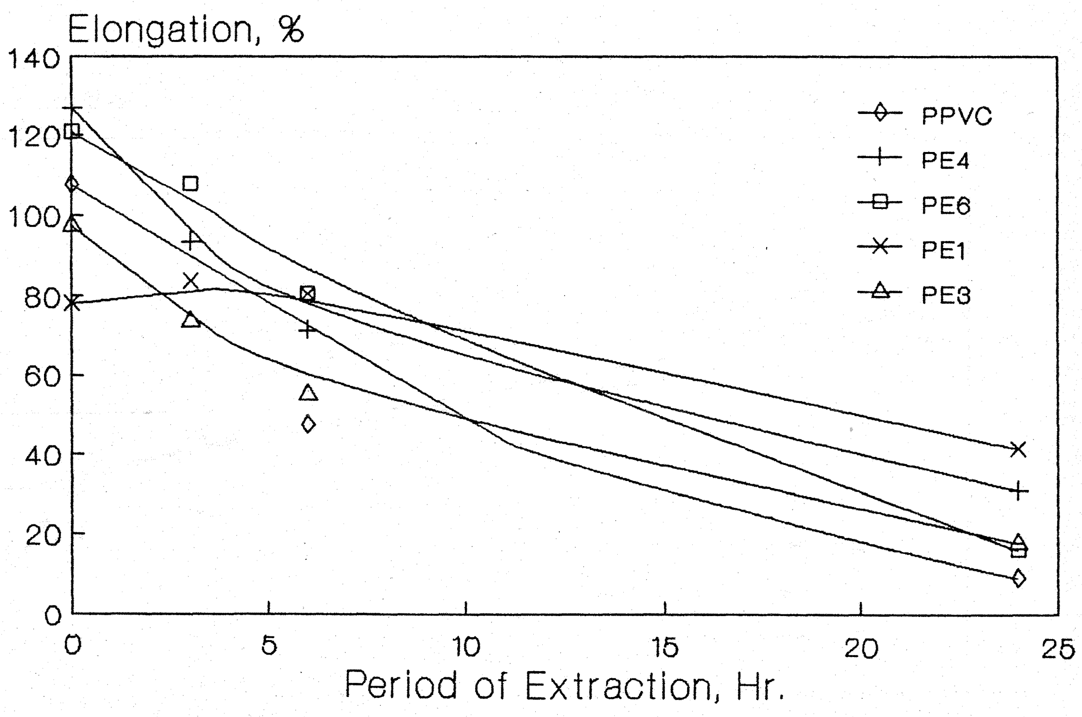


Fig. 4.5.9 Effect of extraction at 70°C in vegetable oil on ultimate elongation

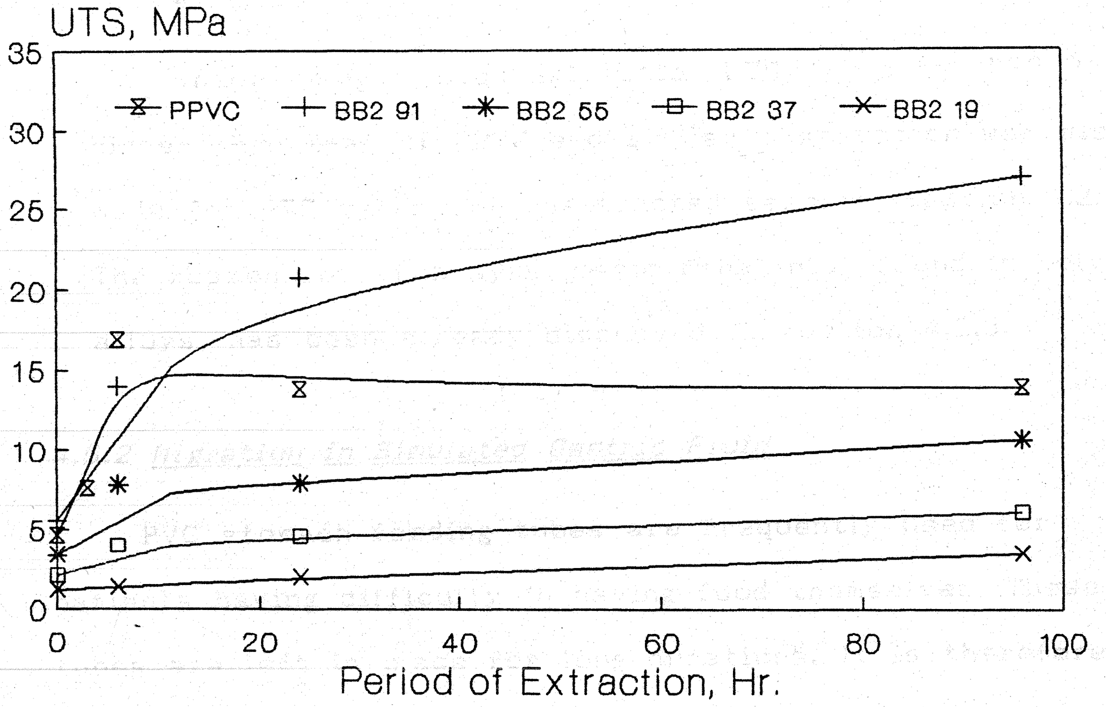


Fig. 4.5.10 Effect of extraction at 70°C
in vegetable oil on UTS

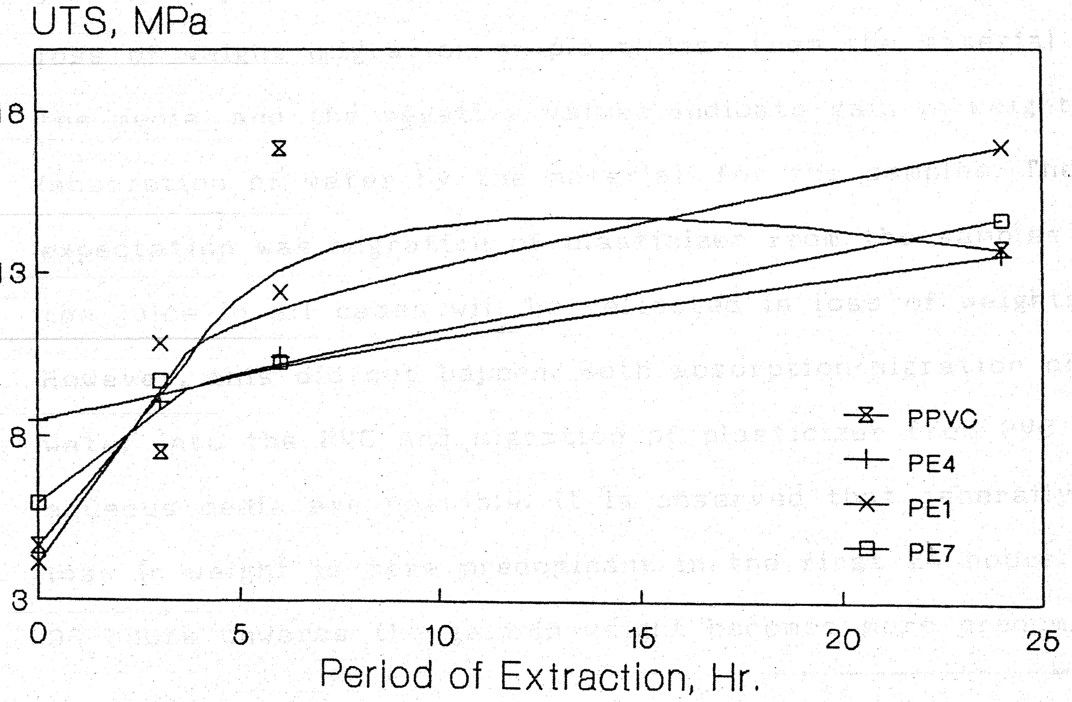


Fig. 4.5.11 Effect of extraction on UTS
in vegetable oil at 70°C

Interestingly, post extraction UTS value for BB2 91 is higher than that of PPVC and similar observation was also made for UTS values of unextracted samples (Section 4.2.3). The reason for such synergistic behaviour, found in polymer alloys, has been already discussed in section 4.2.3.

4.5.2 Migration in Simulated Gastric Fluid

PVC stomach feeding tubes are frequently used for patients having difficulty in having food themselves. These tubes are left in place for long durations. It is therefore relevant to study the effect that the gastric juice may have on PVC based polyblends.

The results of extraction/migration in simulated gastric juice are given in Table 4.5.1. The positive values indicate loss of weight (migration of plasticizer from the material to the media) and the negative values indicate gain in weight (absorption of water by the material) for the samples. The expectation was migration of plasticizer from the samples to the juice in all cases will be reflected in loss of weights. However, this did not happen. Both absorption/migration of water into the PVC and migration of plasticizer from PVC to aqueous media are possible. It is observed that generally the loss in weight is more predominant in the first 24 hours. From 96 hours onwards the gain in weight becomes more predominant.

From the results, it can be concluded that migration takes place both into (water absorption) and away (plasticizer migration) from the material. The amount of plasticizer migration is very low in all cases and no definite conclusion can be made about the relative performance of samples in terms of resistance to plasticizer migration. Generally, water absorption becomes higher than plasticizer migration after 96 hours. Polyester blends seem to absorb less water than other binary blends. PPVC-NBR1 blends, containing large quantities of NBR1 (BB2 37, BB2 19) also seem to absorb less water than PPVC-EVAPVC blends. This behaviour is in contrast to the results obtained for water absorption studies done with distilled water (Section 4.5.3.1). Though, the reasons for this behaviour are not conclusively known, the answer probably lies in the differences in the two media. Derived conclusion would therefore be: the nature of specific aqueous medium and its pH affect migration/water absorption.

TABLE 4.5.1 Migration in Simulated Gastric Juice

Sample Codes	Migration, %			
	Period, Hour			
	6	24	96	168
PPVC	-0.030	-0.050	-0.140	-0.265
BB1 91	0.102	0.094	-0.045	-0.319
BB1 73	0.181	0.197	-0.049	-0.203
BB1 55	0.058	0.131	-0.133	-0.280
BB1 37	0.073	0.163	-0.119	-0.375
BB2 91	0.143	0.155	-0.057	-0.311
BB2 73	0.159	0.208	-0.320	-0.230
BB2 55	0.196	0.270	-0.144	-0.349
BB2 37	0.232	0.304	0.109	0.175
BB2 19	0.460	0.510	0.069	0.066
PE3	0.176	0.280	0.052	-0.06
PE6	0.710	0.910	0.150	0.127
PE9	0.240	0.370	0.110	0.110

4.5.3 *Water Absorption*

In most of the medical applications the PVC products come in contact with aqueous media. In some cases (e.g., giving sets, pump tubing etc.) the contact may be for short durations and in some other cases (like containers for storing injectables) the duration of contact with aqueous media may be very large. Both absorption of water by the PVC and migration of plasticizer from PVC to aqueous media are possible. However in water, the plasticizer migration is known to be very low (Prins, 1979). Too much water absorption may change some of the desirable properties of the material. For example, water absorption leads to 'blushing' in PVC (Nass, 1976). This in turn affects the clarity. Increased water absorption also may lead to increased permeation of water vapour through a material. It is therefore absolutely necessary to study the water absorption characteristics of PVC based materials, intended for medical applications.

The water absorption (WA) characteristics of three 'pure' components PPVC, EVAPVC and NBR1 are given in Fig. 4.5.12. There is significant difference in WA characteristics and it is in the order PPVC < EVAPVC <NBR1. It is interesting to note that water vapour permeability is also in the same order (Section 4.6.1.2).

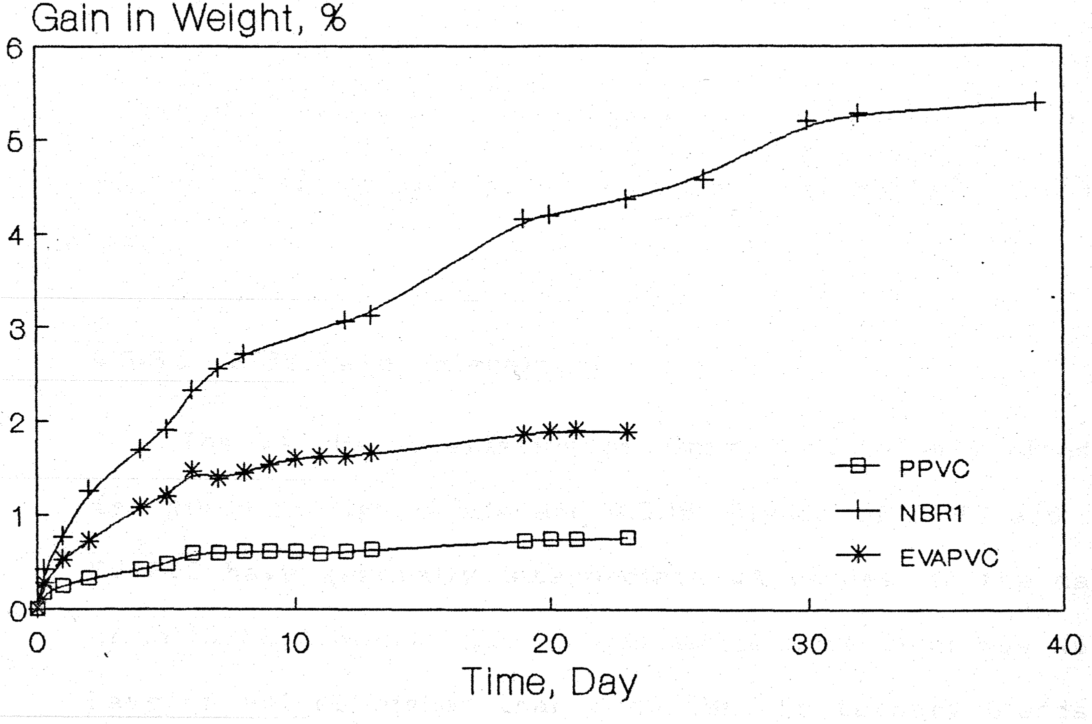


Fig. 4.5.12 Water absorption of PPVC, EVAPVC and NBR1 as a function of time

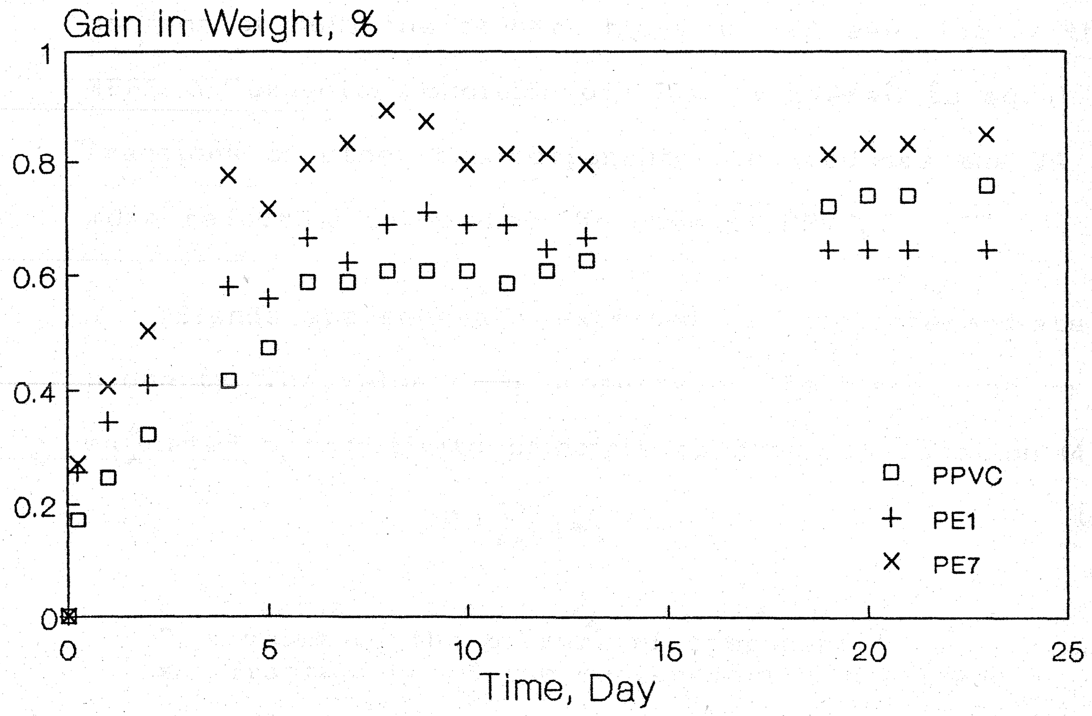


Fig. 4.5.13 Water absorption of PPVC, polyester blends as a function of time

The WA behaviour of representative PE blends are given in Fig. 4.5.13. PE blends have water absorption similar to that of PPVC.

4.5.3.1 Effects on Blending

The WA characteristics of binary and ternary blends are given in Figs. 4.5.14 and 4.5.15. Blends of PPVC and EVAPVC have generally intermediate WA values. In the case of PPVC-NBR1 blends, blends containing more than 50% NBR1 have WA values higher than even NBR1. In ternary blends, addition of NBR1 to equal fractions of PPVC and EVAPVC increases WA till NBR1 content is 60%, beyond which WA comes down. Just as in binary blend system, at around 60% content of NBR1 the ternary blend has WA even higher than NBR1. As expected, addition of PPVC or EVAPVC to equal fractions of other two components also reduces the WA and more reduction takes place in case of PPVC.

Blends are generally expected to have intermediate property. The value of a property of the blends can be calculated by additivity principle as shown in equation (4.23).

$$P = \sum P_1 x_1 \tag{4.23}$$

P = value of the property of the blend
P_1 = value of the property of component 1
x_1 = fraction (w) of the component 1 in the blend

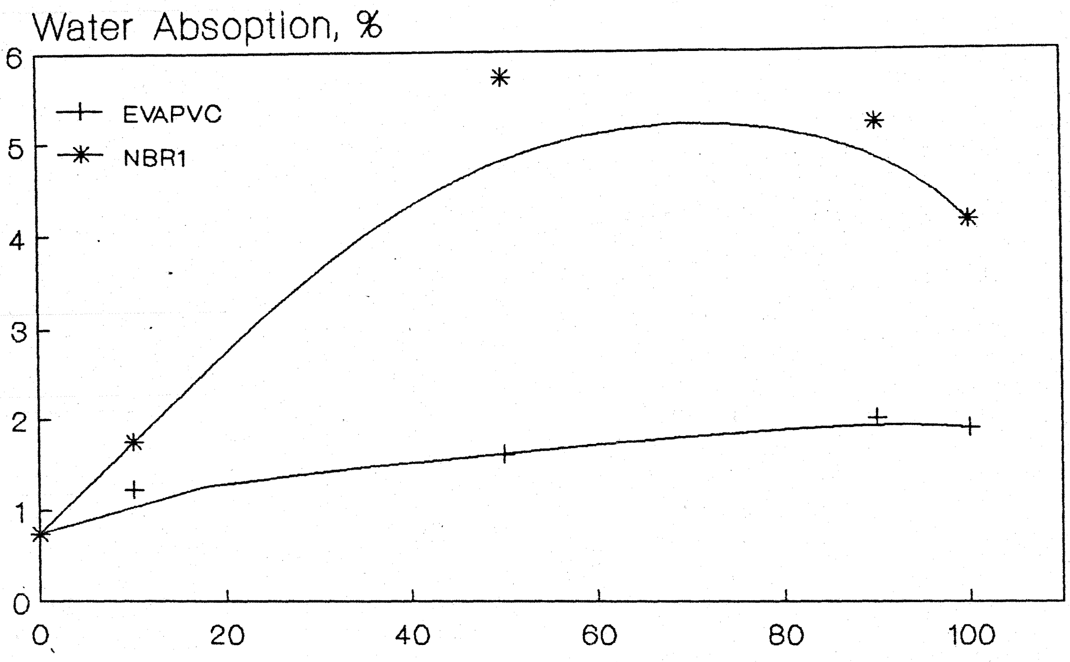


Fig.4.5.14 Water absorption of binary blends of PPVC with EVAPVC and NBR1 at 30°C for period of 3 week

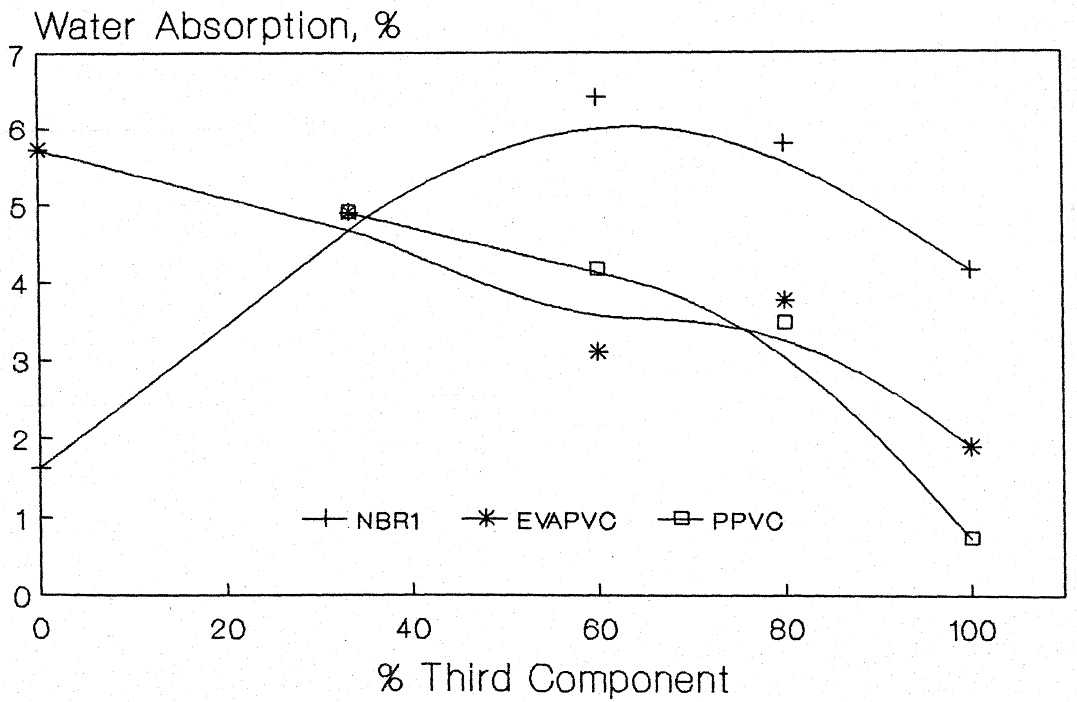


Fig. 4.5.15 Water absorption of ternary blends with equal fractions of two components at 30°C for period of 3 week

Table 4.5.2 lists the values of WA of blends obtained by experiment and additivity principle. It is very interesting to note that in case of all binary and ternary blends, the experimental WA is higher than the expected WA obtained by calculation from the WA values of the 'pure' components. This observation is very similar to the observations made for extraction in vegetable oil (Section 4.5.1.3). The possible reasons for such behaviour also must be similar i.e., polyblends seem to have voids (free volume) and these voids can accommodate more water into the material (Paul, 1982). Inhomogeneity and free volume are expected to be more in ternary blends and also in binary blends where both the components are present in almost equal quantities and this explains why the experimental WA and the deviations from expected values are more for these blends.

TABLE 4.5.2 Experimental and Calculated Water Absorption Values

Sample Codes	Water Absorption in 21 days, %	
	Experimental	Calculated*
PPVC	0.742	
EVAPVC	1.910	
NBR1	4.179	
BB1 91	1.220	0.859
BB1 55	1.619	1.326
BB1 19	2.020	1.793
BB2 91	1.750	1.086
BB2 55	5.725	2.461
BB2 19	5.225	3.835
TB111	4.913	2.254
TB311	4.184	1.663
TB811	3.510	1.203
TB131	3.130	2.130
TB181	3.790	2.020
TB113	6.410	3.038
TB118	5.820	3.608

* Calculated by additivity principle

4.5.3.2 Water Absorption and Density of Blends

The experimental and calculated (by additivity principle) densities of the blends are given in Table 4.5.3. It is observed that generally the experimental densities of the blends have values intermediate between the 'pure' components. For any particular blend, the difference between experimental and calculated values is not significant enough to make very definite conclusion. However, comparison of experimental and predicted density values for all the blends suggest a definite trend that the experimental density values are marginally lower than the predicted ones. This experimental evidence supports the reasoning put forward for the observations made (more than expected) for water absorption and extraction of non-resinous matter in vegetable oil for the blends.

TABLE 4.5.3 Experimental and Calculated Density Values

Sample Codes	Density, gm/cc	
	Experimental	Calculated*
PPVC	1.2011	
EVAPVC	1.1261	
NBR1	1.0063	
BB1 91	1.1751	1.1936
BB1 73	1.1584	1.1786
BB1 55	1.1409	1.1636
BB1 37	1.1522	1.1486
BB1 19	1.1338	1.1386
BB2 91	1.1917	1.1816
BB2 73	1.1333	1.1427
BB2 55	1.0980	1.1037
BB2 37	1.0491	1.0647
BB2 19	1.0149	1.0258
TB111	1.0814	1.1112
TB211	1.0891	1.1337
TB311	1.0965	1.1471
TB811	1.1346	1.1741
TB121	1.0882	1.1149
TB131	1.0998	1.1171
TB112	1.0446	1.0850
TB113	1.0162	1.0692
TB118	1.0209	1.0378

* Calculated by additivity principle

PERMEABILITY

SECTION - 6

4.6 PERMEABILITY

In many of the medical applications PVC based devices are used to store substances (e.g., blood and blood products, drugs and injectables) that require maintenance of constant microclimatic condition without which deterioration of the content takes place. The temperature of storage for such devices could also vary from sub-zero to about 45°C. Knowledge regarding the permeability of gases, present in the atmosphere, through such materials is therefore of practical interest.

In this section, results on the permeability of water vapour at different temperatures are given and detailed discussions regarding the observations made have been attempted. In addition, results of studies on permeability of gases like oxygen, carbon dioxide and nitrogen are also reported.

4.6.1 Water Vapour

4.6.1.1 Plasticized PVC

Results of water vapour permeability for plasticized PVC at 37°C and 60°C are shown in Fig. 4.6.1. Increase in temperature and plasticizer content increase the permeability. Water vapour permeability increases by more than three times when temperature is raised from 37°C to 60°C.

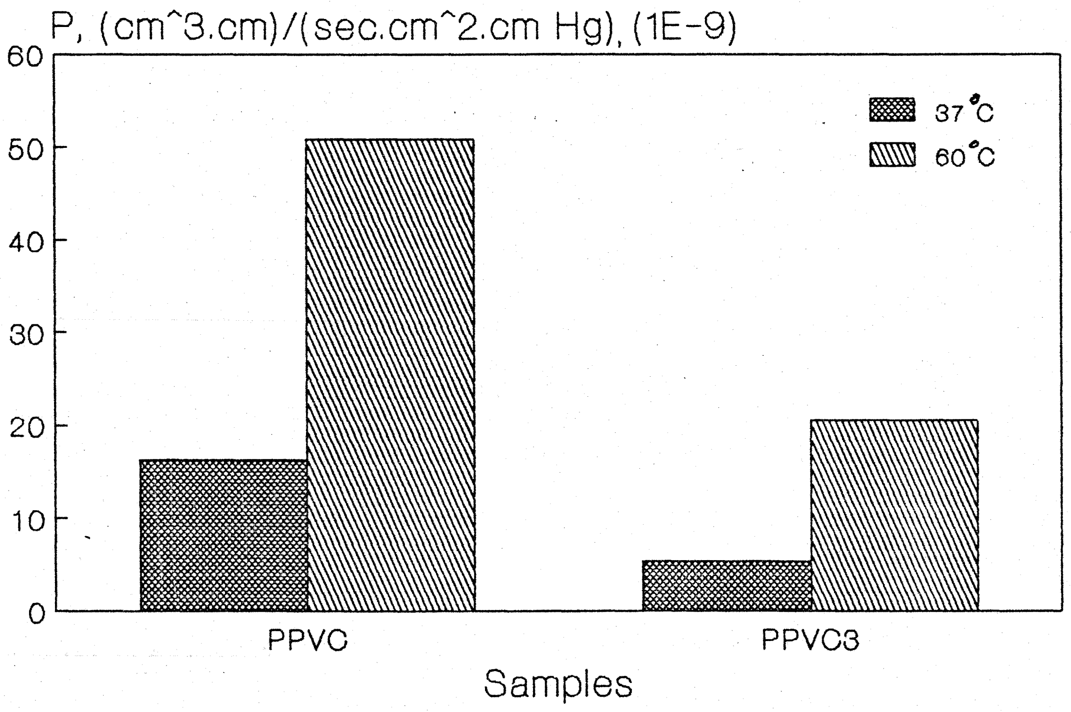


Fig. 4.6.1 Water vapour permeability constants for plasticized PVC samples

Rise in permeability by around three times is also noted for rise in plasticizer level from 25% to 40%. Increase in permeability with temperature is expected because of the increased rate of diffusion of permeate. This is due to the increased mobility of both the permeate and the local chain segment of barrier polymer. Plasticization also increases the molecular mobility of polymer chains (Hammer, 1978) and water vapour can permeate more easily through polymers having increased chain mobility. Additionally, plasticization increases the water absorption. Permeability constant is defined as the product of diffusivity and solubility. The differences in diffusivity in the two plasticized PVC may not significantly affect the permeability. Increased water absorption means increased solubility and therefore permeability goes up with increase in the level of plasticizer.

4.6.1.2 'Pure' Components

The results of water vapour permeability for the 'pure' components are shown in Table 4.6.1. At all the temperatures studied, water vapour permeability is in the order PPVC < EVAPVC <NBR1. It may be recalled that this order is same as noted for water absorption (Section 4.5.3). The order of permeability for the 'pure' components can

therefore be explained by considering solubility of water in the barrier films. Kojima et al.(1983) also observed that in atactic poly(vinyl alcohol) films, the permeability of water vapour is dependent on degree of swelling of the film.

It is very interesting to note that rise of temperature from 4° to 37° and 60°C results in increased permeability by 26 and 84 times for PPVC, 15 and 48 times for EVAPVC and 13 and 23 times for NBR1. The difference in permeability between the three 'pure' components at 4°C reduces as temperature is increased. This is also reflected in the permeability ratios shown in Table 4.6.2. This behaviour can be explained by considering the T_g of the 'pure' components. The T_g values of the 'pure' components are around 17°, -1° and -9°C for PPVC, EVAPVC and NBR1 (Section 4.3.1.2) respectively. 4°C is above the T_g of both EVAPVC and NBR1 and below the T_g of PPVC. And therefore PPVC has very restricted chain mobility and this results in low permeability. However, 37° and 60°C are above the T_g for PPVC and the permeabilities are much higher at these temperatures. For EVAPVC and NBR1 the changes in permeabilities at these three temperatures are not as dramatic as for PPVC because all the three temperatures are above T_g for both these materials.

TABLE 4.6.1 Water Vapour Permeability for 'Pure' Components at different Temperatures

Sample Codes	Water Vapour Permeability Constant $\frac{(cm^3)(cm)}{(cm^2)(\text{sec})(cm.Hg)}, 10^{-9}$		
	4°C	37°C	60°C
PPVC	0.606	16.277	50.900
EVAPVC	1.380	20.737	66.100
NBR1	4.450	34.172	102.00

TABLE 4.6.2 Water Vapour Permeability Ratio for 'Pure' Components at different Temperatures

Sample Codes	Ratio of Permeability Constants		
	4°C	37°C	60°C
EVAPVC : PPVC	2.28	1.27	1.30
NBR1 : PPVC	7.34	2.10	2.00

4.6.1.3 Binary and Ternary Blends

Figs. 4.6.2 and 4.6.3 show the results of water vapour permeabilities at 4°C, 37°C and 60°C for binary and ternary blends of PPVC, EVAPVC and NBR!. As expected, the effect of temperature on the permeability constants for all the blends are similar to the 'pure' components. Blends generally have intermediate permeabilities (of the 'pure' components) at all temperatures. The minor deviation from the intermediate behaviour is too small to consider significant.

In applications like injectable crystalloids, blood bags containing anticoagulant solution, CAPD bags containing dialysis fluids etc., loss of too much water during storage may change the concentration of the salt solution to an unacceptable level. While recommending the blends for such applications, the difference in water vapour permeability with conventional materials like PPVC should be an important consideration.

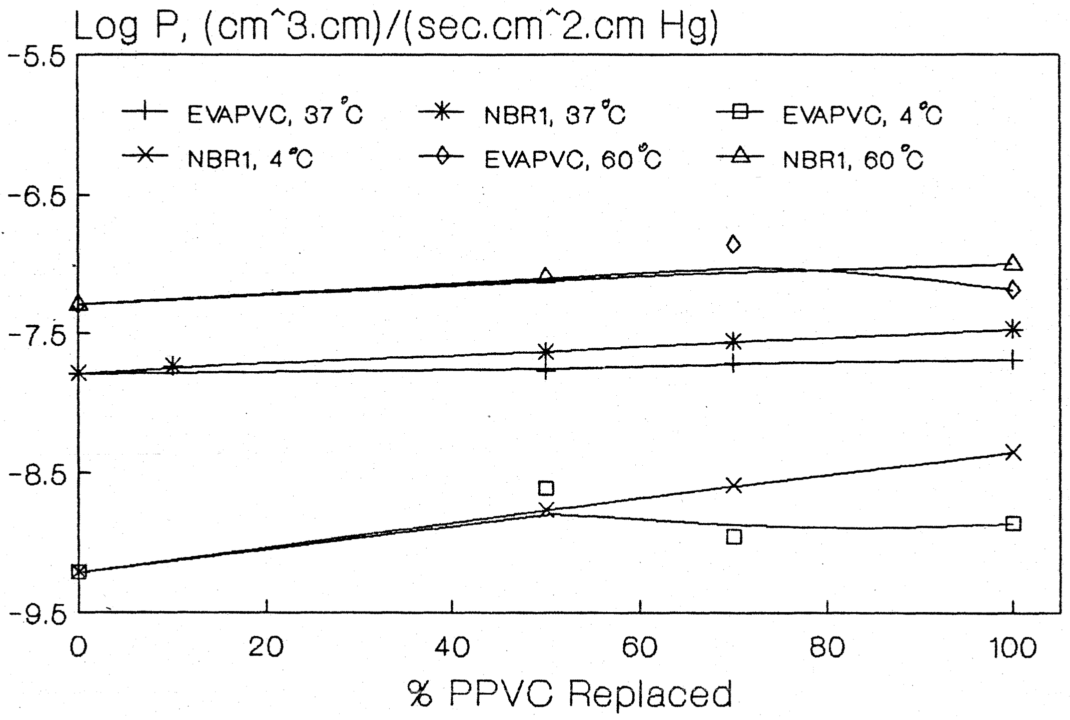


Fig. 4.6.2 Water vapour permeability constants for binary blends

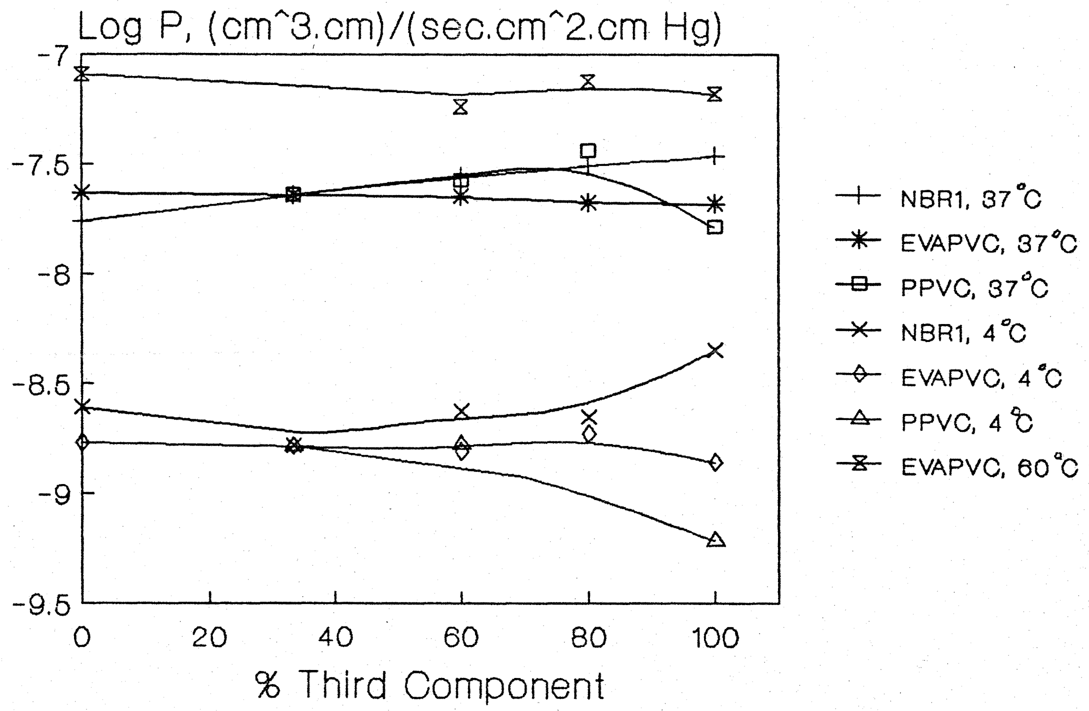


Fig. 4.6.3 Water vapour permeability constants for ternary blends with equal fractions of two components

4.6.2 *Oxygen, Nitrogen and Carbon dioxide*

Results of oxygen, nitrogen and carbon dioxide permeability studies are shown in Table 4.6.3 and for having a better clarity of the trend of the results, the data are presented graphically in Figs. 4.6.4 to 4.6.6. All the samples studied, have carbon dioxide permeability few times higher than those of oxygen and nitrogen. The nitrogen permeability is the lowest. Both the trend and the permeability values for the 'pure' components agree well with the data reported in the literature (Rogers, 1976). Permeability values also compare well with the films used for blood bags (Table 4.6.3). The large difference in P values of gases can have practical significance for multistage concentration and separation of gases. Tejar et al. (1971) reported such possibilities.

Comparison of P values for PPVC and PPVC2 indicates plasticization increases permeability for all the three gases studied. Same is the observation for water vapour permeability. The reasons for this behaviour have been explained in section 4.6.1.1 and the trend is also in agreement with other studies (Rogers, 1976).

Blending of PPVC with a second polymer reduces the P values (Fig. 4.6.5) for all the three gases. The observation for ternary blends are similar to binary systems (Fig. 4.6.6). Paul et al.(1982) and Masi et al. (1982) also made similar observations for other systems and they observed that gas permeation rates through two miscible polymer blends were well below any additive predictions. These observations are of great practical significance, since, reduced permeabilities of gases are expected to maintain the contents of a device, made from such blends, better. Reduced oxygen permeability is likely to reduce deterioration due to oxidation and reduced carbon dioxide permeability is expected to result in better maintenance of pH of the contents.

Permeability depends on the chemical structure, morphology and polarity of the polymer, nature of the permeate, temperature and thickness of barrier film (Ashley, 1985; Subramanian, 1985). For a coherent polymer film, the permeability is the result of two distinct processes: solubility of the permeate in the polymer and diffusion. In case of non-interacting gas molecules, diffusion is the predominant factor. The rate of diffusion through a polymer film is governed by the number and size distribution of pre-existing 'holes' and the ease of 'hole' formation (Rogers, 1976). The first factor is dependent on chain packing and is related to the free volume and density. The ease of 'hole' formation depends on the thermal motions of the polymer chain segments as related to chain stiffness and cohesive energy forces of the polymer. The local segmental mobility or chain stiffness in compatible polyblends gets affected by chain interactions arising from hydrogen bonding, polar group interactions etc. The presence of such interactions in the blends studied have been established by FTIR studies (Section 4.4.2).

From the above discussions and the experimental results it therefore becomes apparent that, in case of O_2, CO_2 and N_2 permeabilities for binary and ternary blends, the chain interactions between the polymers make 'ease of hole formation' difficult and therefore permeabilities of the blends are lower than both the 'pure' components. The predominant factor here is the 'ease of hole formation'. On the other hand for water vapour permeability (Section 4.6.1), the concentration of water in the blends (as reflected in water absorption, Section 4.5.3) and larger free volume (lower density, Section 4.5.3.2) are the predominant factors that govern the permeability.

TABLE 4.6.3 Permeability Constant of Blends for O_2, N_2, and CO_2

Sample Codes	Permeability Constant for Gases $\frac{(cm^3)(cm)}{(cm^2)(sec)(cm.Hg)}, 10^{-10}$		
	O_2	N_2	CO_2
PPVC	4.03	1.71	16.1
PPVC2	2.71	0.81	8.43
EVAPVC	3.59	1.82	15.5
NBR1	1.59		
BB1 91	2.90	1.60	9.75
BB1 37	2.59	1.03	6.94
BB2 91	2.72	1.26	8.80
BB2 37	2.65	0.88	14.0
TB111	2.46	1.04	8.01
TB311	3.10	1.08	9.97
TB131	2.51	0.99	8.64
TB113	3.16	1.14	8.14
TJ*	3.15	0.65	21.9
PPL*	2.50	0.74	16.4
PT*	2.60	0.95	14.3

* Materials used in blood bags from three sources

TJ : Terumo, Japan
PPL : Peninsula Polymers, India
PT : SCTIMST, India

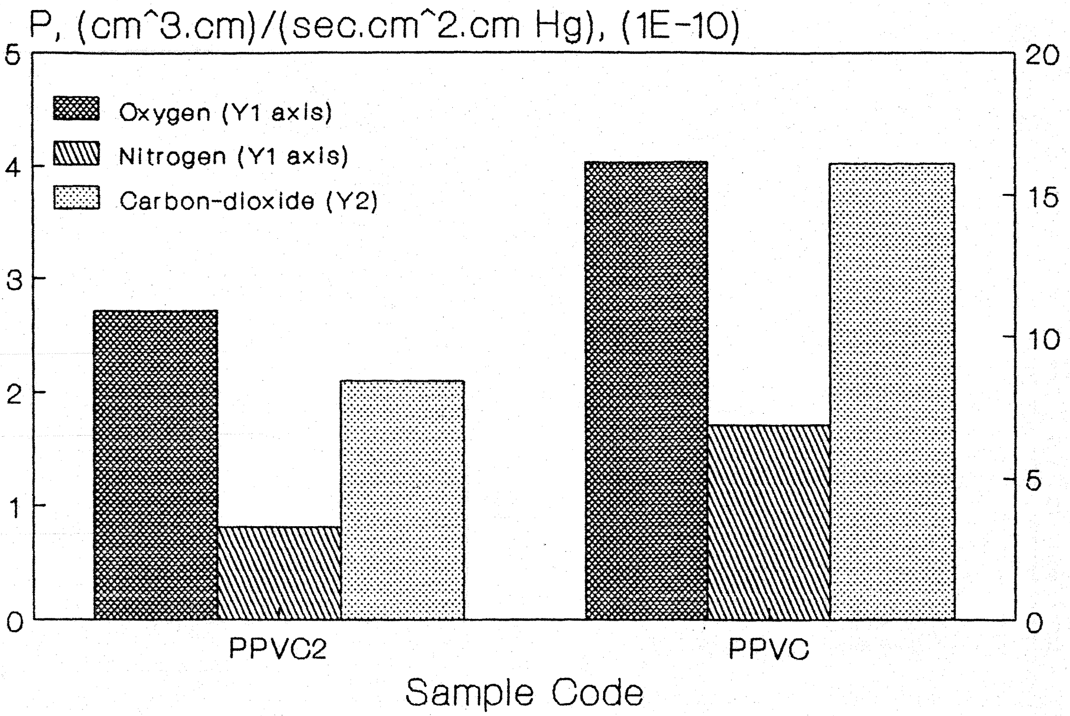


Fig. 4.6.4 Gas permeability constants for plasticized PVC samples

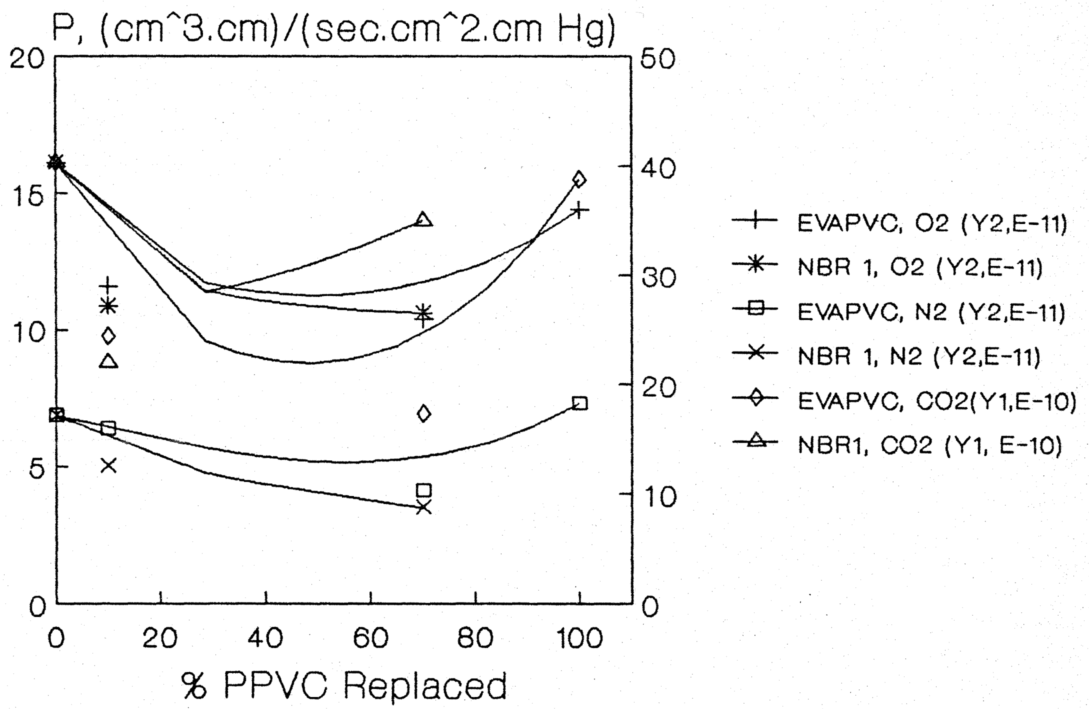


Fig. 4.6.5 Gas permeability of binary blends of PPVC with EVAPVC and NBR1

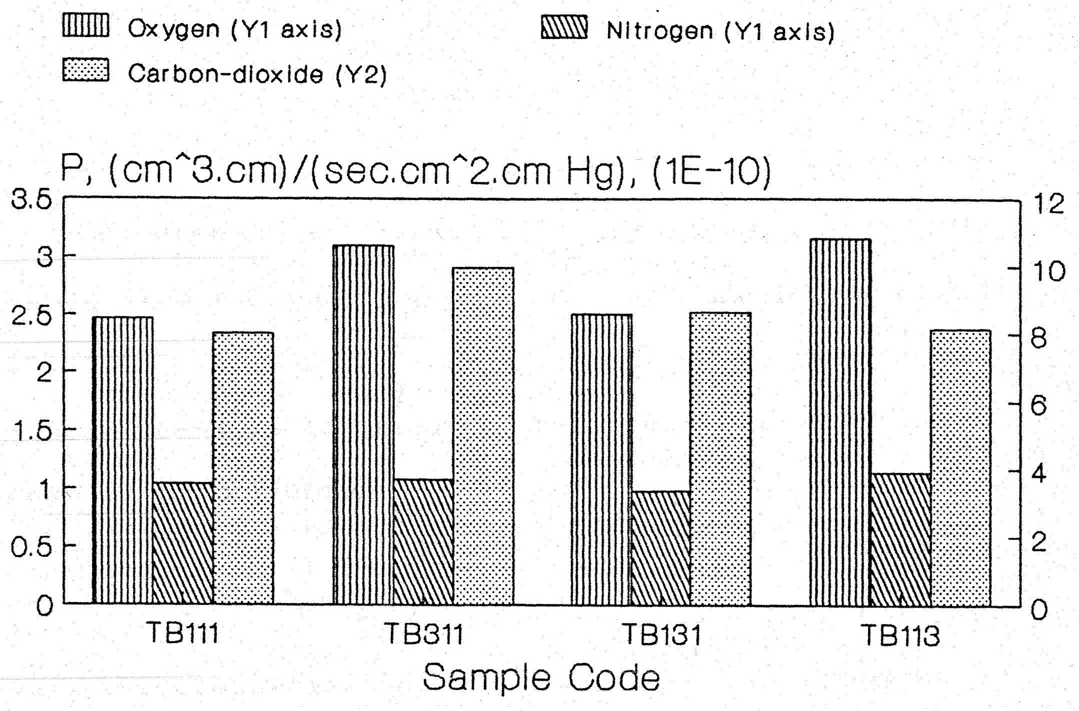


Fig. 4.6.6 Gas permeability constants for ternary blends

4.6.3 *Model*

Prediction of permeabilities of gases through polymer films is very difficult because a large number of variables govern the permeability. Salame (1970) and Robeson et al. (1973) have suggested empirical relationships for predicting the permeability. In a recent study, Swinyard et al. (1990) used the following expression to calculate the water vapour permeability of polyblends.

$$\ln P = \sum \phi_1 \cdot \ln P_1 \tag{4.24}$$

However, they reported that the calculated values differed from that of experimental ones. An empirical model consisting of terms for permeabilities and weight fractions of 'pure' components is suggested for predicting the permeabilities of the blend systems studied for this investigation. The model is:

$$\frac{1}{P} = \sum \frac{x_1}{P_1} \tag{4.25}$$

P = Permeability constant for the blend
P_1 = Permeability constant of the component 1
x_1 = fraction (w) of the component 1 in the blend,
volume fraction of component 1 = ϕ_1

4.6.3.1 Water Vapour

Using the model suggested (equation 4.25), the permeability constants can be calculated and from the values of permeability constants, the water loss through a film can also be predicted. The predicted and experimental loss of water at 37°C through films of binary and ternary blends for period of 21 days are given in Figs. 4.6.7 and 4.6.8. It can be seen that the predictions are quite accurate. The deviation is maximum for TB311 (27%) and for all the other samples the deviations are well within 10%. TB311 being the only sample having double digit deviation, the reason for such deviation can probably be attributed to experimental error for this sample. Depending on the requirements of water vapour permeability, this model can, therefore, be used for designing blend composition.

4.6.3.2 Oxygen, Nitrogen and Carbon dioxide

Due to the very low strength and sticky nature of the NBR1 films, it was difficult to carry out the measurement of permeability. Reproducible results for this film were difficult to get due the the unavoidable stretching and sticking of film surface during fixing on to the cell. It was possible to get three readings which were close only for oxygen permeability. Permeability for nitrogen and carbon dioxide could not be measured . Therefore, in absence of the data for N_2 and CO_2,the model was applied only for oxygen. The predicted and experimental permeability constants for oxygen are presented in Fig. 4.6.9. Though, the predictions are not as accurate as for water vapour, yet these are within 30% of experimental values. In an early study, Stannett et al.(1955) considered prediction of the *P* values within a factor of 2 to be good enough. Therefore, these predictions could be used at least as a rough guide for considering the permeabilities of polyblends while designing the blend formulations. The reason why the model works better for water vapour compared to oxygen is probably the different controlling factors that govern the permeability for these two gases (Section 4.6.2). For reasons of simplicity, the interactions between polymers have not been considered for this model. 'Ease of hole formation' is influenced by the interactions and hence a more complex model with these considerations should probably work better for predicting oxygen permeability.

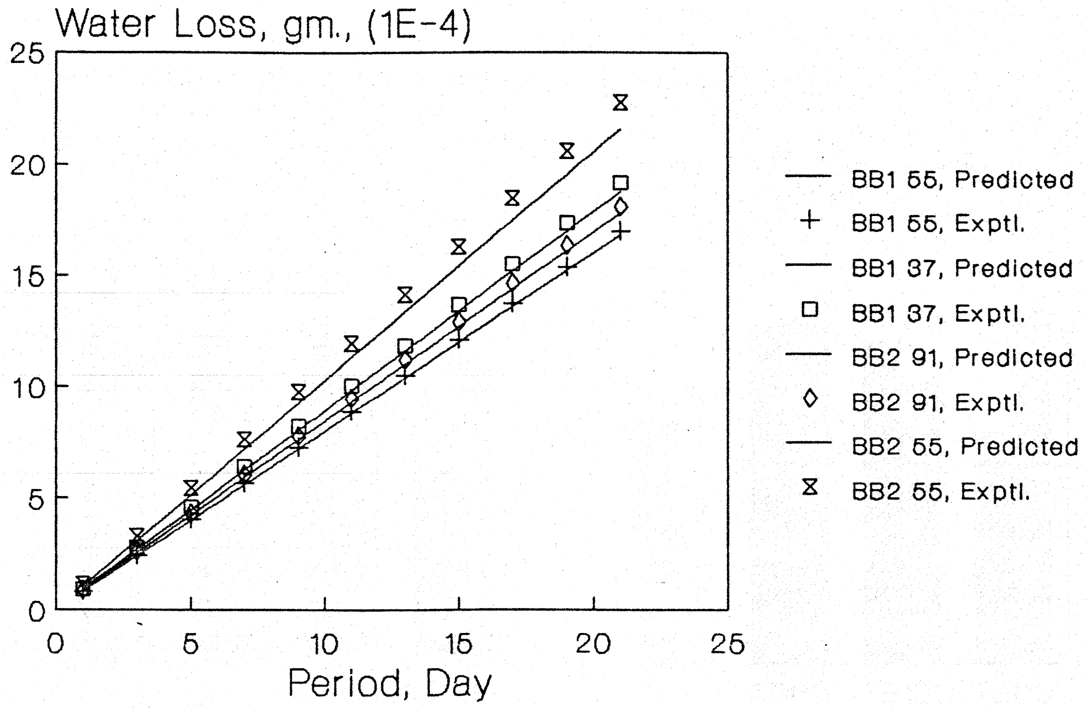


Fig. 4.6.7 Water loss for binary blends at 37°C for unit area, thickness and pressure difference

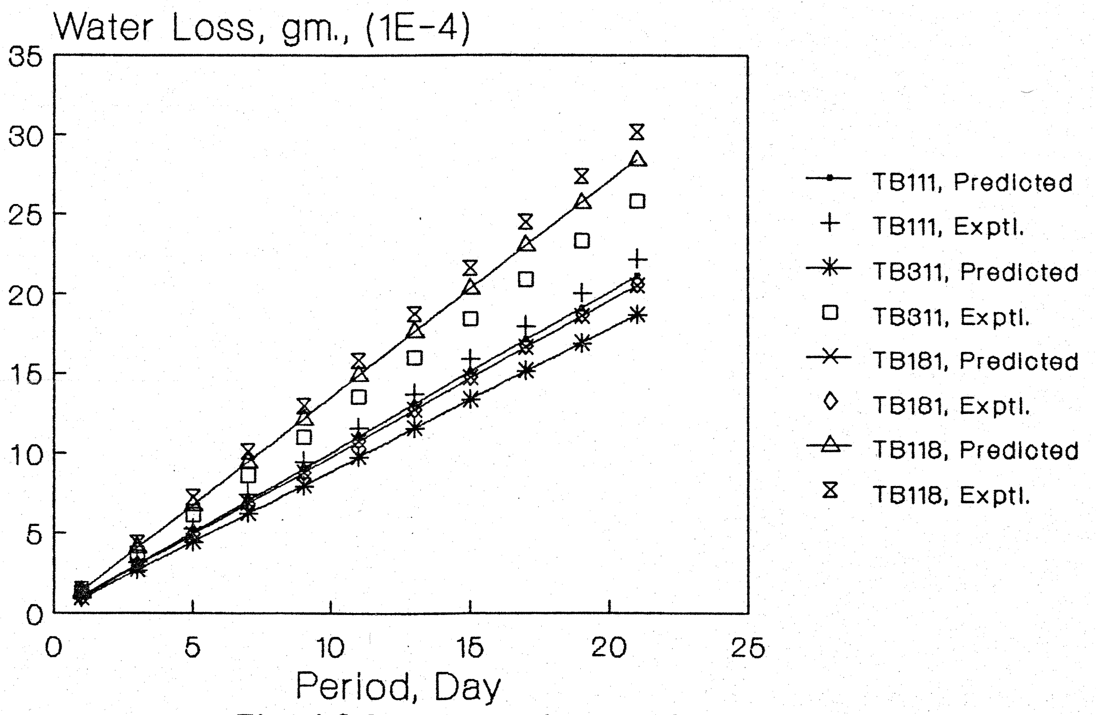


Fig. 4.6.8 Loss of water for ternary blends at 37°C for unit area, thickness and pressure difference

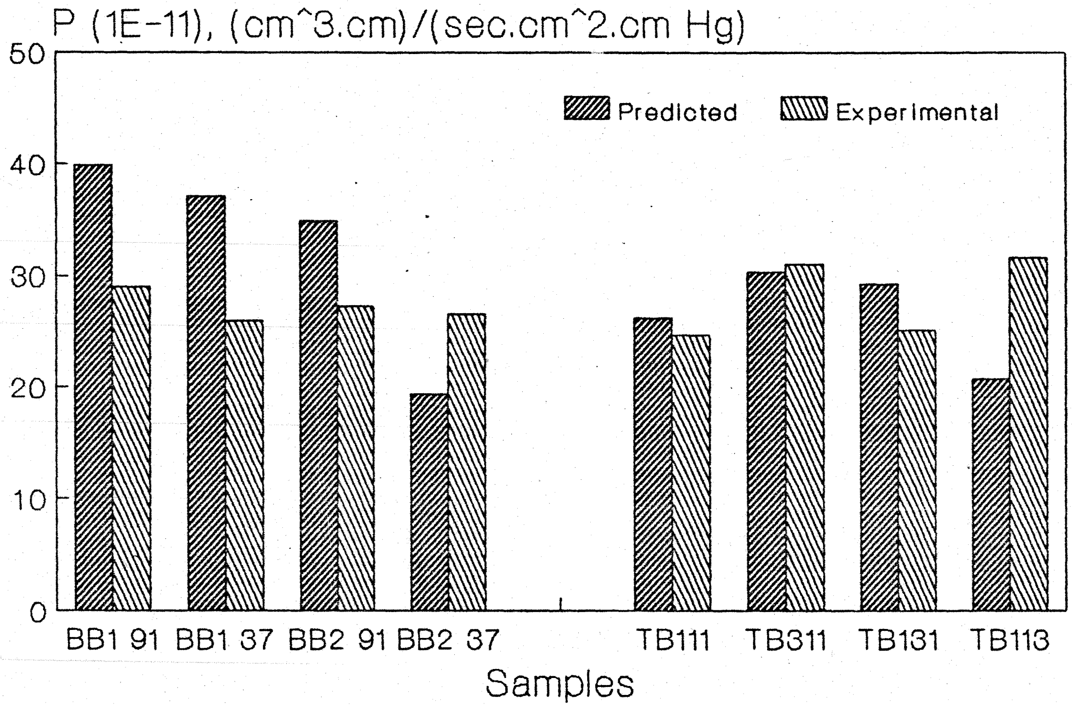


Fig. 4.6.9 Predicted and experimental values of oxygen permeability constants

CLARITY AND HAEMOLYTIC POTENTIAL

SECTION - 7

4.7 CLARITY AND HAEMOLYTIC POTENTIAL

Clarity and haemolytic potential are important considerations for PVC based devices used in medical applications. To avoid contamination, the contents of the PVC based medical devices need to be examined without opening the container. A visual examination of PVC pouches containing I.V. fluids reveals the presence or absence of fungus and other unwanted sediments. The presence of clots or unusual haemolysis in a blood bag can be detected by mere visual examination. Haemolytic potential is a measure of haemolysis (disintegration of red blood cells with liberation of contained haemoglobin) that may be caused by the material when it comes in contact with blood. Presence of traces of unacceptable extractable substances results in drastic haemolysis. Blood bags, blood giving and collection sets, soft shell oxygenator and cardiotomy reservoirs, pump tubings used in open heart surgery are only a few examples where PVC based products come in contact with blood. Haemolytic potential and clarity, therefore, are parameters which must be evaluated for PVC based materials intended for medical applications.

In this section, the results of the study on clarity and haemolytic potential are reported. Discussions have been made for the observed behaviour for the blends studied.

4.7.1 *Clarity*

The amount of light transmitted in the visible region gives the measure of clarity of a material. Percent light transmission for two samples of plasticized PVC is given in Fig. 4.7.1. Transparency is more for PPVC3 which has less plasticizer. This is expected and it happens because of the difference of refractive index between PVC and plasticizer. Transparency at 700 nm is more compared to 400 nm. This is also true for other binary and ternary polyblends studied and representative results are shown in Figs. 4.7.2 and 4.7.3 for binary blends and 'pure' components. From these figures, it is also observed that the transparency is reduced for all the polyblends. This is of course expected because of the loss of incident light due to scattering at the interfaces and different refractive indices in the phase domains of a multiphase system like polyblend (Thomas, 1978). Among the 'pure' components EVAPVC has better transparency than PPVC and NBR1 and these two have similar transparency. However, the PPVC-NBR1 blends have slightly better transparency than PPVC-EVAPVC blends. This is probably because the difference in refractive index is more for the pair PPVC-EVAPVC compared to PPVC-NBR1.

Fig. 4.7.4 shows the change in transparency as PPVC is replaced with a second component. The behaviour is same for both 700 nm and 400 nm, though, the % transmission is lower for 400 nm at all levels of replacement of PPVC. It is interesting to note that the transparency of both the binary blend systems continuously falls and is minimum when PPVC is replaced to the extent of 50-60%, beyond which it again rises. This indicates that scattering of light and inhomogeneity is maximum for binary blends at 50-60 % replacement of PPVC. This result also suggests that phase inversion takes place in this level of replacement of PPVC. Beyond 60% replacement of PPVC, it becomes a dispersed phase. Results of SEM studies also confirm such behaviour (Section 4.4.1.2).

The practical implication of this study is that 50% replacement of PPVC leads to clarity of very low order and this should be avoided. Replacement of PPVC within 30% can have still around 20% light transmission at 700 nm, which is comparable to some of the PVC medical products currently in use. At 700 nm, a film cut from blood bag of Tuta Laboratories was found to have 19% light transmission. From clarity considerations, replacement of PPVC should therefore be restricted within 30%.

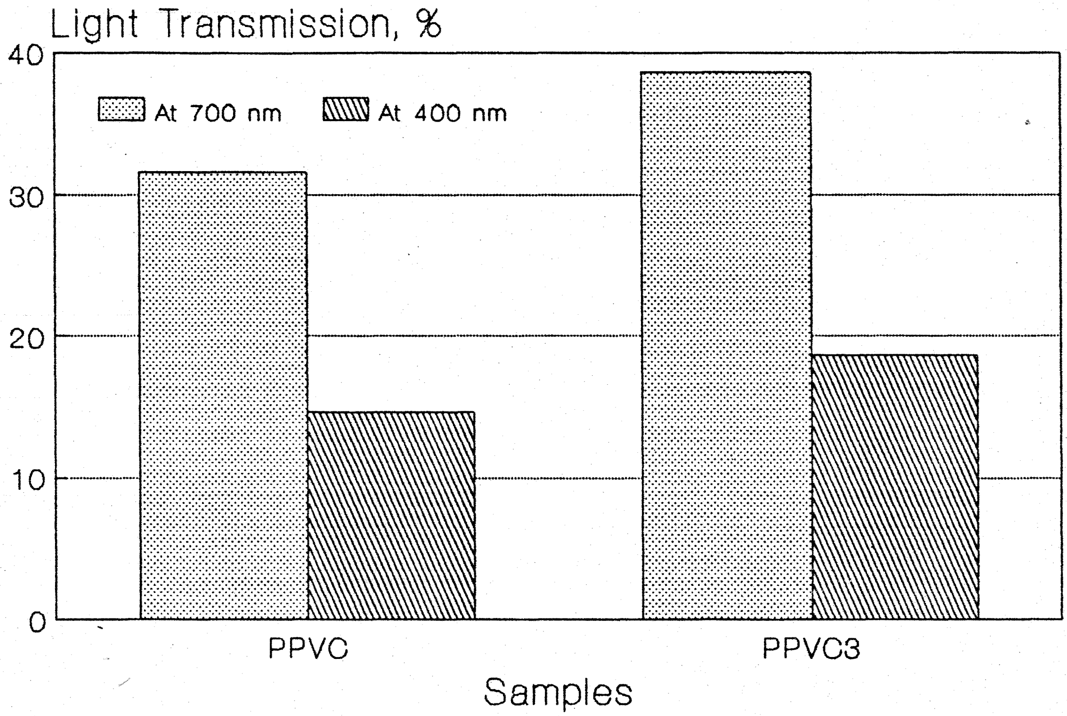


Fig. 4.7.1 Transparency of plasticized PVC samples

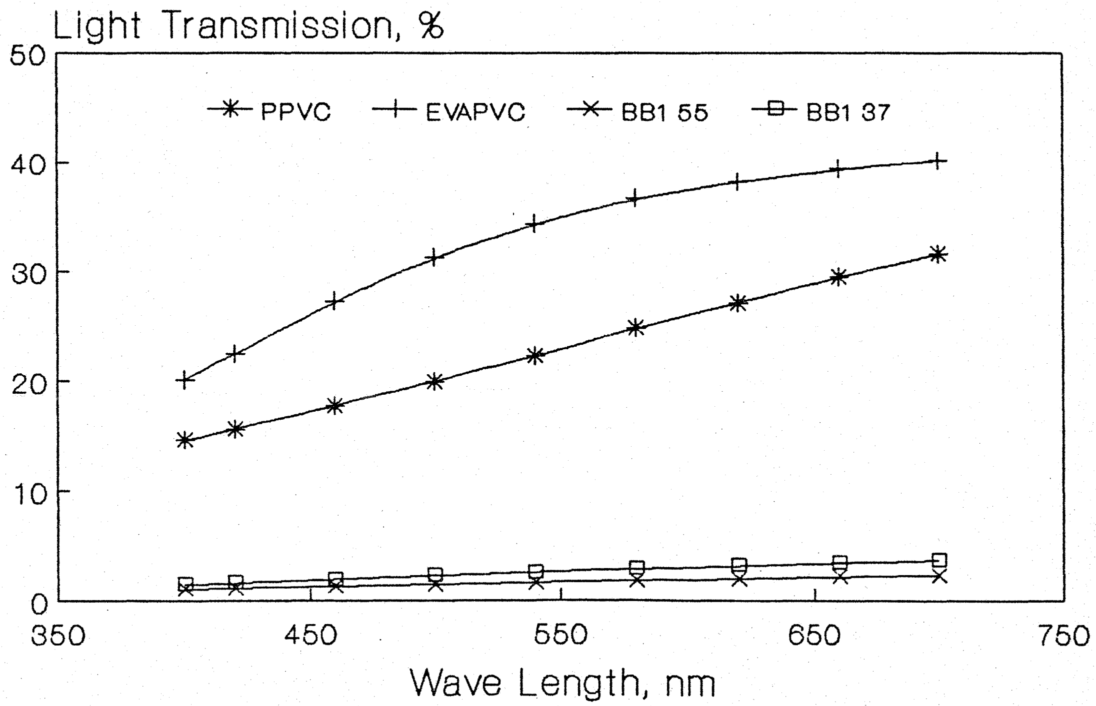


Fig. 4.7.2 Transparency of binary blends of PPVC with EVAPVC

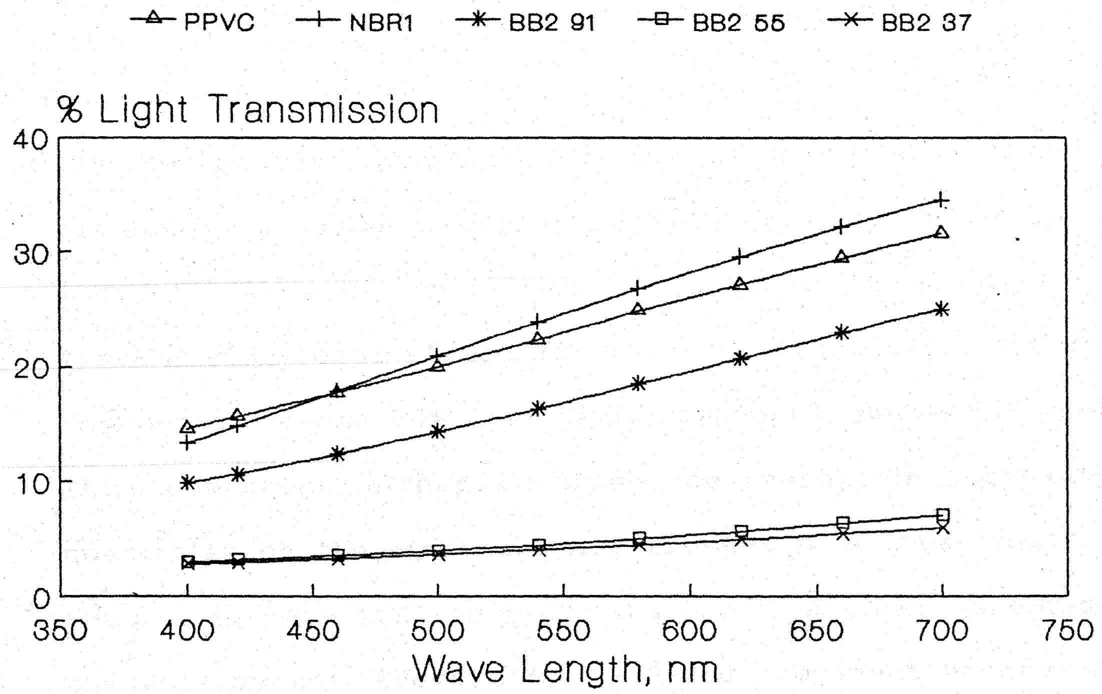


Fig. 4.7.3 Transparency of binary blends of PPVC with NBR1

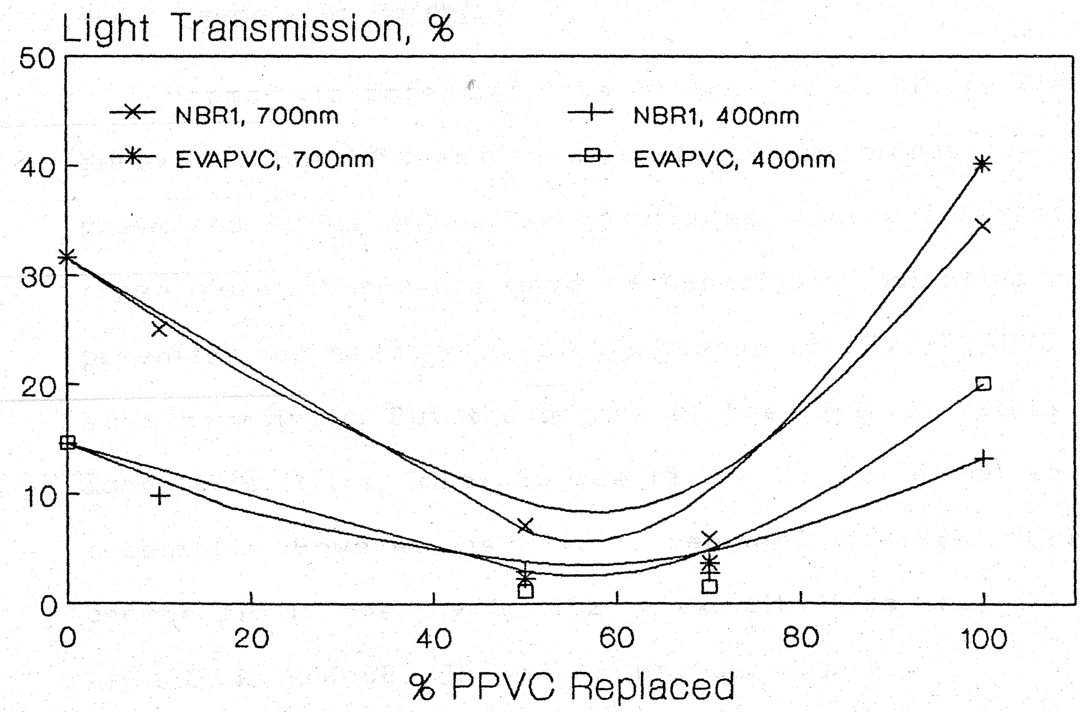


Fig. 4.7.4 Transparency of binary blends of PPVC with EVAPVC and NBR1

It can be expected that the homogeneity should be minimum for ternary blends and this is reflected in the transparency shown in Fig. 4.7.5. When the third component is added to the equal quantities of the other two, % light transmission remains very low for upto 60% addition of third component. Beyond 60% the clarity improves. Below 60% level of third component, either all three are present in substantial quantities or the first two are present in a level that results in poor transparency. Therefore, a clear continuous phase is absent. Above 60%, the third component becomes the matrix and the other two components gradually reduce resulting in improvement of clarity.

4.7.2 Haemolytic Potential

Haemolytic potential data of 'pure' and binary blends are given in Table 4.7.1 and results of ternary blends are presented in Fig. 4.7.6. The results are indeed interesting. All three 'pure' components have 0% haemolysis indicating no potential for haemolysis. Binary blends of PPVC-EVAPVC show some haemolysis. But the degree of haemolyis is within acceptable limits, since 5% haemolysis is considered to be acceptable. However, as PPVC is replaced with NBR1 blends become slowly haemolytic. BB2 91 exhibits less than 5% haemolysis and BB2 55 have 13.6% haemolysis.

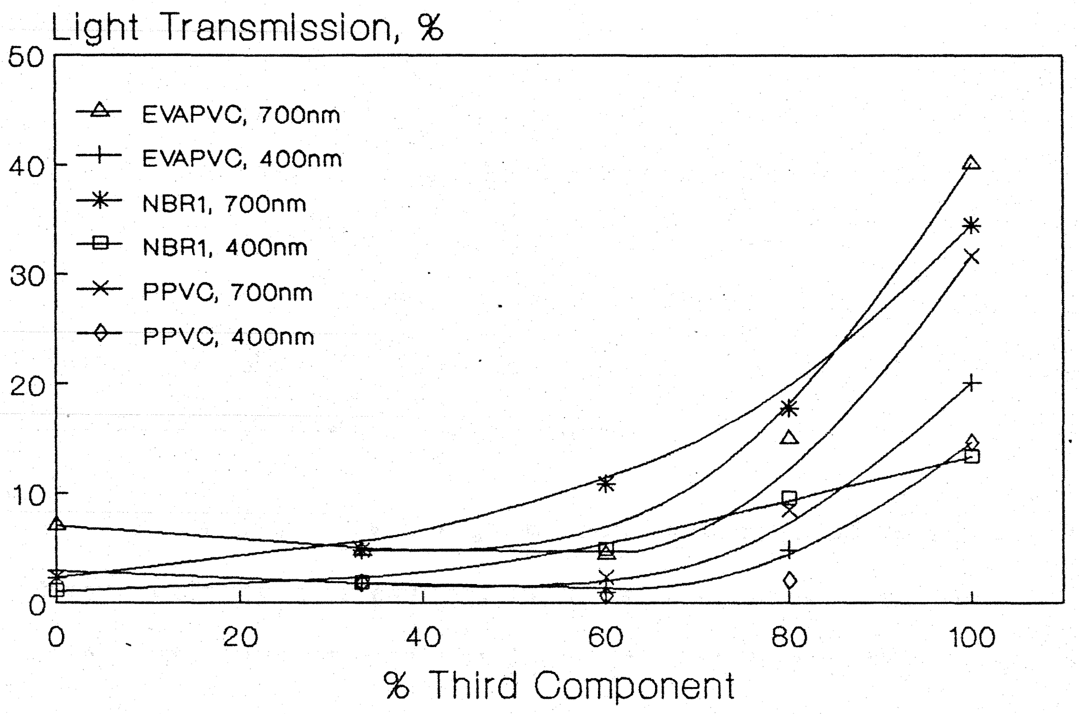


Fig.4.7.5 Transparency of ternary blends with equal fractions of two components

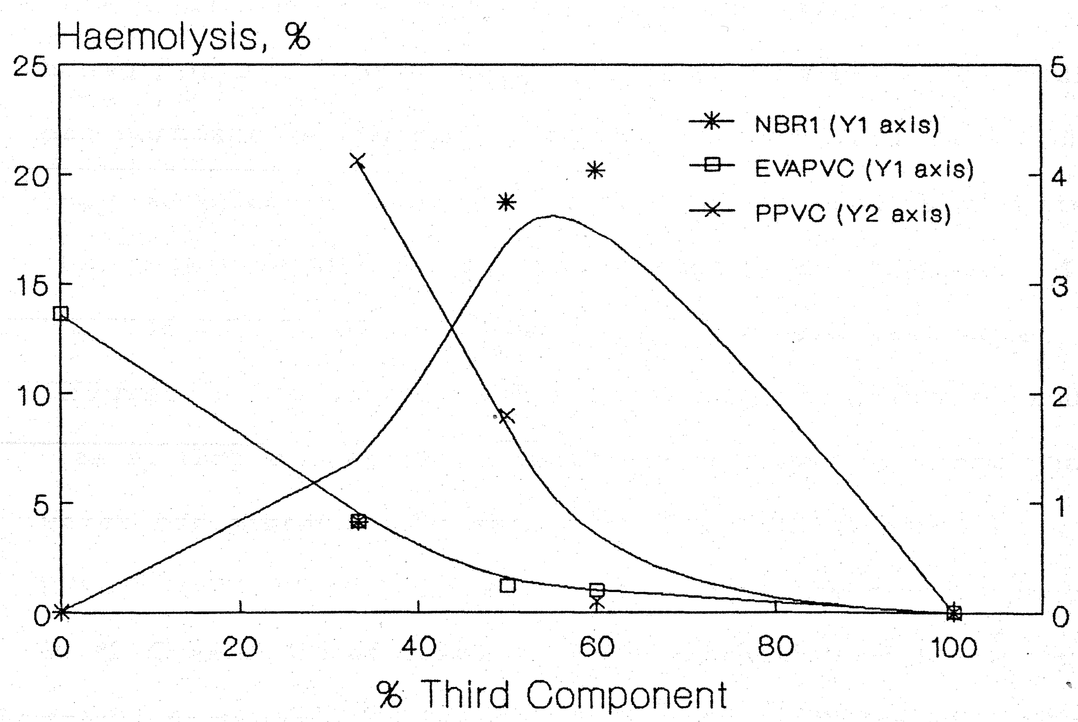


Fig. 4.7.6 Haemolytic potential of ternary blends with equal fractions of two components

Same observation is also made for ternary blends. Addition of both PPVC and EVAPVC to 1:1:1 ternary blends of PPVC, EVAPVC and NBR1 (TB111) reduce haemolysis. But addition of NBR1 to BB1 55 or TB111 increases haemolyis, though, 100% NBR1 does not have any haemolytic potential.

It is known that high molecular weight polymers are not haemolytic by themselves. Results also show that NBR1 is not haemolytic and it can not be said that haemolytic substances are extracted from NBR1. Moreover, unlike the other two, this 'pure' component is a polymer and does not have any easily extractable low molecular weight substance like PPVC. Blending of NBR1 with PPVC seem to result in the extraction of haemolytic substances (e.g., stabilizer) from PPVC. The media can permeate in and out of polyblends much more easily than 'pure' components. This is reflected in the results of water absorption (Section 4.5.3.1) and extraction in vegetable oil (Section 4.5.1.3). Other workers also concluded that water diffuses in the polymer and a water-plasticizer blend exudes (Sears, 1982 c). Results of water absorption also show that water can migrate more easily in PPVC-NBR1 blends than PPVC-EVAPVC blends. Easier permeation of the media (aqueous) in PPVC-NBR1 blends leads to more extraction of low molecular weight haemolytic substances compared to PPVC-EVAPVC blends.

Haemolytic potential is a very sensitive test method, and the test can differentiate differences in extraction between EVAPVC and NBR1 based blend systems even though the differences in extraction may be very small in percentage terms.

TABLE 4.7.1 Haemolytic Potential of 'Pure' and Binary Blend samples

Sample Codes	Haemolysis, %
PPVC	0.00
EVAPVC	0.00
NBR1	0.00
BB1 91	0.22
BB1 55	0.07
BB2 91	2.00
BB2 55	13.6

SUMMARY AND CONCLUSIONS

CHAPTER - V

SUMMARY AND CONCLUSIONS

Use of polymers has revolutionised the present day medical practice. Many of the polymers that are used today, though have contributed in improving the same, have some shortcomings. In medicine, plasticized PVC is used most in disposable applications. However, it suffers from a number of disadvantages, the notable among them being loss of plasticizer and resultant change in mechanical properties. Review of literature indicates that various approaches have been adopted to overcome the shortcomings of plasticized PVC. 'Polymer blend' approach appears to be the most attractive of all. However, there are hardly any reports of studies made on PVC based polyblends for medical applications. While 'polyblending' may result in improvement in a specific property, the need to meet the requirements of other properties, relevant to medical applications, and ease of processing and fabrication should also be considered. With the above aspects in mind, the *scope and objectives* of the present investigation have been formulated.

The *findings of the present investigation* are summarised below:

(a) Polyblends were made by solution and melt *blending techniques.* While no difficulty was encountered in solution blending of PPVC and EVAPVC, NBR1 and NBR2 were not completely soluble in THF and therefore, solution method was found to be not suitable for polyblends containing NBR1 or NBR2. Melt blending was found to be satisfactory for all the blend systems studied. Blending with a second polymer in a two roll mill was not possible in case of PPVC4, which contains very little plasticizer. It is therefore not feasible to consider total replacement of plasticizer for a flexible PVC based polyblend. Pre-mixing in a high speed mixer posed no problems for all the blends excepting those containing NBR2.

(b) Results of *MFI studies* indicate that PE and NBR1 containing blends have lower MFI than PPVC. MFI studies could not be done for pure NBR1 or PPVC-NBR1 blends containing more than 50% NBR1 due to very poor flow and degradation of the material. This limitation has to be taken into account while considering replacement of PPVC by NBR1. However, if replacement is within 30%, no difficulty should arise in processing. PPVC-EVAPVC blends exhibit higher MFI value than PPVC up to 50 percent by weight of EVAPVC, though EVAPVC itself has a lower MFI than PPVC. This observation is of great practical significance from processing point of view and addition of EVAPVC in PPVC-NBR blends should improve the flow behaviour. This is exactly what was observed for ternary blends when EVAPVC was added to a binary blend containing equal amount of PPVC and NBR1. Expectedly, addition of PPVC to 50-50 binary blend of EVAPVC-NBR1 (hypothetical) increased flow while addition of NBR1 to 1:1 PPVC-EVAPVC blend reduced the flow.

(c) *Models for viscosity* are tested for PPVC-EVAPVC binary blend system and predicted results are quite close to the experimental values. From the deviation of predicted and experimental viscosity values, it appears that EVAPVC is predominantly the matrix phase for the blends BB1 73, BB1 55 and BB1 37. SEM studies confirm this.

(d) *Analysis of the viscosity data* indicates that power law is applicable to all samples in the region of experimental $\dot{\gamma}$ values and temperature. Viscosities of all blends have expected temperature dependence, though, the change is least for blends containing more of NBR1.

(e) *"Master plots"* of $\log(\eta/a_r)$ vs. $\log(\dot{\gamma}a_r)$ are tested for the polyblends and predictions are quite satisfactory.

(f) *Die swell ratio,* an indication of normal stress during processing is maximum for PPVC. Blending with a second and/or third polymer reduces the die swell due to chain entanglement and additional resistance to alignment during extrusion. In the experimental range of temperature, increase in temperature generally increases die swell ratio. Experimental range of shear rate has very little pronounced effect on D_R . The data on D_R have been analysed with a composite relation containing terms for shear rate and temperature.

(g) *Principal normal stress difference and recoverable strain* generally show the same trend as D_R and shear modulus exhibits the reverse trend.

synergistic behaviour for both ultimate tensile stress and elongation at break indicating presence of appreciable specific interactions between the polymers. UTS and UE values for PPVC-EVAPVC binary blends are marginally lower than those derived from additivity principle. Ternary blends of PPVC, EVAPVC and NBR1 also have the ultimate properties lower than expected by additivity rule. As expected, the modulus at 100% elongation falls when PPVC is replaced by NBR1 or EVAPVC. However, the fall is marginal if replacement is kept to a level of 25-30%. It can be concluded that 30% replacement of PPVC by NBR1 or EVAPVC improves elongation at break without much of sacrifice in tensile strength and modulus.

(k) *Tensile energy to break* of PPVC improves in a binary blend when it is replaced with EVAPVC or NBR1. In ternary blends of PPVC, EVAPVC and NBR1, improvement in TEB over binaries of equal fractions of the other two is seen when NBR1 is present up to 60% and EVAPVC is present at a level higher than 50%. The ability to improve TEB of PPVC by blending it with EVAPVC and/or NBR1 has important practical utility, particularly, in medical applications.

(l) Both PPVC and NBR1 and binary blends of these two do not exhibit any *permanent set* for the periods and load used in the experiments. EVAPVC and blends containing EVAPVC on the other hand, exhibited creep. For applications, in which materials continuously experience stress, even if at a low level, the use of EVAPVC should be kept to a minimum.

(q) *SEM studies* confirm that the morphology of blends depend on the method of sample preparation. The binary and ternary blends have uniformly distributed separate phases, though distinct phase boundaries are not seen. The matrix and the continuous phases are determined by the relative amounts of the components present in a system. The polyblends studied have components that are fairly compatible and the noted inhomogeneity in microlevel (and homogeneity at macrolevel) can be improved by proper selection of processing conditions.

(r) *Migration studies* for samples of plasticized PVC *in vegetable oil* which simulates the lipid component of blood, have helped in identifying the critical plasticizer level below which extraction of non-resinous matter is reduced drastically. PPVC-NBR1 blends having different levels of non-resinous matter also confirm this trend. It is also noted that the resistance to extraction is more pronounced in PVC compared to PPVC-NBR1 blends containing the same amount of plasticizer. PE blends do not improve the extraction resistance in vegetable oil. An important finding is that, permanence, judged from the change in mechanical properties of pre- and post-extracted samples, is achieved to a large degree in PPVC-NBR1 blends containing around 30% NBR1. PE blends do not provide permanence in properties.

(s) The conclusions made from the *migration studies in simulated gastric juice* are: (i) migration takes place both into (absorption) and away (plasticizer migration) from the material, (ii) the amount of migration is very low for all the samples studied, and (iii) nature of specific aqueous media and its pH affect migration and water absorption.

(t) The amount of *water absorption* of three 'pure' components is found to be in the order PPVC<EVAPVC<NBR1. It is interesting to note that the blends have more water absorption than expected from additivity principle. Presence of additional free volume in the blends, as supported by data on density measurements, is attributed for such observation.

(u) Increased plasticization increases *permeability for water vapour,* O_2, CO_2 and N_2 due to increased chain mobility. The trend for water vapour permeability for 'pure' components is the same as observed for WA suggesting solubility of water in barrier films is the predominant factor that determines water vapour permeability in these cases. While temperature increases permeability, the change is faster as the materials cross the region of T_g. Blending PPVC with a second and/or third polymer results in reduced O_2, CO_2 and N_2 permeability. This improvement in property is of great practical significance and interest, since, in medical applications plasticized PVC is mainly used for storing substances which are affected by permeating gases.

(v) *Clarity* is affected when PPVC is replaced with a second and/or third polymer. However, the replacement can be maintained at a level which leads to polyblends having clarity comparable to some of the existing PVC based medical products.

(w) *Haemolytic potential* is not affected due to the replacement of PPVC with EVAPVC. Though NBR1 itself has 0% haemolysis, blends containing substantial quantities of NBR1 exhibit haemolytic potential and therefore, to restrict haemolysis within acceptable limits, content of NBR1 should not exceed 30%.

The present investigation has resulted in an understanding of the blend behaviour and in generating comprehensive data base for the entire range of composition for the polyblend systems studied. Studies carried out demonstrate that improvement in 'permanence' can be achieved through 'polymer blend approach' without making compromise with other desirable properties that are relevant to medical applications.

Further rational step would be (i) to identify specific end products like pump tubings, tubings for administration sets, blood bags, CAPD containers, etc., and select formulations based on requirements of such end application and the available data on these polyblends, and (ii) to make further specific studies for evaluation of the suitability of the selected formulation for the application. (Studies to evaluate the blend formulations will have to be relevant to the end application and may include detailed biological characterization).

It would also be interesting to *extend the study* of polyblends of other systems for possible medical applications.

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APPENDICES

APPENDIX - A

TABLE A.1 Calculated values of Shear Stress, MFI, Shear Rate and Viscosity

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
PPVC	150	9.11E+04	2.98	6.55E+00	1.39E+05
PPVC	150	1.26E+05	7.62	1.67E+01	7.51E+04
PPVC	150	1.37E+05	8.67	1.90E+01	7.18E+04
PPVC	150	1.71E+05	16.53	3.63E+01	4.72E+04
PPVC	160	9.11E+04	3.67	8.24E+00	1.11E+05
PPVC	160	1.26E+05	10.04	2.26E+01	5.57E+04
PPVC	160	1.37E+05	12.63	2.84E+01	4.81E+04
PPVC	160	1.71E+05	22.98	5.16E+01	3.32E+04
PPVC	165	9.11E+04	8.59	1.95E+01	4.67E+04
PPVC	165	1.11E+05	10.31	2.34E+01	4.73E+04
PPVC	165	1.26E+05	14.91	3.39E+01	3.71E+04
PPVC	165	1.71E+05	40.80	9.27E+01	1.85E+04
PPVC	170	8.02E+04	7.36	1.57E+01	5.10E+04
PPVC	170	9.11E+04	10.16	2.17E+01	4.20E+04
PPVC	170	1.11E+05	19.57	4.18E+01	2.65E+04
PPVC	170	1.26E+05	24.38	5.21E+01	2.41E+04
PPVC2	170	1.37E+05	2.12	6.15E+00	2.22E+05
PPVC2	170	1.45E+05	2.54	7.38E+00	1.97E+05
PPVC2	170	1.56E+05	3.52	1.02E+01	1.53E+05
PPVC2	170	1.71E+05	8.02	2.33E+01	7.35E+04
PPVC2	175	1.26E+05	4.71	1.02E+01	1.23E+05
PPVC2	175	1.37E+05	6.32	1.37E+01	9.98E+04
PPVC2	175	1.45E+05	6.60	1.43E+01	1.02E+05
PPVC2	175	1.71E+05	11.25	2.44E+01	7.02E+04
PPVC2	180	1.26E+05	9.69	2.29E+01	5.49E+04
PPVC2	180	1.37E+05	12.00	2.84E+01	4.82E+04
PPVC2	180	1.45E+05	17.57	4.16E+01	3.50E+04
PPVC2	180	1.71E+05	26.50	6.27E+01	2.73E+04
PPVC2	185	9.11E+04	22.29	5.16E+01	1.76E+04
PPVC2	185	1.11E+05	66.79	1.55E+02	7.16E+03
PPVC2	185	8.02E+04	14.87	3.44E+01	2.33E+04
PPVC2	185	1.26E+05	81.49	1.89E+02	6.66E+03

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
PPVC3	175	1.37E+05	2.53	6.41E+00	2.13E+05
PPVC3	175	1.45E+05	3.21	8.13E+00	1.79E+05
PPVC3	175	1.56E+05	3.50	8.86E+00	1.77E+05
PPVC3	175	1.71E+05	7.06	1.79E+01	9.58E+04
PPVC3	180	1.37E+05	3.51	1.15E+01	1.19E+05
PPVC3	180	1.45E+05	5.17	1.69E+01	8.60E+04
PPVC3	180	1.56E+05	8.17	2.67E+01	5.86E+04
PPVC3	180	1.71E+05	13.75	4.49E+01	3.81E+04
PPVC3	185	1.37E+05	10.60	2.04E+01	6.69E+04
PPVC3	185	1.45E+05	11.79	2.27E+01	6.41E+04
PPVC3	185	1.56E+05	13.84	2.66E+01	5.87E+04
PPVC3	185	1.71E+05	19.16	3.69E+01	4.64E+04
PPVC3	190	1.37E+05	21.59	5.85E+01	2.34E+04
PPVC3	190	1.45E+05	28.22	7.65E+01	1.90E+04
PPVC3	190	1.56E+05	38.57	1.05E+02	1.50E+04
PPVC3	190	1.71E+05	61.39	1.66E+02	1.03E+04
PE1	150	1.26E+05	5.45	1.66E+01	7.60E+04
PE1	150	1.37E+05	7.88	2.39E+01	5.71E+04
PE1	150	1.45E+05	10.95	3.32E+01	4.38E+04
PE1	150	1.56E+05	15.77	4.79E+01	3.27E+04
PE1	160	1.26E+05	10.63	2.57E+01	4.89E+04
PE1	160	1.37E+05	13.74	3.33E+01	4.11E+04
PE1	160	1.45E+05	17.04	4.12E+01	3.53E+04
PE1	160	1.56E+05	21.76	5.27E+01	2.97E+04
PE1	165	1.26E+05	17.58	4.59E+01	2.74E+04
PE1	165	1.37E+05	18.80	4.91E+01	2.78E+04
PE1	165	1.45E+05	26.72	6.98E+01	2.08E+04
PE1	165	1.56E+05	35.18	9.19E+01	1.70E+04
PE1	170	1.26E+05	34.24	6.42E+01	1.96E+04
PE1	170	1.37E+05	38.11	7.14E+01	1.91E+04
PE1	170	1.45E+05	41.91	7.86E+01	1.85E+04
PE1	170	1.56E+05	56.00	1.05E+02	1.49E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
PE2	150	1.26E+05	8.60	1.64E+01	7.69E+04
PE2	150	1.37E+05	10.60	2.01E+01	6.79E+04
PE2	150	1.45E+05	11.45	2.18E+01	6.68E+04
PE2	150	1.56E+05	13.69	2.60E+01	6.01E+04
PE2	160	1.26E+05	8.78	2.33E+01	5.41E+04
PE2	160	1.37E+05	11.43	3.03E+01	4.51E+04
PE2	160	1.45E+05	14.87	3.94E+01	3.69E+04
PE2	160	1.56E+05	20.38	5.40E+01	2.89E+04
PE2	165	1.26E+05	15.02	3.46E+01	3.63E+04
PE2	165	1.37E+05	18.60	4.29E+01	3.18E+04
PE2	165	1.45E+05	22.11	5.10E+01	2.85E+04
PE2	165	1.56E+05	29.20	6.74E+01	2.32E+04
PE2	170	1.26E+05	21.87	5.12E+01	2.45E+04
PE2	170	1.37E+05	27.68	6.48E+01	2.11E+04
PE2	170	1.45E+05	33.00	7.73E+01	1.88E+04
PE2	170	1.56E+05	43.20	1.01E+02	1.54E+04
PE3	150	1.26E+05	8.27	1.67E+01	7.51E+04
PE3	150	1.37E+05	9.41	1.90E+01	7.18E+04
PE3	150	1.45E+05	11.39	2.30E+01	6.31E+04
PE3	150	1.56E+05	13.57	2.75E+01	5.69E+04
PE3	160	1.26E+05	12.26	2.49E+01	5.05E+04
PE3	160	1.37E+05	14.08	2.86E+01	4.78E+04
PE3	160	1.45E+05	16.33	3.32E+01	4.39E+04
PE3	160	1.56E+05	20.50	4.16E+01	3.76E+04
PE3	165	1.26E+05	12.75	3.10E+01	4.06E+04
PE3	165	1.37E+05	16.55	4.02E+01	3.40E+04
PE3	165	1.45E+05	20.82	5.06E+01	2.88E+04
PE3	165	1.56E+05	26.13	6.35E+01	2.46E+04
PE3	170	1.26E+05	18.36	4.03E+01	3.12E+04
PE3	170	1.37E+05	25.76	5.66E+01	2.42E+04
PE3	170	1.45E+05	28.41	6.24E+01	2.33E+04
PE3	170	1.56E+05	36.47	8.01E+01	1.95E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
PE7	150	1.26E+05	6.37	1.30E+01	9.64E+04
PE7	150	1.37E+05	6.58	1.35E+01	1.01E+05
PE7	150	1.45E+05	7.04	1.44E+01	1.01E+05
PE7	150	1.56E+05	9.18	1.88E+01	8.32E+04
PE7	160	1.26E+05	7.51	1.60E+01	7.84E+04
PE7	160	1.37E+05	8.23	1.76E+01	7.78E+04
PE7	160	1.45E+05	10.94	2.34E+01	6.22E+04
PE7	160	1.56E+05	11.38	2.43E+01	6.44E+04
PE7	165	1.26E+05	10.43	2.52E+01	4.99E+04
PE7	165	1.37E+05	13.42	3.24E+01	4.22E+04
PE7	165	1.45E+05	16.19	3.91E+01	3.72E+04
PE7	165	1.56E+05	21.80	5.26E+01	2.97E+04
PE7	170	1.26E+05	18.27	4.49E+01	2.80E+04
PE7	170	1.37E+05	25.23	6.20E+01	2.20E+04
PE7	170	1.45E+05	31.33	7.70E+01	1.89E+04
PE7	170	1.56E+05	38.97	9.58E+01	1.63E+04
PE8	150	1.26E+05	3.62	8.36E+00	1.50E+05
PE8	150	1.37E+05	4.95	1.14E+01	1.20E+05
PE8	150	1.45E+05	5.48	1.27E+01	1.15E+05
PE8	150	1.56E+05	7.77	1.80E+01	8.71E+04
PE8	160	1.26E+05	6.31	1.63E+01	7.70E+04
PE8	160	1.37E+05	9.05	2.34E+01	5.84E+04
PE8	160	1.45E+05	10.79	2.79E+01	5.21E+04
PE8	160	1.56E+05	14.67	3.80E+01	4.12E+04
PE8	165	1.26E+05	8.65	2.29E+01	5.49E+04
PE8	165	1.37E+05	13.56	3.59E+01	3.81E+04
PE8	165	1.45E+05	16.72	4.43E+01	3.29E+04
PE8	165	1.56E+05	21.13	5.59E+01	2.80E+04
PE8	170	1.26E+05	16.40	4.04E+01	3.11E+04
PE8	170	1.37E+05	20.59	5.08E+01	2.69E+04
PE8	170	1.45E+05	27.06	6.67E+01	2.18E+04
PE8	170	1.56E+05	33.87	8.35E+01	1.87E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
PE9	150	1.26E+05	4.08	9.63E+00	1.31E+05
PE9	150	1.37E+05	6.25	1.48E+01	9.26E+04
PE9	150	1.45E+05	7.23	1.71E+01	8.52E+04
PE9	150	1.56E+05	8.80	2.08E+01	7.53E+04
PE9	160	1.26E+05	7.22	1.74E+01	7.21E+04
PE9	160	1.37E+05	9.90	2.39E+01	5.71E+04
PE9	160	1.45E+05	11.78	2.84E+01	5.11E+04
PE9	160	1.56E+05	15.02	3.63E+01	4.31E+04
PE9	165	1.26E+05	9.38	2.20E+01	5.71E+04
PE9	165	1.37E+05	13.50	3.17E+01	4.32E+04
PE9	165	1.45E+05	15.08	3.54E+01	4.11E+04
PE9	165	1.56E+05	20.37	4.78E+01	3.27E+04
PE9	170	1.26E+05	14.22	3.45E+01	3.64E+04
PE9	170	1.37E+05	18.97	4.61E+01	2.97E+04
PE9	170	1.45E+05	23.30	5.66E+01	2.57E+04
PE9	170	1.56E+05	29.25	7.10E+01	2.20E+04
EVAPVC	160	1.37E+05	2.78	6.32E+00	2.16E+05
EVAPVC	160	1.45E+05	3.29	7.46E+00	1.95E+05
EVAPVC	160	1.56E+05	3.67	8.32E+00	1.88E+05
EVAPVC	160	1.71E+05	5.47	1.24E+01	1.38E+05
EVAPVC	170	1.37E+05	5.11	1.32E+01	1.03E+05
EVAPVC	170	1.45E+05	6.62	1.72E+01	8.47E+04
EVAPVC	170	1.56E+05	8.25	2.14E+01	7.31E+04
EVAPVC	170	1.71E+05	10.74	2.78E+01	6.15E+04
EVAPVC	175	1.37E+05	7.54	1.81E+01	7.57E+04
EVAPVC	175	1.45E+05	8.65	2.07E+01	7.02E+04
EVAPVC	175	1.56E+05	11.39	2.73E+01	5.73E+04
EVAPVC	175	1.71E+05	14.18	3.40E+01	5.04E+04
EVAPVC	180	1.37E+05	11.09	2.57E+01	5.32E+04
EVAPVC	180	1.45E+05	13.07	3.03E+01	4.80E+04
EVAPVC	180	1.56E+05	15.34	3.56E+01	4.40E+04
EVAPVC	180	1.71E+05	20.40	4.73E+01	3.62E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
BB1 91	160	9.11E+04	7.71	1.72E+01	5.31E+04
BB1 91	160	1.11E+05	12.83	2.86E+01	3.88E+04
BB1 91	160	1.26E+05	17.66	3.93E+01	3.20E+04
BB1 91	160	1.37E+05	22.66	5.04E+01	2.71E+04
BB1 91	165	9.11E+04	9.53	2.05E+01	4.45E+04
BB1 91	165	1.11E+05	18.07	3.88E+01	2.86E+04
BB1 91	165	1.26E+05	23.18	4.97E+01	2.53E+04
BB1 91	165	1.37E+05	28.29	6.07E+01	2.25E+04
BB1 91	170	9.11E+04	12.02	2.65E+01	3.44E+04
BB1 91	170	1.11E+05	19.36	4.26E+01	2.60E+04
BB1 91	170	1.26E+05	28.76	6.33E+01	1.99E+04
BB1 91	170	1.37E+05	34.53	7.60E+01	1.80E+04
BB1 91	175	9.11E+04	16.93	3.25E+01	2.80E+04
BB1 91	175	1.11E+05	29.46	5.66E+01	1.96E+04
BB1 91	175	1.26E+05	35.25	6.78E+01	1.86E+04
BB1 91	175	1.37E+05	40.83	7.85E+01	1.74E+04
BB1 73	160	9.11E+04	7.39	1.67E+01	5.45E+04
BB1 73	160	1.11E+05	13.99	3.16E+01	3.50E+04
BB1 73	160	1.26E+05	19.93	4.51E+01	2.79E+04
BB1 73	160	1.37E+05	23.54	5.32E+01	2.57E+04
BB1 73	165	9.11E+04	12.56	2.67E+01	3.42E+04
BB1 73	165	1.11E+05	20.28	4.31E+01	2.57E+04
BB1 73	165	1.26E+05	27.90	5.93E+01	2.12E+04
BB1 73	165	1.37E+05	32.86	6.98E+01	1.96E+04
BB1 73	170	9.11E+04	18.20	3.83E+01	2.38E+04
BB1 73	170	1.11E+05	26.65	5.61E+01	1.97E+04
BB1 73	170	1.26E+05	42.38	8.93E+01	1.41E+04
BB1 73	170	1.37E+05	47.90	1.01E+02	1.35E+04
BB1 73	175	9.11E+04	26.28	5.45E+01	1.67E+04
BB1 73	175	1.11E+05	52.39	1.09E+02	1.02E+04
BB1 73	175	1.26E+05	66.92	1.39E+02	9.06E+03
BB1 73	175	1.37E+05	76.33	1.58E+02	8.63E+03

Sample Codes	Temp ºC	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
BB1 55	160	9.11E+04	4.74	1.11E+01	8.23E+04
BB1 55	160	1.11E+05	7.91	1.85E+01	6.00E+04
BB1 55	160	1.26E+05	12.91	3.01E+01	4.17E+04
BB1 55	160	1.37E+05	15.10	3.52E+01	3.88E+04
BB1 55	170	9.11E+04	11.92	2.67E+01	3.41E+04
BB1 55	170	1.11E+05	18.99	4.25E+01	2.61E+04
BB1 55	170	1.26E+05	26.94	6.03E+01	2.09E+04
BB1 55	170	1.37E+05	32.96	7.38E+01	1.85E+04
BB1 55	175	9.11E+04	15.25	3.46E+01	2.63E+04
BB1 55	175	1.11E+05	23.95	5.43E+01	2.04E+04
BB1 55	175	1.26E+05	34.64	7.85E+01	1.60E+04
BB1 55	175	1.37E+05	43.05	9.76E+01	1.40E+04
BB1 55	180	9.11E+04	21.81	4.70E+01	1.94E+04
BB1 55	180	1.11E+05	33.07	7.12E+01	1.56E+04
BB1 55	180	1.26E+05	46.03	9.91E+01	1.27E+04
BB1 55	180	1.37E+05	55.22	1.19E+02	1.15E+04
BB1 37	160	9.11E+04	2.56	6.19E+00	1.47E+05
BB1 37	160	1.11E+05	4.34	1.05E+01	1.06E+05
BB1 37	160	1.26E+05	6.23	1.51E+01	8.35E+04
BB1 37	160	1.37E+05	8.43	2.04E+01	6.71E+04
BB1 37	170	9.11E+04	6.22	1.41E+01	6.44E+04
BB1 37	170	1.11E+05	10.37	2.36E+01	4.70E+04
BB1 37	170	1.26E+05	14.24	3.24E+01	3.89E+04
BB1 37	170	1.37E+05	18.01	4.09E+01	3.34E+04
BB1 37	175	9.11E+04	7.96	1.78E+01	5.12E+04
BB1 37	175	1.11E+05	12.57	2.81E+01	3.94E+04
BB1 37	175	1.26E+05	17.68	3.95E+01	3.18E+04
BB1 37	175	1.37E+05	21.90	4.90E+01	2.79E+04
BB1 37	180	9.11E+04	11.35	2.40E+01	3.80E+04
BB1 37	180	1.11E+05	18.65	3.94E+01	2.81E+04
BB1 37	180	1.26E+05	24.38	5.15E+01	2.44E+04
BB1 37	180	1.37E+05	28.86	6.10E+01	2.24E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
BB1 19	160	1.11E+05	2.02	4.85E+00	2.28E+05
BB1 19	160	1.26E+05	3.14	7.56E+00	1.66E+05
BB1 19	160	1.37E+05	4.07	9.79E+00	1.40E+05
BB1 19	160	1.45E+05	4.32	1.04E+01	1.40E+05
BB1 19	170	1.11E+05	4.61	1.13E+01	9.81E+04
BB1 19	170	1.26E+05	6.48	1.59E+01	7.92E+04
BB1 19	170	1.37E+05	8.46	2.07E+01	6.60E+04
BB1 19	170	1.45E+05	10.33	2.53E+01	5.75E+04
BB1 19	175	1.11E+05	6.62	1.41E+01	7.86E+04
BB1 19	175	1.26E+05	9.23	1.97E+01	6.40E+04
BB1 19	175	1.37E+05	11.43	2.44E+01	5.61E+04
BB1 19	175	1.45E+05	12.59	2.68E+01	5.42E+04
BB1 19	180	1.11E+05	8.73	1.89E+01	5.85E+04
BB1 19	180	1.26E+05	11.72	2.54E+01	4.95E+04
BB1 19	180	1.37E+05	14.57	3.16E+01	4.32E+04
BB1 19	180	1.45E+05	16.50	3.58E+01	4.07E+04
BB2 91	165	9.11E+04	2.19	5.65E+00	1.61E+05
BB2 91	165	1.11E+05	4.05	1.05E+01	1.06E+05
BB2 91	165	1.26E+05	6.81	1.76E+01	7.15E+04
BB2 91	165	1.37E+05	9.21	2.38E+01	5.74E+04
BB2 91	170	9.11E+04	2.99	7.15E+00	1.27E+05
BB2 91	170	1.11E+05	5.77	1.38E+01	8.02E+04
BB2 91	170	1.26E+05	8.14	1.95E+01	6.45E+04
BB2 91	170	1.37E+05	10.92	2.61E+01	5.23E+04
BB2 91	175	9.11E+04	6.22	1.55E+01	5.88E+04
BB2 91	175	1.11E+05	10.41	2.59E+01	4.28E+04
BB2 91	175	1.26E+05	16.71	4.16E+01	3.02E+04
BB2 91	175	1.37E+05	23.59	5.87E+01	2.33E+04
BB2 91	180	9.11E+04	12.82	2.85E+01	3.19E+04
BB2 91	180	1.11E+05	22.55	5.02E+01	2.21E+04
BB2 91	180	1.26E+05	30.27	6.74E+01	1.87E+04
BB2 91	180	1.37E+05	39.09	8.70E+01	1.57E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
BB2 73	165	1.26E+05	1.23	4.18E+00	3.01E+05
BB2 73	165	1.37E+05	2.21	7.50E+00	1.82E+05
BB2 73	165	1.45E+05	2.83	9.60E+00	1.51E+05
BB2 73	165	1.56E+05	4.25	1.44E+01	1.09E+05
BB2 73	165	1.71E+05	6.67	2.26E+01	7.58E+04
BB2 73	170	9.11E+04	0.71	1.97E+00	4.62E+05
BB2 73	170	1.11E+05	1.06	2.96E+00	3.74E+05
BB2 73	170	1.26E+05	2.91	8.12E+00	1.55E+05
BB2 73	170	1.37E+05	3.78	1.06E+01	1.29E+05
BB2 73	175	1.26E+05	3.26	9.73E+00	1.29E+05
BB2 73	175	1.37E+05	6.43	1.92E+01	7.12E+04
BB2 73	175	1.45E+05	7.96	2.38E+01	6.12E+04
BB2 73	175	1.56E+05	10.04	3.00E+01	5.22E+04
BB2 73	180	9.11E+04	1.72	4.63E+00	1.97E+05
BB2 73	180	1.11E+05	3.06	8.26E+00	1.34E+05
BB2 73	180	1.26E+05	4.27	1.15E+01	1.09E+05
BB2 73	180	1.37E+05	8.52	2.30E+01	5.95E+04
BB2 55	165	1.26E+05	0.90	2.83E+00	4.44E+05
BB2 55	165	1.37E+05	1.42	4.49E+00	3.04E+05
BB2 55	165	1.56E+05	2.40	7.60E+00	2.06E+05
BB2 55	165	1.71E+05	3.68	1.16E+01	1.47E+05
BB2 55	170	1.26E+05	1.00	2.86E+00	4.39E+05
BB2 55	170	1.37E+05	1.42	4.04E+00	3.38E+05
BB2 55	170	1.56E+05	1.88	5.36E+00	2.92E+05
BB2 55	170	1.71E+05	4.40	1.25E+01	1.37E+05
BB2 55	175	1.26E+05	1.11	3.42E+00	3.68E+05
BB2 55	175	1.37E+05	2.25	6.94E+00	1.97E+05
BB2 55	175	1.56E+05	3.09	9.52E+00	1.64E+05
BB2 55	175	1.71E+05	5.31	1.64E+01	1.05E+05
BB2 55	180	1.26E+05	1.72	3.84E+00	3.27E+05
BB2 55	180	1.37E+05	3.03	6.76E+00	2.02E+05
BB2 55	180	1.56E+05	3.34	7.44E+00	2.10E+05
BB2 55	180	1.71E+05	6.03	1.34E+01	1.28E+05

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
TB111	170	1.26E+05	2.60	6.51E+00	1.93E+05
TB111	170	1.37E+05	3.16	7.93E+00	1.72E+05
TB111	170	1.45E+05	3.87	9.71E+00	1.50E+05
TB111	170	1.71E+05	6.38	1.60E+01	1.07E+05
TB111	175	1.26E+05	3.19	8.14E+00	1.54E+05
TB111	175	1.37E+05	4.10	1.05E+01	1.30E+05
TB111	175	1.45E+05	4.90	1.25E+01	1.16E+05
TB111	175	1.71E+05	8.08	2.06E+01	8.30E+04
TB111	180	1.26E+05	5.78	1.30E+01	9.66E+04
TB111	180	1.37E+05	6.13	1.38E+01	9.90E+04
TB111	180	1.45E+05	6.45	1.45E+01	1.00E+05
TB111	180	1.71E+05	10.30	2.32E+01	7.39E+04
TB111	185	1.26E+05	6.41	1.53E+01	8.20E+04
TB111	185	1.37E+05	8.15	1.95E+01	7.01E+04
TB111	185	1.45E+05	9.35	2.24E+01	6.50E+04
TB111	185	1.71E+05	14.70	3.52E+01	4.87E+04
TB211	170	1.26E+05	4.69	1.14E+01	1.10E+05
TB211	170	1.37E+05	5.76	1.41E+01	9.72E+04
TB211	170	1.45E+05	6.80	1.66E+01	8.77E+04
TB211	170	1.71E+05	11.33	2.76E+01	6.20E+04
TB211	175	1.26E+05	6.29	1.49E+01	8.43E+04
TB211	175	1.37E+05	8.58	2.04E+01	6.71E+04
TB211	175	1.45E+05	9.53	2.26E+01	6.44E+04
TB211	175	1.71E+05	15.18	3.60E+01	4.76E+04
TB211	180	1.26E+05	9.02	2.17E+01	5.80E+04
TB211	180	1.37E+05	11.07	2.66E+01	5.13E+04
TB211	180	1.45E+05	13.36	3.21E+01	4.53E+04
TB211	180	1.71E+05	20.37	4.90E+01	3.50E+04
TB211	185	1.26E+05	12.12	2.88E+01	4.37E+04
TB211	185	1.37E+05	14.78	3.51E+01	3.90E+04
TB211	185	1.45E+05	17.70	4.20E+01	3.46E+04
TB211	185	1.71E+05	26.81	6.36E+01	2.69E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
TB311	165	1.26E+05	4.57	1.06E+01	1.19E+05
TB311	165	1.37E+05	5.89	1.36E+01	1.00E+05
TB311	165	1.45E+05	7.01	1.62E+01	8.98E+04
TB311	165	1.71E+05	9.63	2.22E+01	7.70E+04
TB311	170	1.26E+05	5.32	1.35E+01	9.32E+04
TB311	170	1.37E+05	7.12	1.81E+01	7.57E+04
TB311	170	1.45E+05	8.46	2.14E+01	6.78E+04
TB311	170	1.71E+05	13.57	3.44E+01	4.98E+04
TB311	175	1.26E+05	7.78	1.81E+01	6.96E+04
TB311	175	1.37E+05	8.87	2.06E+01	6.64E+04
TB311	175	1.45E+05	12.23	2.84E+01	5.13E+04
TB311	175	1.71E+05	17.02	3.95E+01	4.34E+04
TB311	180	1.26E+05	12.11	2.62E+01	4.81E+04
TB311	180	1.37E+05	13.83	2.99E+01	4.57E+04
TB311	180	1.45E+05	17.13	3.70E+01	3.93E+04
TB311	180	1.71E+05	23.05	4.98E+01	3.44E+04
TB811	165	1.26E+05	7.09	1.59E+01	7.92E+04
TB811	165	1.37E+05	8.46	1.89E+01	7.22E+04
TB811	165	1.45E+05	8.86	1.98E+01	7.33E+04
TB811	165	1.71E+05	14.93	3.35E+01	5.12E+04
TB811	170	1.26E+05	8.20	1.96E+01	6.42E+04
TB811	170	1.37E+05	10.79	2.57E+01	5.31E+04
TB811	170	1.45E+05	12.71	3.03E+01	4.80E+04
TB811	170	1.71E+05	19.94	4.76E+01	3.60E+04
TB811	175	1.26E+05	11.61	2.58E+01	4.88E+04
TB811	175	1.37E+05	16.57	3.68E+01	3.72E+04
TB811	175	1.45E+05	18.25	4.05E+01	3.59E+04
TB811	175	1.71E+05	27.06	6.01E+01	2.85E+04
TB811	180	1.26E+05	16.09	3.58E+01	3.51E+04
TB811	180	1.37E+05	19.34	4.30E+01	3.18E+04
TB811	180	1.45E+05	22.62	5.03E+01	2.89E+04
TB811	180	1.71E+05	34.97	7.78E+01	2.20E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
TB121	165	1.26E+05	4.34	1.07E+01	1.18E+05
TB121	165	1.37E+05	6.90	1.70E+01	8.05E+04
TB121	165	1.45E+05	7.73	1.90E+01	7.64E+04
TB121	165	1.71E+05	12.71	3.13E+01	5.48E+04
TB121	170	1.26E+05	6.27	1.41E+01	8.94E+04
TB121	170	1.37E+05	7.74	1.74E+01	7.87E+04
TB121	170	1.45E+05	8.68	1.95E+01	7.47E+04
TB121	170	1.71E+05	13.15	2.95E+01	5.81E+04
TB121	175	1.26E+05	8.10	1.76E+01	7.15E+04
TB121	175	1.37E+05	9.95	2.16E+01	6.32E+04
TB121	175	1.45E+05	11.17	2.43E+01	5.99E+04
TB121	175	1.71E+05	15.75	3.42E+01	5.00E+04
TB121	180	1.26E+05	10.05	2.32E+01	5.42E+04
TB121	180	1.37E+05	13.49	3.11E+01	4.39E+04
TB121	180	1.45E+05	14.27	3.29E+01	4.42E+04
TB121	180	1.71E+05	22.10	5.10E+01	3.36E+04
TB131	165	1.26E+05	4.63	1.10E+01	1.14E+05
TB131	165	1.37E+05	5.15	1.23E+01	1.11E+05
TB131	165	1.45E+05	6.47	1.54E+01	9.43E+04
TB131	165	1.71E+05	9.79	2.33E+01	7.35E+04
TB131	170	1.26E+05	5.23	1.35E+01	9.28E+04
TB131	170	1.37E+05	7.30	1.89E+01	7.22E+04
TB131	170	1.45E+05	8.52	2.21E+01	6.58E+04
TB131	170	1.71E+05	14.45	3.75E+01	4.57E+04
TB131	175	1.26E+05	7.36	1.85E+01	6.81E+04
TB131	175	1.37E+05	10.47	2.63E+01	5.20E+04
TB131	175	1.45E+05	12.13	3.04E+01	4.78E+04
TB131	175	1.71E+05	19.04	4.78E+01	3.59E+04
TB131	180	1.26E+05	10.96	2.57E+01	4.89E+04
TB131	180	1.37E+05	15.17	3.56E+01	3.84E+04
TB131	180	1.45E+05	16.03	3.76E+01	3.87E+04
TB131	180	1.71E+05	24.02	5.64E+01	3.04E+04

Sample Codes	Temp ℃	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
TB181	165	1.26E+05	5.12	1.13E+01	1.12E+05
TB181	165	1.37E+05	5.92	1.30E+01	1.05E+05
TB181	165	1.45E+05	6.82	1.50E+01	9.70E+04
TB181	165	1.71E+05	11.25	2.47E+01	6.93E+04
TB181	170	1.26E+05	6.99	1.63E+01	7.70E+04
TB181	170	1.37E+05	7.75	1.81E+01	7.55E+04
TB181	170	1.45E+05	9.51	2.22E+01	6.55E+04
TB181	170	1.71E+05	14.96	3.49E+01	4.91E+04
TB181	175	1.26E+05	8.27	1.96E+01	6.42E+04
TB181	175	1.37E+05	10.43	2.47E+01	5.53E+04
TB181	175	1.45E+05	12.33	2.92E+01	4.97E+04
TB181	175	1.71E+05	19.21	4.55E+01	3.76E+04
TB181	180	1.26E+05	11.22	2.60E+01	4.83E+04
TB181	180	1.37E+05	14.90	3.46E+01	3.95E+04
TB181	180	1.45E+05	16.75	3.89E+01	3.74E+04
TB181	180	1.71E+05	26.51	6.15E+01	2.78E+04
TB112	170	1.26E+05	3.25	7.74E+00	1.62E+05
TB112	170	1.37E+05	3.61	8.59E+00	1.59E+05
TB112	170	1.56E+05	4.83	1.15E+01	1.36E+05
TB112	170	1.71E+05	6.76	1.61E+01	1.06E+05
TB112	175	1.26E+05	3.40	8.57E+00	1.47E+05
TB112	175	1.37E+05	3.69	9.32E+00	1.47E+05
TB112	175	1.56E+05	6.66	1.68E+01	9.31E+04
TB112	175	1.71E+05	7.73	1.95E+01	8.78E+04
TB112	180	1.26E+05	3.76	9.89E+00	1.27E+05
TB112	180	1.37E+05	6.03	1.59E+01	8.62E+04
TB112	180	1.56E+05	7.70	2.02E+01	7.72E+04
TB112	180	1.71E+05	10.49	2.76E+01	6.21E+04
TB112	185	1.26E+05	4.81	1.20E+01	1.04E+05
TB112	185	1.37E+05	6.21	1.55E+01	8.79E+04
TB112	185	1.56E+05	8.22	2.06E+01	7.60E+04
TB112	185	1.71E+05	11.24	2.81E+01	6.09E+04

Sample Codes	Temp °C	Apparent Shear stress N/m^2	MFI gm/10 min	Corrected Shear rate sec^{-1}	Viscosity Poise
TB113	170	1.37E+05	2.69	6.95E+00	1.97E+05
TB113	170	1.45E+05	3.29	8.50E+00	1.71E+05
TB113	170	1.56E+05	3.83	9.91E+00	1.58E+05
TB113	170	1.71E+05	5.05	1.30E+01	1.31E+05
TB113	175	1.37E+05	3.25	7.83E+00	1.75E+05
TB113	175	1.45E+05	3.30	7.96E+00	1.83E+05
TB113	175	1.56E+05	4.00	9.64E+00	1.62E+05
TB113	175	1.71E+05	5.28	1.27E+01	1.34E+05
TB113	180	1.37E+05	3.34	8.90E+00	1.54E+05
TB113	180	1.45E+05	4.66	1.24E+01	1.17E+05
TB113	180	1.56E+05	5.56	1.48E+01	1.06E+05
TB113	180	1.71E+05	6.75	1.80E+01	9.52E+04
TB113	185	1.37E+05	3.81	1.03E+01	1.32E+05
TB113	185	1.45E+05	5.52	1.50E+01	9.72E+04
TB113	185	1.56E+05	6.25	1.69E+01	9.23E+04
TB113	185	1.71E+05	8.35	2.26E+01	7.57E+04
TB118	175	1.45E+05	1.89	5.17E+00	2.82E+05
TB118	175	1.56E+05	2.12	5.77E+00	2.71E+05
TB118	175	1.71E+05	4.26	1.16E+01	1.47E+05
TB118	180	1.45E+05	2.17	6.91E+00	2.11E+05
TB118	180	1.56E+05	2.72	8.65E+00	1.81E+05
TB118	180	1.71E+05	4.40	1.40E+01	1.22E+05
TB118	185	1.45E+05	2.52	8.50E+00	1.71E+05
TB118	185	1.56E+05	3.77	1.27E+01	1.23E+05
TB118	185	1.71E+05	5.28	1.78E+01	9.61E+04

APPENDIX - B

SYNOPSIS

Polymer Blends are physical mixtures of structurally different homo or copolymers where one polymer is dispersed in one or more other polymers. The extent of dispersion depends on the method of mixing, the amount of thermodynamic compatibility desired and the properties of individual polymer. Poly blends can easily be adopted to specific needs and can be modified for improvement of one property at the minimum sacrifice of the other properties.

For medical applications, some of the polymers in the virgin or normal commercially available form do not ideally meet the requirements of use. For example, conventional grades of nontoxic plasticized poly(vinyl chloride) are far from ideal due to their "non permanence". Low molecular weight additives migrate to the media in contact, and this leads to problems of possible toxicity and changes in original property. Both of these are not desirable for medical applications. Ease of modification, processing and fabrication and the low cost have made the total replacement of plasticized PVC a very difficult proposition inspite of these disadvantages. Attempts have earlier been made to modify plasticized PVC by different methods like internal plasticization, use of alternative non-conventional plasticizer etc. Some information is also now available regarding industrial applications of PVC based poly-blends. But there is hardly any information available regarding the use and suitability of PVC based poly-blends for medical applications.

The present work deals with the studies on PVC based polymer blends. The systems studied are binary blends of a) PVC- - Polyesters (PE) with different molecular weights of polyester,) Plasticized PVC (PPVC) - Acrylo Nitrile Butadiene Rubber (NBR) rom two sources, c) PPVC - (Ethylene Vinyl acetate copolymer)-g-PVC (EVAPVC) and ternary blends of PPVC, NBR, and EVAPVC. The main emphasis of the work was to study the blend behaviour in terms of blendability, processibility and other properties that are relevant to medical applications.

Chapter I is essentially an abstract of the Thesis and gives an overall view of the total work. Each Chapter begins with a summary of the contents of the Chapter.

Chapter II deals with introduction and critical discussions on significance of the problem, current status and literature survey related to the various aspects of the present work. The scope and objectives of the work are included at the end of his Chapter.

Chapter III describes the materials used and the experimental techniques adopted during the course of the nvestigation. These include blending methods and studies on melt low, extrusion, mechanical properties, dynamic mechanical property, morphology and blend interaction, barrier properties, optical properties and brittleness temperature. Sample prepara-ion, test methods and equipment used are also discussed.

Results and discussions have been given in Chapter IV which ontains seven sections.

Section 1 of Chapter IV discusses the rheological and rocessing behaviour of blends. The effect of temperature and pm variation on equilibrium torque of PPVC, PPVC-NBR and VC-PE blends are reported and reasons for the variations observed are discussed. Results of the studies on Melt Flow Index (MFI) for binary blends PVC-PE, PPVC-NBR, PPVC- EVAPVC and ternary blends of PPVC, NBR, and EVAPVC at different temperature and shear stress conditions are discussed. As expected, binary blends PVC-PE and PPVC-NBR showed lower MFI than PPVC. But blends of PPVC with EVAPVC showed higher MFI than PPVC for replacement of PPVC upto 50% by EVAPVC, though EVAPVC formulation itself had much lower MFI value than PPVC. This is an interesting and important finding and is of great significance from processing point of view. The observation made for binary blends is also reflected in the results of ternary blends. Values of Die-swell ratio showed similarity with PPVC for PE series, and initial drop for upto 30% replacement of PPVC by EVAPVC followed by a continuous rise, and continuous reduction for replacement of PPVC by NBR. Viscosity - Shear rate plots showed temperature dependency of all blends, though the variation was least for blends of PPVC-NBR. Plots of $\log(\eta/a_r)$ vs. $\log(\dot{\gamma}a_r)$ for each sample showed a very good agreement of experimental results with predicted values. Discussions have been made for other blend parameters like flow behaviour index, principal normal stress difference, recoverable normal strain, and apparent shear modulus. Results of the study with an extruder give the output, pressure in the die head, and torque parameters for three 'pure' components. Prediction of apparent viscosity of PPVC- EVAPVC blends from the values of 'pure' components with logarithmic additive rule agreed well with experimental values.

Section 2 discusses the mechanical properties of blends. Representative stress-strain plots of 'pure' components and blends are given for comparison. Generally, the blends have intermediate property. Ultimate Elongation (UE) improved when PPVC was replaced with both NBR and EVAPVC. Ultimate Tensile Strength (UTS) was more or less unaffected till 30% replacement of both binary and ternary blends are intermediate. The transition peaks became broader as second/third component was added to a ‘pure’ component. Absence of additional peak and broader transition peaks for blends indicate good homogeneity in macro level and possibility of some inhomogeneity in micro level. Two transitions for EVAPVC was also reflected in the blends of PPVC-EVAPVC and the second minor transition was drawn inwards and finally merged with PPVC as the content of PPVC increased in the blends. Loss tangent values for EVAPVC and its blends remained high compared to other components. PPVC had brittleness temperature lower than other ‘pure’ components and blends studied, though, PPVC had T_g higher than both NBR and EVAPVC.

Studies on blend morphology and interactions are given in Section 4. SEM pictures clearly demonstrate that the morphology of both ‘pure’ and blends are dependent on method of sample preparation. Solvent cast films of both ‘pure’ as also blends of PPVC-EVAPVC show total absence of phase boundaries even at 1000 magnification. But, the milled samples of PPVC show uniformly distributed globular morphology and the blends have distinct dispersed phase with occasional agglomeration distributed in continuous phase. A clear boundary is absent in all blends. For binary blends the dispersed phase slowly becomes the continuous phase as 50% or more of PPVC is replaced by other components. Ternary blends with equal fraction of all components is the least homogeneous. Scanning electron micro photographs of low magnification (X 20) did not suggest any inhomogeneity though, the pictures taken at high magnification (X 1000) showed two phases in blends. This indicated that the blend systems studied had macro homogeneity and micro inhomogeneity. The interactions in the blends, studied by FTIR differential spectroscopy and identified by the shifts in IR absorption peaks, were found to be of higher degree for PPVC-EVAPVC compared to PPVC-NBR blends.

of the blends. A simple model has been proposed to predict the gas permeability of blends. Agreement with experimental data is within reasonable limits.

Results and discussions on optical clarity and haemolytic potential are given in Section 7. Results on haemolytic potential indicated that the 'pure' components PPVC, NBR and EVAPVC had 0% haemolysis, but all the blends showed some amount of haemolysis. Though % haemolysis was within acceptable limits for most of the blends, blends containing 50% or more of NBR had unacceptable levels of haemolysis. Considering the fact that PPVC is not likely to be replaced by NBR to the extent of 50%, this observation should not create any problems in applications. As expected, blending reduced the clarity, the minimum clarity being for around 50% replacement of PPVC in case of binary blends and ternary blends showed improvement in clarity only when one component was 70% or more. This observation also matches the findings of blend morphology by SEM technique.

Chapter V contains the summary and conclusions of the work and future prospects. The present work has led to understanding the behaviour of PVC based poly-blends and recommendations have been made for appropriate amount of replacement that lead to optimum properties relevant to medical applications. Suggestions have been made for further investigations in related area.