

**SOME STUDIES ON THE BLENDS OF POLY (VINYL ACETATE)
AND POLY(ETHYL METHACRYLATE) .**

BY

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JULY, 1984.

DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

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THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by Miss M. K. Ibiyeye entitled, "Some Studies on the Blends of Poly(Vinyl acetate) and Poly(Ethylmethacrylate), be accepted in partial fulfilment of the requirements for the degree of M.Sc. Polymer Science and Technology.

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DEDICATION

Dedicated to my dearest mother,
Mrs. D. E. Ibiyeye.

In memory of my late father and
my two brothers; Pa Abdu Ibiyeye,
Raifu Ibiyeye and Moses Jegede.

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ABSTRACT

Studies have been conducted on blending of Polyvinylacetate with Polyethylmethacrylate. Polyvinylacetate and Polyethylmethacrylate samples were prepared using emulsion polymerisation method under different conditions to obtain polymers of varying molecular characteristics. The viscosity average molecular weight of each polymer was determined. Four different methods were used to assess and characterise the type of interaction taking place in the two polymers when blended together.

Study of the blends of PVAc and PEMA by dilute solution viscosity revealed two types of interactions viz PVAc - PEMA intermolecular interaction which increases with molecular weight of PEMA and molecular weight ratio of the polymers. This type of interaction leads to formation of blends with co-operative forces of stabilisation which are superior to those of the pure polymers.

The other type of interaction is the PVAc or PEMA intramolecular interaction which leads to independent behavior of the two polymers, and decreases with increase in molecular weight of PEMA and the molecular weight ratio of the polymers.

From the Melt Flow Index study of the melt form of PEMA and PVAc blends, one form of interaction predominates, namely the PVAc - PEMA intermolecular interaction which increases with the molecular weight of PEMA and therefore leads to an improvement in the melt flow characteristics of either of the two polymers. Also a mode of interaction has been suggested in which PEMA acts as a surface on which PVAc is arranged, thus improving the macromolecular arrangement in the melt.

Mechanical study of films of the blends were carried out on the Instron testing Machine. Two types of interaction existed between the polymers namely the PVAc - PEMA intermolecular interaction which leads to blends which are strong and of superior properties to those of the individual polymers, and the other from weak Vander Waals forces due to the PVAc or PEMA intermolecular and possibly intramolecular attractions between the molecules of the polymers, leading to the formation of inferior blends. These properties are strongly depended on the molecular weight ratio (M_v) for the two polymers i.e. $\frac{M_v}{PEMA} / \frac{M_v}{PVAc}$.

Optical microscopy was also used to aid in determining not only the presence but the connectivities of the phases representing each polymer.

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CHAPTER ONE1.0 I N T R O D U C T I O N

The mixing together of different polymers has been carried out for many years for various purposes. Rubbers have been used to flexibilize rigid plastics, and rigid plastics have been used to stiffen rubbers. Many adhesives, sealants and coatings have been based upon blend of polymers, yet it was only recently that it was realised that most polymers are basically incompatible with each other (1). It appears therefore that many of the succesful results of mixing polymers are attributable to the properties obtained from two-phase systems.

As is so often the case, the historical development of polyblends can be characterised as technological rather than scientific, by this, it means that polymers are mixed together to improve properties and to discover useful compositions prior to knowledge of the incompatibility of polymers, the microstructure of two phase systems and the resulting mechanical properties.

1.1 THEORIES OF POLYMER COMPATIBILITY.

In the following discussion compatibility will be taken to mean the ability of two or more substances to mix with each other to form a homogeneous composition with useful and possibly improved properties (2).

This is the sense in which the term is used in the production of plastic materials. It contrast with it's use in the application of plastics in which compatibility means that the polymer does not interact unfavourably or otherwise with it's environment e.g it does swell, dissolve etc (3).

In some cases polymer compatibility refers to the total miscibility on a molecular scale of homopolymers and of random copolymers in various combinations. In this connection, it is understood that miscibility on a molecular scale is not necessarily random. Interaction between similar or different molecules may lead to a small amount of clustering or other non random arrangements of the polymer segments. Miscibility in polymer blends is restricted to amorphous regions in the polymers. Crystallizable polymers are dealt with only in those cases in which the polymer remains at least partially amorphous and in which the miscibility with other polymer was investigated in the amorphous state (1).

To some workers, compatible polymers are those that produce blends of desirable physical properties when mixed. To other workers, compatible polymers are those that do not exhibit any gross symptoms of phase separation when blended. All the above definitions of polymer

compatibility are somewhat interrelated since it is only reasonable to suppose that polymer blends exhibiting no gross symptoms of phase separation on blending and having desirable properties, show at least some mixing or interaction of polymer segments on a macroscopic scale. This implies either a certain amount of thermodynamic compatibility or a physical constraint that prevents such demixing such as grafting, cross-linking, the presence of block copolymer, interpenetrating network formation or the quenching of a mixed system to a temperature at which demixing is thermodynamically but not kinetically favoured.

Due to some problems (4) associated with bulk mixture of polymers, a number of workers preferred studying polymer compatibility in solution in mutual solvents (5). When two liquids are mixed, their incompatibility is easily ascertained by observing whether one or two phases result. When two incompatible polymers are blended by mastication the demixing into two distinct phases of the two constituents is impossible because of lack of mobility of the polymeric chains. In many cases, this mixture will then consist of a discrete phase of one polymer dispersed in a continuous phase of the other polymer.

In some cases, the two polymers will form interpenetrating networks with neither polymer being clearly the discrete phase. If two polymers are compatible, the mixture is most often transparent rather than opaque. Transparency can be observed, however in an incompatible polyblend if the refractive indices of the two polymers are about the same value.

Many methods have been reported in literature for investigating polymer-polymer compatibility. Such methods include studies of:

- (i) the viscosities of polymer mixtures in solution (6) and in bulk (7),
- (ii) tensile strength, elongation at break and other mechanical properties (8) of polymer mixtures,
- (iii) thermal oxidative degradation of polymer mixtures.

Recently, Kulezneve et al, (9) and Hourston and Hughes (10) have indicated that the viscometric and sonic velocity measurements may reveal various aspects of the compatibility of polymer blends in highly viscous or solid forms.

1.2 POLYMER BLENDS

Polymer blends are physical mixtures of structurally different homo- or copolymers (11). A polyblend can be considered to be a dispersion of one polymer in another, the extent of dispersion depends on the method of mixing and the amount of thermodynamic compatibility desired or achievable.

In addition, there are two related polymeric systems; the first is a mixture of copolymers that have different comonomer unit ratios, and the second includes block and graft copolymers which in themselves are not blends but form solid arrays that physically resemble mixtures. All three types have contributed substantially to the development of commercial polymer mixtures.

The importance of blending has increased recently because it has become a useful approach to the preparation of materials with new desirable properties, absent in the component polymers. The blending of polymers may result in the reduction of basic cost, improved processing and also may enable properties of importance for the fabrication of the blends to be maximized (1). However, the manifestation of superior properties depends upon compatibility or the miscibility of homopolymers at molecular levels. Depending upon the degree of molecular

mixing, the blends may be categorized thus:- totally miscible or compatible blends, semi-miscible or semi-compatible blends, and immiscible or incompatible blends. The extent of compatibility or miscibility results in altogether different morphologies of the blends ranging from single phase to multiphase systems.

1.3 THERMODYNAMICS OF MIXING.

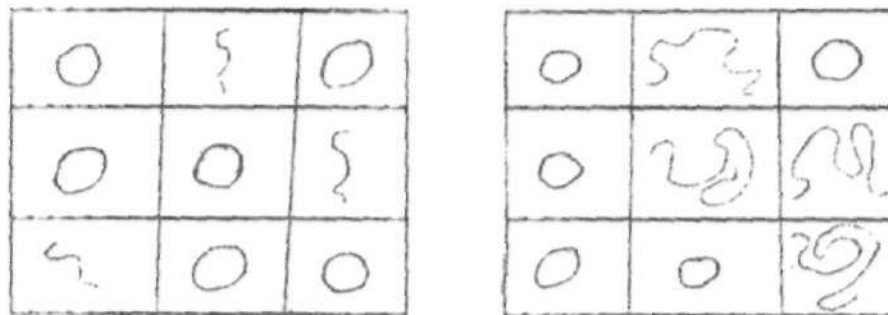
Mixing process is a reaction which is also governed by the normal thermodynamic equation:-

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \dots(1-1)$$

relating the free energy G_m , heat of mixing H_m and the entropy S_m of mixing of two substances. For any process to occur spontaneously the free energy of the process must decrease. Homogeneity in mixtures therefore depends on the heat and entropy of mixing. Mixing is always accompanied by entropy gain but the heat of mixing in most cases is endothermic i.e. energy is absorbed into the system. Mutual compatibility therefore depends on which of the two factors i.e. heat and entropy of mixing is predominant. With increase in molecular size of a set of molecules being mixed the importance of entropy

decreases whereas that of the heat of mixing remains approximately the same. The reason for this is that entropy change depends on the number of molecules per unit volume which decreases with increase in molecular size (12). Heat of mixing per unit volume is a function of the number of molecular unit contacts, which remains nearly constant with increase in molecular size, when the components of the mixture are polymers see Dig. 1, entropy change per unit volume will be extremely small and heat of mixing alone will determine the homogeneity of the mixture,

Diagram 1



Small molecules $\Rightarrow$ large polymer molecules

Since mixing is often an endothermic process, polyblends are expected to be heterogeneous. Endothermic mixing results when the energy for association in the mixture is greater than the mean of the energies of association in the pure components. There are two processes viz:- H-bonding and stereo isomerization which clearly provides a more favourable association energy in the mixture and therefore gives rise to homogeneous polyblend. The effect of H-bonding on mixtures has been demonstrated by Smith and coworkers (13). They found that on mixing aqueous solutions of poly(acrylic acid) and poly(ethylene oxide), a precipitate was formed which had properties different from those of the individual polymers. Spontaneous mixing can therefore occur only if the two structures are similar enough to have a small heat of mixing or have attractive forces to produce a negative heat of mixing (14).

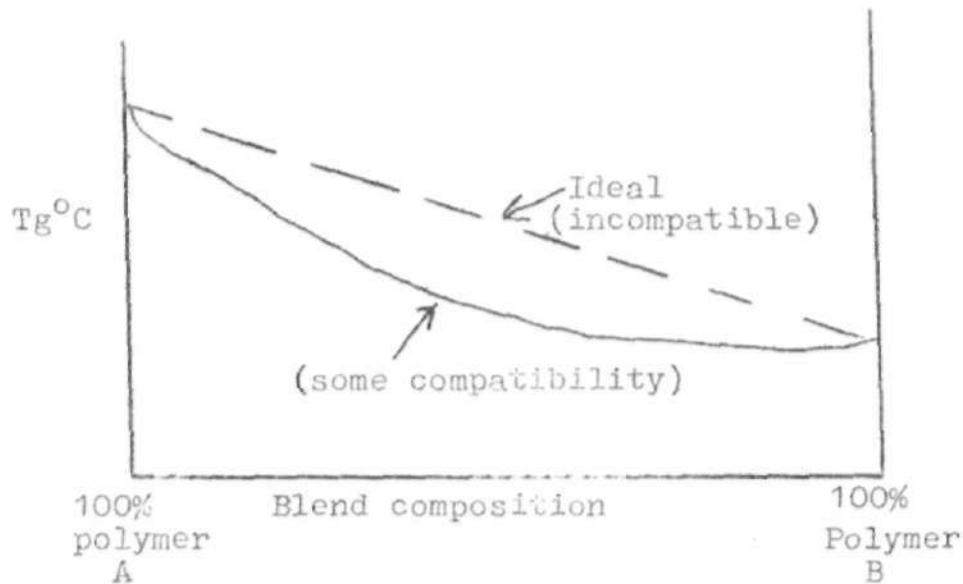
In all cases of polyblends, the important criterion for homogeneity is the size of the domain and not the heat of mixing.

Hsu et al (14) found that the effect on compatibility of unequal molar volumes of two polymers was similar to the effect deduced by Scott (15). Also the presence of

a low molecular weight polymer in a polymer mixture was found to promote the solubility of the high molecular weight polymer in the solvent.

1.4 PHYSICAL MIXTURES.

When two polymers which are incompatible in all the senses defined earlier are physically mixed, as by bulk mixing or by co-aquation of their two lattices, the resulting product is of necessity heterogeneous. The domains of one polymeric constituents can vary (i) in size and (ii) in distribution of sizes, depending upon the physical properties of the two polymers and the method of mixing them (9). Many gross properties of the mixtures, such as tensile strength, elongation and hardness, usually lie between those of the two separate constituents (16). The molecular properties such as melting point (T_m) and glass transition temperature (T_g) of the two constituents retain their separate identities (1) in the mixtures. The molecules of the mixture behave close to ideal, experiencing little attractive or repulsive interactions (12). This is indicated in Diagram 2.

Diagram 2

For this type of incompatible mixture the equation:-

$$P_{AB} = P_A^0 N_A + P_B^0 N_B \quad \dots(1-2)$$

would be approximately obeyed, where P_A^0 and P_B^0 are the properties of the pure components A and B respectively and N_A , N_B are their mole ratios in the mixture. The degree of deviation from this expression might be a judgement of the extent of the interactions between the molecules.

1.5 PREPARATION OF POLYBLENDS

1.5.1 MELT MIXING:-

Melt mixing of polymers avoids the contamination and removal problems of diluents and assures a system that will not change in molding operations. However, because of the amount of heat necessary to maintain low viscosity and the shearing rates needed for thorough mixing, a degradation of either or both polymers can occur.

Cross-linking, block and graft formation and chain scission reaction can also result because of the degradative conditions. The resulting blended polymers are therefore often physically different from what might be expected for the composite. For example, mastication of natural rubber-neoprene systems in the cold at high shear force results in a polymer blend with gel content (18). The product consists of a complex mixture of block, graft and cross-linked copolymers.

In melt mixing, the polymers are mixed and fluxed together in a Banbury mixer or on a Two-roll Rubber Mill or Torgue Rheometer at a particular temperature depending on the polymer.

1.5.2 LATEX MIXING.

Latex mixing is one of the most important techniques for the preparation of commercial polyblends. In a latex, polymers are present as suspended microspheres. Interactions of neighbouring spheres are prevented by the suspending medium (soap) after blending a mixture of two latexes with different polymers containing a random suspension of dissimilar particle each unaffected by the other. Co-aqulation too, is random because the rate of flocculation is dependententirely on the soap concentration and not on polymer characteristics (17).

1.5.3 SOLUTION BLENDING.

In solution blending, a diluent is added to lower the temperature and shear force requirements for satisfactory mixing without degradation. However, attempts to remove the diluent can often lead to changes in the domain sizes of the blends e.g. through solvation, and in severe cases this may cause complete polymer separations. As solvent is removed from a one-phase mixed polymer solution, contacts of dissimilar solvated polymers might bring about phase separation. One of the polymer usually has a greater affinity for the solvent, causing the other to selectively precipitate.

The mixture then has a gradient favouring one polymer in one region and the second in another.

Precipitation by addition of a non-solvent leads to nearly the same result (19). In this case, macroheterogeneous systems are obtained. If anything but macroheterogeneity is desired, the conditions favourable to solution precipitation of polyblends are obviously even more stringent than those necessary from the thermodynamic point of view for the formation of one-phase systems.

1.6 POLYMER PLASTICIZATION.

Polymer plasticization plays a part in polymer blends.

There are two methods of plasticising a polymer viz:- external and internal plasticization. The type of plasticization which may probably be referred to in this research is the internal plasticization.

Internal plasticization involves the modification of the polymer molecules themselves by introducing appropriate spaced groups of proper polarity and desired properties and dimensions along the main polymer chains.

The major molecular effects of both mechanical treatment and the addition of foreign materials are to alter the local mobility of chains and the magnitude of intermolecular forces (20). From the above discussion, this method of plasticization represents the theoretical ideal way of adopting a plastic for practical use. Also plastics which have been internally plasticized do not exhibit adequate strength at one temperature, when they have been designed for satisfactory flexibility at some lower temperatures. This severely limits the useful temperature range of internally plasticized polymers (20).

Plasticizing a polymer internally can be relatively simple when it essentially involves physical mixture of the two components concerned.

1.7 INTERACTION BETWEEN POLYMERS.

Miscibility of non polar polymers of substantial molecular weight occurs only when their solubility parameters (δ) are precisely matched (21). This fact is shown in the equation given below, called:-

$$\Delta H_{\text{mix}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad \dots(1-3)$$

Assume that one of the polymers is the solvent and the other the solute with solubility parameters δ_1 , δ_2 respectively. In equation (1-3) V is the volume of the system, while ϕ_1 and ϕ_2 are the volume fractions of the polymers.

The enthalpy of mixing can be negative or the mixing reaction exothermic. If polar polymers are involved with favorable interactions ΔG_{mix} might be negative inspite of the small entropy. These interactions may arise from a variety of mechanisms such as dipole-dipole forces, hydrogen bonding etc as suggested by Olayemi et al (5).

It is however useful to introduce the terms for donor and acceptor groups, in analogy to hydrogen bonding. As a result it may be possible to select two polymers having chemical moieties within or attached to the chain which have the proper complementary dissimilarity to yield an exothermic heat of mixing although it should be recognised that there will still be an endothermic contribution from the dispersion interactions or van der waals forces between the remaining parts of the structures that do not interact (1) specifically. This has been illustrated nicely by some calorimetric data or model compound designed to understand the solvating power of cyclic ethers and ketones for PVC (22).

Also Olabisi (23) recently proposed the possibility of charge interactions between poly(vinyl chloride) and the ester oxygen groups on poly(ϵ -caprolactone)' to explain the negative interaction parameter estimated from solvent problems of the miscible blends in the inverse gas chromatographic technique and from spectroscopic measurements.

Nishi et al (24) also showed that the heat of mixing parameter in classical theory of melting point depression has a negative value for miscible blends of poly(vinylidene fluoride) PVF₂ and PMMA and following that lead, Imken et al (25) demonstrated that the interaction parameter, χ is similarly negative for miscible PVF₂ blends with PEMA, PMA and PEA.

The work of Imken et al (25) makes it possible to relate the magnitude of the interaction parameter to the availability of the carbonyl for interaction with the PVF₂ segment. This rank order also agrees well with that estimated from the literature values of solution dipole moments of the amorphous polymers, a result that suggests that strong dipolar interactions can be responsible for the observed miscibility.

1.8 PHASE SEPARATION IN POLYMER SOLUTION.

Incompatibility of certain high polymers towards each other has been observed for a long time, especially in the field of varnishes and paints.

Experiments to improve such products by blending different constituents have often been frustrated by the incompatibility of the products. Incompatibility of polymers can be easily recognized from the films obtained from the mixtures which are not homogeneous and transparent but turbid or opaque and possess mechanical properties which are inferior to those of the films obtained from the separate constituents.

The molecular weight of the polymer is of great importance in polyblends. The higher it is, the less compatible are the samples and the more the possibility for phase separation (16) towards the higher concentrations. Dobry et al (16) also found out that the molecular weight together with the shape of the dissolved molecules in a polyblend influence the extent of compatibility. They also found that branched chain molecules do not have the same separation limits as linear molecules.

They further reported that there was no known obvious relationship between the compatibility of two polymers and the chemical nature of their monomers, and that the similarity of their chains would not be sufficient to ensure miscibility of the two polymers.

1.9 ANALYTICAL METHODS FOR THE CHARACTERISATION OF POLYBLEND.

The behavior of two polymers in a mixture will not necessarily correspond to the behavior of each of the isolated polymers as stated previously. Therefore, methods must be found that can determine the function of each polymer in its new environment and questions must be answered concerning:-

- (i) the separation of phases,
- (ii) the identification of the predominant phase
- (iii) the character of the dispersed phase and
- (iv) the interactions between the polymers.

This also leads to the question of how a change in morphology will affect the stress or strain distribution in the localized phases of a bulk material under load.

It is clear, however, that to answer these questions information must first be obtained on the final morphology.

Due to the fact that many levels of structure may exist in a polyblend, each with its own characteristic dimension more than a single characterisation method will be required in order to understand how all levels relate to each other and to the properties of interest.

A number of polyblends have been characterised by the use of instrumental and phase separation techniques. Qualitative (26) and in some cases even quantitative analysis of systems containing as many as four different repeating units and up to three separate polymer types have been made with infra red spectroscopy (i.r.).

Whether applied quantitatively or qualitatively, infrared spectroscopy remains one of the foremost non destructive tools for the analysis of polymers. Haslam and Willis (25) pointed out that the infrared spectra of Acrylonitrile butadiene styrene (ABS) resins are suitable for quantitative applications.

Gesner (26) also found that with natural ABS resins the application of infrared calibration curves gives reasonable values for the three components in the system.

Valuable information on dispersed particles have also been obtained through electron microscopy (13) which provides information about the internal structure.

Yuen and Kisinger (27) used the light scattering method for characterizing the inhomogeneity in a polyblend.

Hourston et al (10) found that blends of polyvinylidene fluoride and polymethylmethacrylate are compatible up to a certain extent using the dynamic mechanical study of the blends. Singh et al (6) and Kuleznev (9) have also employed viscometric and ultrasonic techniques to characterize polyblends. They both came to a conclusion that for a plot of absolute viscosity against composition, and ultrasonic velocity for solutions of blends against composition of blend, a linear behavior denotes a total miscibility of the polymers and the presence of a peak denotes some kind of interactions.

Olayemi et al (5) have studied the compatibility of polyvinylacetate with polymethylmethacrylate using the tensile mechanical properties of films of blends. They concluded that some specific interactions existed between the two polymers.

1.10 POLYMER TESTING.

1.10.1 MECHANICAL PROPERTIES OF POLYMERIC SUBSTANCES.

These are the totality of properties determining the response of bodies to external mechanical influences manifested in the ability of the substance to develop reversible or irreversible deformations and to resist failure. The basic characteristics of the mechanical properties of solids are normally determined by tests resulting in various deformation-versus-stress dependencies such as stress-strain. One of the chief concern of any Polymer Scientist and Technologist is to summarize and correlate physical data, particularly finding the correlation between physical characteristics and chemical structure. Many standards by which polymers, especially plastics, can be compared with one another and with other materials have been established (28).

Among the most important standard are the mechanical, thermal, permanence, optical, electrical and chemical tests. Of interest here however are the various tests used to characterise a polymer mechanically viz tensile strength, elongation at break and initial modulus of elasticity. These are collectively called technical tests and can be used to determine the specification of a particular polymer for use in various industrial applications.

Tensile strength may be defined as the maximum tensile stress which a material can sustain and is taken to be maximum load exerted on the film sample during the test, divided by the original cross-section of the sample. No definite rule has been stated in literature about the dependence of tensile strength on molecular weight, other than, the tensile strength increases with increasing molecular weight of polymers finally reaching a maximum and then levelling off then decreasing slightly (28). It was also discovered that in the case of linear polymers like PMMA, the tensile strengths are high because the kinked or curled macromolecule can stretch out and straightened. Also linear molecules may slip past each other slightly. Thus during the stretching operation,

the groups responsible for secondary valence forces may become aligned and thus increase the tensile strength of the material. If a high degree of cross-linking exists, the material cannot be stretched to any greater extent, but leaves the tensile strength generally high (28).

Elongation is usually measured at the point where the film breaks and is expressed as the percentage of change of the original length of the test film. Its importance is as a measure of the ability of film's to stretch.

Young's modulus or the modulus of elasticity is the ratio of stress to strain over the range for which this ratio is constant i.e. up to the yield point.

1.10.2 MECHANICAL PROPERTIES AND STRUCTURE OF POLYMERIC SUBSTANCES.

A phenomenological description of the mechanical properties of polymers appeared long before the first conceptions of the molecular nature of these bodies were formed. The discovery that polymer molecules are very large and are flexible if their structure is

linear led to a new stage in the development of the theory of the mechanical properties of polymeric bodies. This stage no longer confines itself to a mere description of the mechanical properties peculiar to polymeric substances but wants to establish the relationships between their mechanical properties and the basic characteristics of macromolecules. These characteristics are:

- (i) size of the macromolecules i.e. their degree of polymerization;
- (ii) flexibility and
- (iii) the characteristics of intermolecular interaction.

Establishment of the relationships between these characteristics gives an insight into the reasons for the appearance of any particular properties, and thus makes it possible to find ways of synthesizing new polymers of desired properties. The theory of the mechanical properties of polymeric substances was based on two main premises (29):-

- (a) Deformation of the polymer depends wholly on the behavior of its molecules, reversible deformations being due to changes in conformations of the molecules and irreversible deformations to the displacement of the molecules.

- (b) Isotropic amorphous polymeric substances are homogeneous substances consisting of randomly arranged macromolecules, while isotropic crystalline polymeric substances result from the ordering of some regions of the polymer into microcrystals.

Yuen et al (27) discovered in their work that the mechanical and physical properties of solid polymers depend on their degree of inhomogeneity - due to the presence of two phases of the polymer blends. They also found that in the case of solid mixtures such as polyblends, the degree of inhomogeneity also determines, relatively, the mutual compatibility of the compounds. Jordan et al (30) also studied the mechanical and viscoelastic properties of nitrile rubber blends with PVC and vinyl chloride (vinyl stearate copolymers, they found out from their study that the mechanical properties of the blends depend on blend compositions.

1.10.3 FILM DEPOSITION TECHNIQUE.

A film is a flat section of a thermoplastic resin or a regenerated cellulose material, which is very thin in relation to it's length and breadth. Films are formed by many techniques such as melt extrusion, calendering, chemical regeneration or by solvent casting.

Films or molded objects made from mutually miscible or compatible polymers are optically clear and have good mechanical integrity whereas those made from incompatible polymers are usually translucent or opaque and often have properties which are inferior to those of pure components.

Yuen and Kisinger (27) have shown that only a small amount of a second incompatible polymer needs be added to cause a film to appear opaque. They showed that for PMMA produced in the presence of polystyrene, as little as 0.01% by weight of polystyrene causes the resulting film to appear opaque. Although a film of any two amorphous, compatible polymers are always clear, absolute judgement on the compatibility of the two polymers cannot be made on this basis alone. It is also claimed that under special circumstances, films made from blends of two incompatible or semi compatible polymers can be optically clear (27).

Jenckel and Herwig (31) have suggested that the clarity observed in heterogeneous blends of PVAc and PMMA was probably due to the dispersed domains of PVAc in PMMA matrix. In addition to film clarity, blends of compatible polymers exhibit superior mechanical properties to those of individual components, especially tensile strength,

1.11 RHEOLOGICAL PROPERTIES OF POLYBLENDS.

From a rheological view point one can consider polymer blends as dispersion of deformable, liquid like particles. Hence the rheological behavior is governed by the state of dispersion and the shape and orientation of the dispersed phase, as well as particle-particle interaction. The rheology of dispersion can be studied at two levels; the macrorheological level, which involves measurement of the rheological properties of the dispersion itself, such as the viscosity and normal stresses, and the microrheological level, which concentrates on the detailed motions of the individual particles themselves (32).

Oene (33) in the study of dispersion in a finely divided mixture of two incompatible polymers coextruded, found two basic types of dispersions viz:-

dispersions in fluids that exhibit large normal stresses in shearing flows, and dispersions in newtonian media, where normal stresses are essentially absent.

Kuleznev (9) studied the dependence of melt viscosity upon composition for mixtures of polymers, and concluded that the mixture was poly dispersed especially if from the solutions of the individual polymers. There may be migration of low molecular weight fractions from the phase of one polymer to that of another and this may change the viscosity of the system due to the change in the viscosity of each phase.

In the case of polyblend systems with strong interactions, such as PVC-ester urethanes, Galimor et al (34) reported the presence of a ~~maximum~~ for each of viscosity and density versus composition relationships. They explained this as due to the presence of a rather strong hydrogen-bonded network in the blends.

Knowledge of the melt flow characteristics is essential to the polymer manufacturer who must tailor his polymer product to flow properly in numerous applications and to the fabrication engineer, who must

choose the proper material, or device a proper fabrication procedure for this purposes. Such knowledge might relate either to the phenomenological behaviour of the melt viscosity or to it's molecular origin or to both.

In this research work, the rheological properties of polyblends will be studied by employing two measurements viz:- the dilute solution viscosity measurement, and the melt flow measurements. The MFI (Melt Flow Index) is a measure of the melt viscosity which in turn, is related to the macromolecular structure, including molecular weight. It is determined by an extrusion plastometer with a standard orifice. In summary (32) concurrent flow or bicomponent extrusion of two polymer melts is in general a non stable flow; extremely sensitive to the precise inlet conditions.

1.12 SCOPE OF PRESENT INVESTIGATION.

As evident from the previous discussion the primary objectives of this work are:-

- i) preparation of polyvinylacetate and polyethyl methacrylate samples of different macromolecular properties by the emulsion polymerisation method.

- ii) Blending of the various polymer samples of PEMA with PVAc of various molecular characteristics.
- iii) Determination of the tensile mechanical properties of each of these systems with a view of assessing effect of blending on the properties of the individual components of the blends.
- iv) The use of the melt flow index measurement and the dilute solution viscosity method to determine the rheological properties of the blends and also for assessment of compatibility and miscibility of PVAc and PEMA.
- v) The use of optical microscopy to determine the extent of homogeneity or phase separation in the blends of the polymers.

The ultimate goal is to determine the technological value of such blends and the possibility of using one of the

polymers to probe the macromolecular structure of the other in the blend. To achieve this goal, the methodology available and considered likely to reveal useful and relevant information are the dilute solution viscosity, melt viscosity, microscopy and tensile mechanical property study.

CHAPTER TWO2.0 E X P E R I M E N T A L2.1 MATERIALS.2.1.1 Purification of Monomers.

(i) Ethylmethacrylate (EMA): Ethyl methacrylate was purified by washing repeatedly with 2% sodium hydroxide solution in a separating funnel to remove the quinol inhibitor. A clear aqueous layer was obtained which indicate complete removal of inhibitor. The organic layer was first washed with small quantities of distilled water to remove traces of alkali and distilled over anhydrous calcium sulphate. It was then then dried under reduced pressure at 79°C . The distillate was collected into a brown bottle and stored in a refrigerator until needed.

(ii) Vinylacetate (VAc):- Vinyl acetate monomer was purified using the method described for the purification of ethyl methacrylate except that distillation was carried out at 46°C . The purified vinyl acetate was stored in a refrigerator.

2.1.2 Purification of nitrogen gas.

Commercial nitrogen gas was purified by passing it over Fieser's solution (35) for absorption of oxygen.

Fieser's solution was prepared by dissolving potassium hydroxide (20g) in distilled water (100ml) and adding sodium guthra quinono- β -sulfonate (2g) (Antraquinone-2-sulphonic acid) and sodium hyposulphite $\text{Na}_2\text{S}_2\text{O}_4$ (15g) in the warm solution. The mixture was stirred until a clear blood red solution was obtained. The solution i.e. Fieser's solution was cooled in an ice bath and maintained at room temperature.

Traces of unwanted gas in the nitrogen from the tank and in the flow line were removed by passage of the latter through wash bottles containing the Fieser's solution and three other wash bottles containing calcium hydroxide, concentrated sulphuric acid and a saturated solution of lead acetate in that order before finally passing into the reaction mixture.

2.1.3 Other Reagents.

Methanol, ethylacetate, sodiumlauryl sulphate potassium persulphate, dipotassium hydrogen phosphate were all analytical grade reagents, also obtained from BDH.

2.1.4 Apparatus.

A five necked 1L reaction kettle, a condenser, a monomer dropper, beakers, stirrer, a thermostat for constant temperature and a water bath were used for the emulsion polymerisation experiments.

2.2 PROCEDURES.

2.2.1 Emulsion polymerisation of ethylmethacrylate.

Polymerisation experiments were carried out at the same temperatures of $50 \pm 0.05^\circ\text{C}$ in a constant temperature water bath. Four concentrations of the sodium lauryl sulphate (emulsifier) below the critical micelle concentration (c.m.c. = $8.9 \times 10^{-3} \text{ m/l}$ (36) were used. The initiator concentration was the same for all the polymerisation reactions.

The kinetics of the emulsion polymerisation of the ethyl methacrylate was studied.

The recipe for the polymerisation reactions are given in table 2.1.

TABLE 2.1

Polymerisation recipe for PEMA production

Polymeri- sation	Concentration of initiator $\text{m/L} \times 10^{-3}$	Concentration of emulsifier $\text{m/L} \times 10^{-2}$	Concentration of monomer $\text{m/L} \times 10^{-2}$	Volume of distilled water (cm^3)	Total volume of reaction mixture (cm^3)
A	2.22	0.69	5.96	215	250
B	2.22	1.39	5.96	210	250
C	2.22	2.00	5.96	205	250
D	2.22	2.77	5.96	200	250

The reaction mixture without the monomer was made in the five-necked reaction kettle. The mixture was stirred with a metal stirrer attached to the reaction kettle to allow the initiator to dissolve. A condenser was also attached to one inlet of the kettle. Before the addition of the monomer, purified nitrogen was bubbled through the mixture in the kettle while attaining the bath temperature. The monomer was then added using a monomer dropper after about 15 minutes of bubbling nitrogen gas. Monomer addition was completed within 10 secs. Polymerisation was allowed to take place. Sampling for rate determination was accomplished by pipetting a sample of 25cm^3 out of the mixture at suitable intervals while stirring was still going on. Polymerisation reaction of the 25cm^3 sample was stopped by pouring each aliquots into a cold solution of methanol. The solid which separated out was filtered using a suction flask and washed thoroughly with distilled water to remove traces of contaminants. The clear product was dried to constant weight in a vacuum oven at 40°C . The polymerisation experiments were labelled (A - D) according to the concentration of the emulsifier used.

2.2.2 Emulsion polymerisation of vinylacetate.

Polymerisation procedure of vinyl acetate is similar to that described in 2.2.1 for ethyl methacrylate, except that the conditions were different.

Polymerisation was carried out at the temperature $60 \pm 0.05^{\circ}\text{C}$ in a constant temperature water bath. Two different concentrations of the initiator ($\text{K}_2\text{S}_2\text{O}_8$) were used. The emulsifier concentration was the same for both polymerisations. The kinetics of polymerisation was also studied in each case.

The recipe for the polymerisations are given in table 2.2.

TABLE 2.2

Polymerisation recipe for PVAc production

Polymeri- sation	Concentration of initiator $\text{m/l.} \times 10^{-3}$	Concentration of emulsifier used $\text{m/L} \times 10^{-3}$	Concentration of monomer $\text{m/L} \times 10^{-2}$	Volume of Buffer cm^3 (Stock solution $765 \cdot \text{dm}^{-3}$)	Volume of distilled water (cm^3)	Total volume of reaction mixture (cm^3)
E	3.70	4.51	7.89	10	198.75	250
F	3.70	4.51	7.98	10	198.75	250
G	1.85	4.51	7.98	10	198.75	250
H	1.85	4.51	7.89	10	198.75	250
I	1.85	4.51	7.89	10	250	250

2.2.3 RECOVERY OF POLYMERS.

The polymers recovered in each polymerisation were dried thoroughly to constant weight and the (%) conversion of the monomer to the polymer were calculated using the equation (2.1) below:-

$$(\%) \text{ conversion} = \frac{\text{wt. of yield(g)}}{\text{wt. of monomer(g)}} \times 100 \quad \dots(2-1)$$

2.3 MOLECULAR WEIGHT DETERMINATION BY VISCOSITY MEASUREMENTS.

Dilute solution viscosity method was used in the study. Solution viscosity is basically a measure of the size and extension in solvent of polymer molecules. It is empirically related to the molecular weight, for linear polymers in the Mark-Houwink Sakurada equation (2-2) given below:

$$[\eta] = k\bar{M}^{\alpha} \quad \dots\dots(2-2)$$

where $[\eta]$ - intrinsic viscosity

and for a given polymer-solvent system and temperature, k and α are constants.

The Mark-Houwink Sakurada equation is strictly valid only for linear polymers and require modification for non linear or branched polymers (37).

In this research work, PEMA and PVAc are regarded to be linear polymers to be able to apply the Mark-Houwink Sakurada equation.

2.3.1 Experimental methods

(i) Polyethyl methacrylate: The viscosity of each PEMA sample in ethyl acetate at $35^{\circ} \pm 0.02^{\circ}\text{C}$ was determined using an Ubbelohde dilution type viscometer.

The viscometer was first cleaned with chromic acid cleaning solution and then washing thoroughly with large quantities of distilled water before thorough drying.

10cm^3 of pure ethyl acetate was measured accurately into the scrupulously clean and dry dilution viscometer. The viscometer was placed in the water bath maintained at $35^{\circ} \pm 0.02^{\circ}\text{C}$ to thermally equilibrate. The efflux time (η_0) for ethylacetate was determined repeatedly until reproducible to within ± 0.2 sec. The viscometer was emptied and allowed to dry. 10cm^3 of the polyethyl-methacrylate solution was measured accurately into the viscometer and the efflux time at $35^{\circ} \pm 0.02^{\circ}\text{C}$ was determined as before.

Five stepwise dilutions i.e. 3cm^3 stepwise addition of ethyl acetate at a time, of the PEMA solution in the viscometer were made and the efflux time determined after each addition of the 3cm^3 of ethyl acetate. From the values of the efflux time, the specific (η_{sp}) and the relative (η_{sp}/c) viscosity values were calculated and a linear plot of (η_{sp}/c) versus the concentration of PEMA g.dm^{-3} was made to obtain the limiting viscosity $[\eta]$ or intrinsic viscosity by extrapolation to zero solution concentration.

The viscosity average molecular weight of PEMA was obtained from the Mark-Houwink (36) equation:-

$$[\eta] = k \bar{M}_v^\alpha$$

where at 35°C and for PEMA-ethylacetate system,

$$k = 8.6 \times 10^{-5} \text{ mL/g} \quad \alpha = 0.71$$

$\bar{M}_v$ - viscosity average molecular weight.

ii) Polyvinyl acetate:- The method of determining the limiting viscosity of PVAc is the same as that described in (i) for PEMA, except that methanol (analytical grade) was used as the solvent and the bath temperature was $30^\circ \pm 0.02^\circ\text{C}$.

The viscosity average molecular weight of PVAc was also obtained from the limiting viscosity $[\eta]$ using the Mark-Houwink equation where at 30°C and for PVAc-methanol system,

$$K = 31.4 \times 10^{-5} \text{ mL/g}$$

$$\alpha = 0.60.$$

2.4 DILUTE SOLUTION VISCOSITY MEASUREMENTS OF PEMA AND PVAc BLEND.

2.4.1 Materials.

- i) Ubbelohde Viscometer:- It was cleaned thoroughly with chromic acid and distilled water.
- ii) Chloroform:- It was supplied by BDH Chemical Ltd, Poole England. It was a reagent grade and was further purified by distillation.
- iii) Polyethylmethacrylate and Polyvinylacetate samples:- They were those reported in 2.2.1 and 2.2.2 respectively.

2.4.2 Procedure.

The solution for the different blend composition of PEMA and PVAc were prepared by dissolving different quantities of the polymers in chloroform to make a total concentration of $0.06\text{g}/100\text{cm}^3$. The percent weight of PEMA in the solution was varied from 0 - 100%.

Efflux time of each blend of PEMA and PVAc was determined using an Ubbelohde viscometer.

The specific viscosity (η_{sp}/c) was also calculated from the efflux time of the solvent and that of the solution.

The bath temperature was $30 \pm 0.02^\circ\text{C}$.

2.5 MELT FLOW MEASUREMENTS.

2.5.1 Materials.

(i) Melt-flow indexer, Model 3, Davenport apparatus.

ii) Dichloromethane:- The dichloromethane used was supplied by BDH Chemicals Ltd, Poole England. It was of reagent grade and was further purified by distillation under vacuum.

- iii) Melting point apparatus (Gallenkhamp)
- iv) Magnetic stirrer.
- v) Beakers (IL)
- vi) Melting point tubes (glass)

2.5.2 Polymers

- (i) Poly(ethylmethacrylate) (PEMA) samples:- were those reported in 2.2.1.
- (ii) Poly(vinylacetate) (PVAc) samples:- was supplied by BDH Chemicals Ltd, Poole England.

TABLE 2.3

Polymers used for MFI study

PEMA	$\bar{M}_v \times 10^6$	PVAc	$\bar{M}_v$
A.	1.514	J	450,000
B	2.212		
C	3.008		
D	3.816		

2.5.3 Blending of polymers (PVAc/PEMA) for MFI study.

The PVAc and PEMA blend in this case was prepared by dissolving different quantities of the polymers i.e. PEMA and PVAc in dichloromethane to give different blend compositions, evaporating the solvent while the mixture was being stirred with a magnetic stirrer until it became highly viscous. Remnant solvent was removed in the vacuum oven at 40°C to get solid blends of constant weight.

The percentage weight of PEMA in the mixture was varied from 0 - 100%.

2.5.4 Determination of melting temperature of the polymer blends.

The melting temperature of the polymer blends prepared in 2.5.3 were determined using a Gallenkamp melting point apparatus. A little quantity of the powdered polymer blend was put in the meltingpoint tubes. The tubes were then placed in the melting point apparatus. The temperature was allowed to increase gradually while observing the powder in the tube. The temperature range over which the powder melted was recorded.

2.5.5 Melt flow index measurements.

The melt flow index (MFI) is the weight in grams of polymer extruded through a standard orifice in 10 minutes.

The melt flow measurements were carried out on Devenport Indexer Model 3/2264 as described in the manufacturers manual . . . The MFI was calculated in each case using the equation below:-

$$MFI = \frac{10w}{T} \quad \dots(2-3)$$

where

MFI = melt flow index (gf/10 minutes).

w = Average cut-off weight (gf)

T = extrusion time per cut-off (mins)

2.6 STUDY OF MECHANICAL PROPERTIES.

The determination of these properties is considered under the same heading because the same equipment was used to measure each of them. The measurement of the properties however involved the use of polymer film strips.

There are various types of testing machines for studying the mechanical properties of polymer films. The principle and mode of operation of all these are however the same.

Basically, it involves holding a film strip at one end by a fixed clamp and at the other end by a movable one. The clamps are then drawn apart and the tension in the strip measured at various clamp separation distances. The load versus extension is measured and plotted on a chart by the machine.

For accuracy and reliability results, it is necessary that the film strip be aligned vertically in the clamps, so that the stresses are uniform across the width of the strip and parallel to the direction of the load. Since the upper clamp is usually suspended from a pivot, vertical alignment is more easily obtained if the strip is fastened in this clamp first. Also the use of self aligning grips will greatly reduce the problem of uneven loading.

The solutions were prepared by dissolving the required amounts of polyethylmethacrylate and polyvinyl acetate together as a mixture in chloroform which is a common solvent for both of them.

The total weight of polymer mixture was always 0.7g in 25cm³ of chloroform. Details about the preparation of the solutions are given in table 2.4.

TABLE 2.4Preparation of chloroform solution of PVAc/PEMA blends

Blend	Weight of PVAc (g)	Weight of PEMA (g)	(%) weight of PEMA in the mixture	Total weight of sample (g) Approx.
1	0.700	0.000	0	0.700
2	0.665	0.035	5	0.700
3	0.630	0.070	10	0.700
4	0.560	0.140	20	0.700
5	0.490	0.210	30	0.700
6	0.420	0.280	40	0.700
7	0.350	0.350	50	0.700
8	0.280	0.420	60	0.700
9	0.140	0.560	80	0.700
10	0.000	0.70	100	0.700

iii) Casting of polymer films.

The homogeneous solution of the blend was poured on the clean mercury surface in a petri-dish in a fume cupboard to allow the solvent to evaporate and the film to cast. The cast film was given time to dry, it was then removed by means of a sharp razor blade and kept

between two filter papers in a desiccator at room temperature. Care was taken to avoid any nick or imperfections at the film edges during the cutting in order to prevent failure due to tearing during subsequent testing.

Each film was cut into five strips of equal dimensions of 4.0cm by 1.0cm at different directions of the film. The average thickness of each thin strip was measured using a micrometer screw gauge. The recorded values of the measured properties are thus the averages for the five strips from the same film cast.

2.6.1 Testing of the film strips.

The mechanical properties of the cut strips were studied with the Instron testing machine Model "1026".

Gauge length of each strip was 2.5cm. A maximum shear load of 2kg was used with chart speed of 50mm.min^{-1} and a cross head speed of 50mm.min^{-1} . This made chart to cross head speed ratio equal 1:1. From the stress-strain curves obtained, the following tensile mechanical properties were calculated:-

Tensile strength (Nm^{-2}):- This was calculated using the formula:-

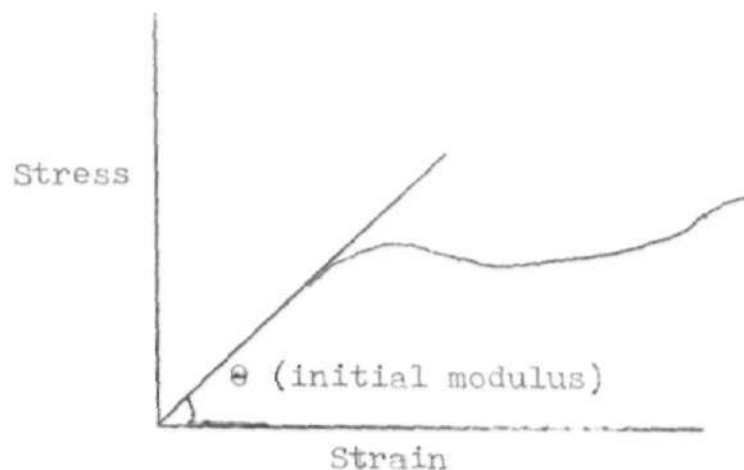
$$\frac{\text{Breaking load (N)}}{\text{Cross-sectional area (m}^2\text{)}} \quad \dots(2-4)$$

Percentage elongation at break:- This was calculated using the formula given below:-

$$\frac{\text{Chart extension}}{\text{gauge length}} \times \frac{\text{Cross head speed}}{\text{Chart speed}} \times 100 \quad \dots(2-5)$$

Initial modulus:- This was obtained from the chart by measuring the strain and stress at different points of the chart, plotting the stress - strain curve and then calculating the tangent over the range for which this is constant up to the yield point i.e. the linear portion of the curve

Stress-strain curve



Using the above procedures, the mechanical properties of all the types of poly(vinyl acetate) and poly(ethylmethacrylate) blends were determined. Descriptions of polymers used for this study are given in table 2.5

TABLE 2.5

Polymers used for tensile mechanical study

PVAc	$\bar{M}_v \times 10^{-6}$	PEMA	$\bar{M}_v \times 10^{-6}$
I	0.531	A	1.513
F	0.570	B	2.212
H	0.638	C	3.008
G	0.721	D	3.616
E	0.745		

CHAPTER THREE

3.0

RESULTS AND DISCUSSION

3.1

EMULSION POLYMERISATION OF ETHYLMETHACRYLATE AND VINYL ACETATE.

3.1.1

Influence of emulsifier and initiator concentrations on (%) conversion of EMA to PEMA.

Figure 3.1 represents the results obtained from the kinetic study of the emulsion polymerisation of ethylmethacrylate using different concentrations of sodium laurylsulphate emulsifier, a constant initiator concentration of $2.22 \times 10^{-3} \text{ m/L}$ and a constant monomer concentration of $5.96 \times 10^{-2} \text{ m/L}$. All the emulsifier concentrations are below the critical micelle concentration (cmc) of $8.9 \times 10^{-3} \text{ m/L}$ for sodium lauryl sulphate. The plots are characterised by three regions. The first is an initial polymerisation immediately after the induction period which shows a slight inflexion at conversion which increased with emulsifier concentration, this observation is in agreement with Harkin's (38) prediction on the kinetics of emulsion polymerisation of vinyl acetate.

The second region represents the actual range over which conversion is linear. The range depends on the emulsifier concentration. For very low emulsifier concentration of about $6.94 \times 10^{-3} \text{ m/L}$, conversion is linear

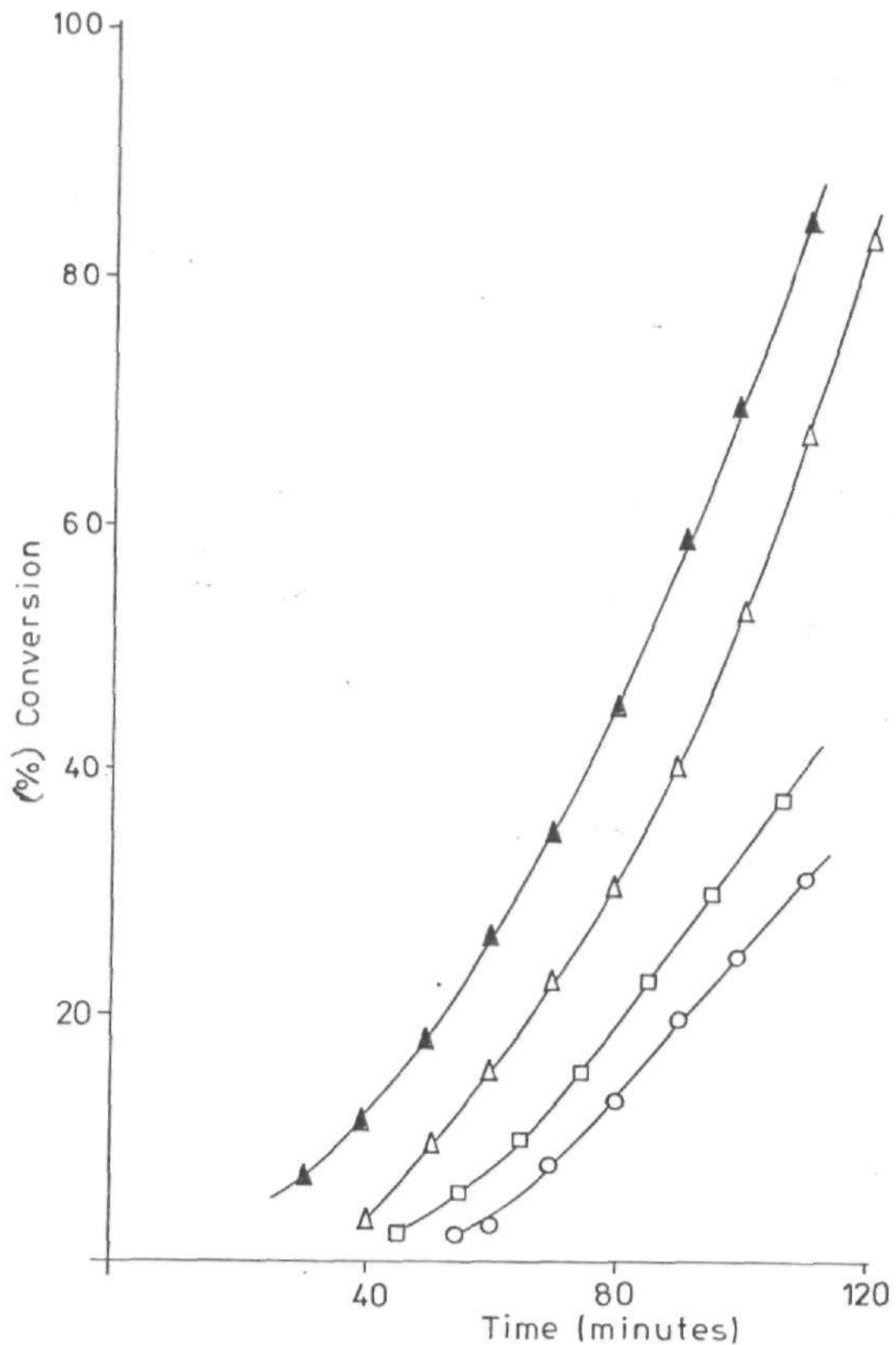


Fig. 3.1 (%) Conversion versus time of polymerisation of ethylmethacrylate using
 (○) 2×10^{-3} , (□) 4×10^{-3} , (Δ) 6×10^{-3} , (▲) 8×10^{-3} ,
 g.dm $^{-3}$ of emulsifier and 0.60 g.dm $^{-3}$ of the initiator (K₂ S₂ O₈)

from about 7% to 30% (figure 3.1). For the same recipe but higher emulsifier concentration of about 2.77×10^{-2} the linearity occurs at a higher (%) conversion of the PEMA. This suggests that conversion increases with the emulsifier concentration below the cmc. The above discussion therefore suggests that below the cmc of sodium lauryl sulphate as an emulsifier a mechanism of polymerisation of PEMA which is essentially different from those predicted by the classical theory of Smith and Edwart (39) begins to undergo a transition into the classical form. In summary the deviation from the expectations of the classical theory would be largely determined by the extent to which the emulsifier concentration is lower than the cmc of the emulsifier.

The third region represents the range where there is an abrupt increase in the (%) conversion with time of polymerisation. This third region is absent in the lowest emulsifier concentration, whereas the (%) conversion at which it occurred in the other polymerisations increased with the emulsifier concentration. It can therefore be concluded that the rate of polymerisation and (%) conversion of the EMA to PEMA increased with emulsifier concentration. This is in agreement with Bikales (40)

study, who reported an increase in rate of polymerisation of styrene and methylmethacrylate with increase in emulsifier concentration.

For each polymerisation there was an induction period i.e. period of delay to polymerisation before the initial polymerisation. From table 3.1, the induction period increased with decrease in emulsifier concentration. This strongly supports a mechanism of 'delayed interaction' proposed by Olayemi et al (41), taking place between the initiator and the monomer as the emulsifier concentration is decreased. The higher the emulsifier concentration that will solubilise the monomer or mix it with water, the shorter the induction period. This observation is in contrast with Olayemi et al's (41) work where the increase in emulsifier concentration increases the induction period in the polymerisation of vinyl acetate.

The influence of initiator and emulsifier concentrations on the (%) conversion of vinyl acetate of Polyvinyl acetate is same as has been described by Olayemi et al (41).

TABLE 3.1

CONDITIONS FOR PRODUCTION AND CHARACTERISTICS OF THE PEMA SAMPLES

Solvent for viscosity measurement:- Ethylacetate

Temperature of measurement - 35°C

k and values for PEMA/ethylacetate at 35°C

are $k = 8.6 \times 10^{-5} \text{ ml/g} = 0.71$

Polymeri- sation	Emulsifier concentration m/L x 10^{-2}	Monomer concentration m/L x 10^{-2}	Initiator concentration m/L x 10^{-3}	ATD mins	(%) conversion	$\bar{M}_v$ x 10^{-6}
A	0.69	5.96	2.22	50	63.56	1.513
B	1.39	5.96	2.22	40	70.62	2.212
C	2.08	5.96	2.22	30	63.40	3.008
D	2.77	5.96	2.22	20	61.23	3.816

Note: ATD in table means apparent time of delay
to polymerisation.

TABLE 3.2

Conditions for production and characteristics of PVAc Samples

Solvent for viscosity measurement - methanol
 temperature of measurement: - 30°C
 k and values for PVAc/methanol at 30°C
 are $k = 31.4 \times 10^{-5} \text{ ml/g}$ and $\eta = 0.6$

Polymeri- sation	Emulsifier concentration $\text{m/L} \times 10^{-3}$	Monomer concentration $\text{m/L} \times 10^{-2}$	Initiator concentration $\text{m/L} \times 10^{-3}$	(%) Conversion	$\bar{M}_v \times 10^{-6}$
E	4.51	7.89	3.7	80.70	0.745
F	4.51	7.89	3.7	40.35	0.570
G	4.51	7.89	1.85	30.11	0.721
H	4.51	7.89	1.85	69.15	0.638
I	4.51	7.89	1.85	40.29	0.531

3.1.2 Viscosity average molecular weight ($\bar{M}_v$) of the PEMA and PVAc Samples Used.

The data obtained from the dilute solution viscosity measurement of some PEMA and PVAc samples detected from several polymerisation products are shown in tables 3.1 and 3.2 respectively. The molecular weights of the polymers were calculated from the determined values of their intrinsic viscosities using Mark-Houwink equation as quoted by Billmeyer (37). The intrinsic viscosities of the polymer solutions were obtained by extrapolating the straight line obtained from the plot of the specific viscosity versus the concentration of the solution to infinite dilution. From Huggin's equation (42), the calculated viscosity average molecular weights ($\bar{M}_v$) are also shown in tables 3.1 and 3.2 for PEMA and PVAc respectively.

From table 3.1 and figure 3.2, the viscosity average molecular weight of PEMA was found to increase with emulsifier concentration for preparation of comparable conversion of about 63%. Increase in molecular weight of PEMA with emulsifier concentration might be possible only for polymerisations below cmc as proposed by Friis (43), who discovered in his study of the development of molecular weight in vinylacetate emulsion polymerisation

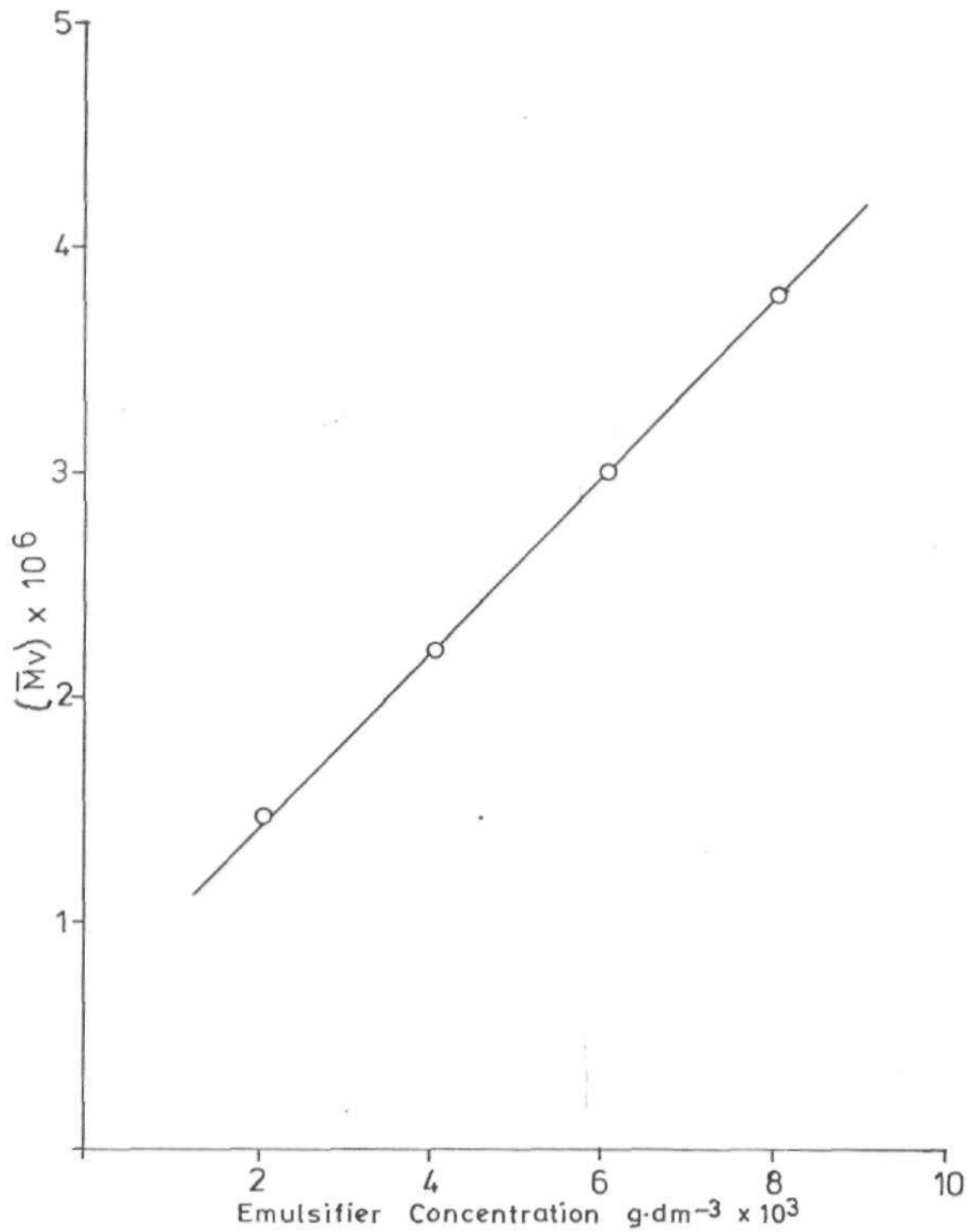


Fig. 3-2 Plot of $(\bar{M}_v)$ of PEMA against emulsifier Concentration at about 64% monomer conversion using 0.60 g.dm^{-3} of initiator $(\text{K}_2 \text{S}_2 \text{O}_8)$

that above the cmc, chain transfer reaction leading to branching of the polymer backbone is very pronounced, thereby reducing the molecular weight of the polymer formed, Friis concluded that polymers formed below the cmc are expected to have higher molecular weights than those formed above cmc of the emulsifier due to the formation of linear polymers. This suggests clear dependence of $(\bar{M}_v)$ on $[S_o]$ below the cmc.

Izumi et al (44) in their study of the effect of emulsifiers in the emulsion polymerisation of acrylonitrile found that the emulsifier is usually effective at concentrations below it's cmc and that the $(\bar{M}_v)$ does not always increase with increasing concentration of emulsifier but rate of polymerisation increases.

3.1.3 Effect of initiator concentration on the $\bar{M}_v$ of PVAc.

From table 3.2, $(\bar{M}_v)$ of PVAc is independent of the initiator concentration for both the 80% and 40% conversions of the vinylacetate to the polyvinyl acetate. This observation is in agreement with the results reported by Friis et al (43) where the $(\bar{M}_v)$ of polystyrene is independent of the initiator, emulsifier concentrations and also the number of polymer particles formed. Although strictly

speaking, the higher the initiator concentration is, the faster the reaction and the lower the ($\bar{M}_v$) for preparations of the same (%) conversion polymers.

Also Olayemi et al (41) in their study on emulsion polymerisation of vinyl acetate, observed that the conversion of vinyl acetate to polyvinylacetate increased with initiator concentration. They further claimed that the observation may probably be due to the availability of more free initiator radicals in the reaction medium with increase in the initiator concentration thereby increasing the rate of interaction between the radicals and the monomer molecules. This therefore increased the rate at which polymers are formed.

3.2 DILUTE SOLUTION VISCOSITY OF PEMA/PVAc SYSTEM.

3.2.1 Effect of blend composition (w/w) PVAc/PEMA on the specific viscosity (η_{sp}/c) of PVAc.

From figure 3.3, the specific viscosity (η_{sp}/c) of polyvinylacetate in methanol increases up to a maximum or inflexion at about 20% weight of PEMA in the blend. Beyond this concentration of PEMA, there is a slight decrease in the (η_{sp}/c) to an ill-defined minimum at about 35% weight of PEMA in the blend. This is followed by an increase tending towards the value for the pure PEMA

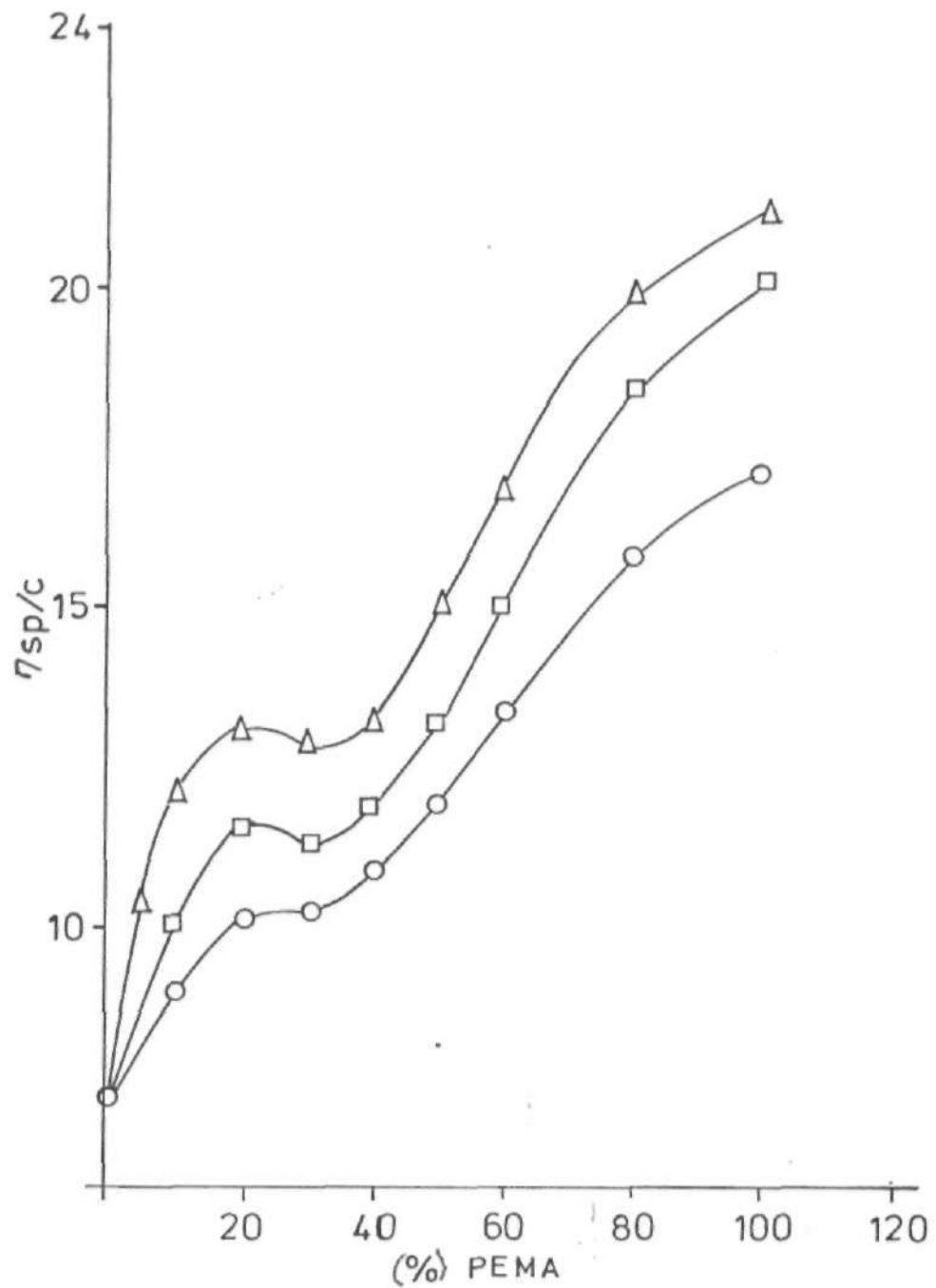


Fig. 3-3 Plot of η_{sp}/c against (%) PEMA for PVAc/PEMA blend, PVAc ($\bar{M}_v$, 0.7205×10^6) (○) PEMA ($\bar{M}_v$, 1.5140×10^6), (□) PEMA ($\bar{M}_v$, 3.0080×10^6) (Δ) PEMA ($\bar{M}_v$, 3.8160×10^6)

sample. A similar trend was observed for different molecular weight PEMA samples when blended with the same PVAc samples.

The plots are not linear for all the three PEMA samples studied here. From Raoult's law, a linear graph would represent an independent behavior of PEMA and PVAc molecules when mixed together. Figure 3.3 shows shapes tending to be binodal, the types observed by Kuleznev (9). The shapes obtained in these plots will be referred to in this study as being due to the occurrence of some kind of interactions between the molecules of PEMA and PVAc, intramolecular or intermolecular in nature.

Kuleznev (9) and Bender (45) in their study on dependence of dilute solution viscosity upon composition for mixtures of polymers referred to non-linear plot as a result of the formation of a two-phase mixture with compatibility between the polymers up to a certain blend composition. They also claimed that in a two-phase mixture of polymers, a change in composition always causes phase inversion with a resulting non-linear property-composition curve. They also advanced that the S-shape of the property-composition curve is characteristic of a colloid system in which the phase reverse upon change

in composition of the blend. It is believed that results of studies based on other methods would be required to make these types of deductions. However the inflexion in the curve (figure 3.3) might be due to the considerable difference between the viscosity of PVAc phase and the viscosity of the PEMA phase thus causing a reversal of phase. Since the overall viscosity of PVAc phase and the viscosity of the blend is largely determined by the viscosity of it's continuous phase, the specific viscosity (η_{sp}/c) of the PVAc decreases at the phase inversion point before increasing gradually to that of the pure PEMA denoting an independent movement of PVAc in a stream of PEMA. The inversion became more pronounced with decrease in the difference in molecular weight of PEMA and PVAc.

The discussion made here is in agreement with Feldman's (46) suggestion that when the dynamic viscosity varies linearly with composition of the blend, it indicates no interaction between the molecules of the polymers.

Deviations from a linear behavior might therefore be due to:

- (i) differences in molecular structure of PEMA and PVAc e.g. molecular weights and branching.

- (ii) differences in their monomeric properties
e.g. polarity
- (iii) differentials in the polymer-solvent
interactions i.e. PEMA-solvent and
PVAc-solvent interaction;
- (iv) formation of intramolecular and intermolecular
linkages between their molecules, bearing in
mind that PEMA intramolecular interactions
might be different from those of PVAc.

Linear plot of viscosity versus composition in a compatible blend of PVAc and PMMA in chloroform denotes formation of a single phase, whereas for incompatible blends of PMMA and PS solutions in toluene, the viscosity versus composition curve is of the S-type indicating two-phase formation with reversal of phases at intermediate composition.

The type of polymer blend discussed above is considered to be a case of ternary system in which there is competition between the types of interactions taking place in the system i.e. polymer/solvent interaction and the two polymer-polymer interactions.

3.2.2 Dependence of the specific viscosity of PVAc on $\bar{M}_v$ of PEMA and the molecular weight ratio of PEMA to PVAc.

The curves in figure 3.3 shows two distinct point or regions with respect to a linear plot drawn to join the specific viscosities of PEMA and PVAc i.e tie-line. The area above the tie-line corresponds to about 20% PEMA concentration and the area below occurred at about 35% PEMA concentration. The areas above and below the straight lines joining properties for the pure polymers were calculated by weighing the cut pieces of the areas concerned on a weighing balance. The data obtained for the areas are given in table 3.3.

TABLE 3.3

Data obtained for the areas below and above the tie-lines at the molecular weight ratios of PEMA and PVAc.

$(\bar{M}_v) \times 10^{-6}$ PEMA	$\frac{\bar{M}_{PEMA}}{\bar{M}_{PVAc}}$	Area above (Arbtr Unit)	Area below Arbtr Units	Transition T(%) PEMA
1.513	2.10	0.0250	0.0115	25
3.008	4.17	0.0586	0.0043	30
3.813	5.30	0.0775	0.0000	35

The areas above and the areas below the ideal line correspond to some kind of interactions between the molecules of the PEMA and the PVAc.

From figure 3.4, the area above increases with the PEMA molecular weight, while the area below the ideal line decreases with the increase in PEMA molecular weight. This area is absent for the PEMA with the highest ($\bar{M}_v$) of 3.816×10^6 . Also the (%) PEMA composition at which transition occurs from one form of interaction to the other increases with the PEMA molecular weight, (check table 3.3). It can therefore be assumed that when molecular weight of PEMA is sufficiently large with constant molecular weight PVAc, the area below the ideal line tends to zero. At this point, it is therefore necessary to refer to the molecular weight ratio of the PEMA and PVAc when $\bar{M}_{PEMA}/\bar{M}_{PVAc}$ is sufficiently large, the area below the ideal line tends to zero while the area above the ideal line becomes more prominent (figure 3.4).

Since Feldman (46) and some other workers have suggested that a linear plot of the (n_{sp}/c) versus composition curve denotes independent interactions

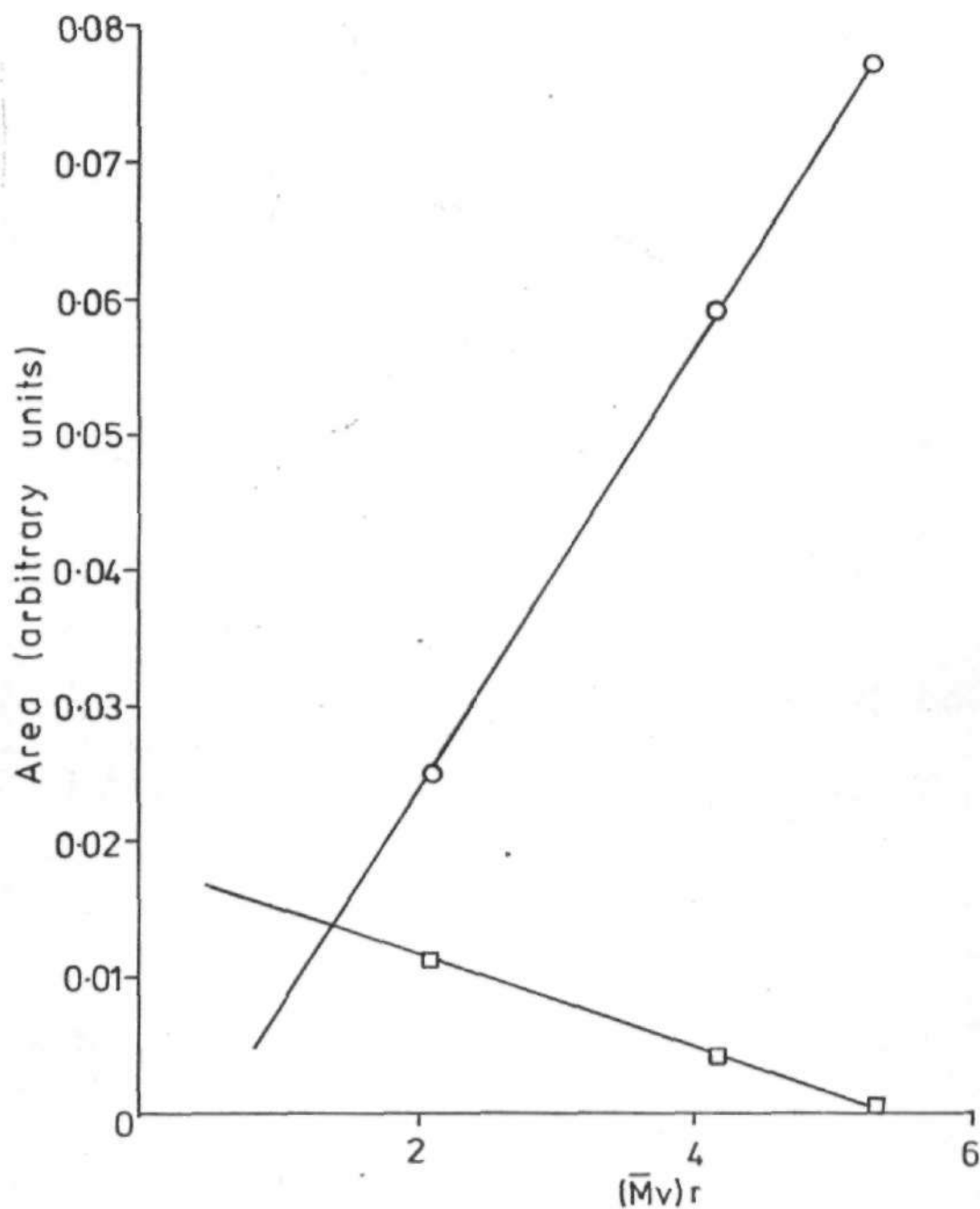


Fig. 3.4 Variation of the areas under and above the tie-lines in figure 3.3 with molecular weight ratio of PEMA and PVAc
(○) area above tie-line (□) area below tie-line

between the macromolecules, it is therefore necessary to interpret this result on their assumption. The area above and below the ideal line will therefore be due to some kind of specific interaction between the molecules of PEMA and PVAc which result to reinforcement of the PVAc by introduction of a certain (%) PEMA composition, interaction favouring the blending of PVAc and PEMA). The area above may also be due to the strong dipole-dipole attraction between the molecules of the polymers. Since this attraction increases with molecular weight, it will be very strong for high molecular weight PEMA in the blend, whereas the attraction will become smallest for monomer-monomer interactions.

The area below the ideal line on the other hand denotes another type of interaction leading to inferior properties of PEMA. It can also be due to transition point of dipole¹ - dipole² through mixture of dipole¹ - dipole² with vander waals forces - to dipole² - dipole¹ interaction, where 1 and 2 stand for PVAc and PEMA molecules respectively. It can thus be concluded from the above discussion that the area above the ideal line can be regarded as region where significant improvement to properties of PVAc occurs, while the area below can be seen as representing interactions leading to inferior properties of PEMA.

The area above ideal line may also be due to intramolecular interactions between the molecules of PEMA and PVA, whereas the area below may be due to intermolecular interactions between them. Also from the results, as PEMA/PVAc molecular weight ratio increases, region corresponding to the area above grows at the expense of the area below. Theoretically when the ratio is sufficiently large, region below ceases to exist. This implies that there is an improvement to the properties of both polymers from the molecular weight ratio of this value and above it. Hence molecular weight ratio is very important and the bigger it is, the more favourable interactions the components of the blend undergo. This can thus be explained in terms of the large PEMA dissolving in the VAc monomer and PVAc dissolving in EMA monomer.

This study is in agreement with Paul's (1) study on miscibility through specific interactions although Paul used thermodynamic equations as given in equation (3-1) to interpret the type of interactions required for good miscibility:-

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}}^{(\text{dis})} - N\Delta H_{\text{mix}}^{(\text{sp})} \quad \dots(3-1)$$

where N - number of interactions

dis - dispersive or vander waals force

sp - specific interaction.

He therefore claimed that for ΔH_{mix} to be exothermic or a sufficiently small positive value (as required for semi-compatible or compatible blends) there must be a sufficiently strong interaction to outweigh the dispersive contribution i.e. vander waals forces. He further concluded that a straight line in the plot of ΔH_{mix} versus number of molecules denotes that the contributions from specific and dispersive interactions are simply additive as one might expect. The point of intersection of the two plots on figure 3.4 may be taken as the molecular weight ratio at which the two types of interactions may probably become additive.

3.3 MELT VISCOSITY STUDY.

3.3.1 Melting point of the blends of IEMA and PVAc Samples.

The data obtained for the melting temperature range of the pure polymers and their blends are given in table 3.4.

TABLE 3.4Melting point of PEMA/PVAc blends

Blend (%) PEMA/Melting point	C range ($^{\circ}\text{C}$)
0	122 - 125 $^{\circ}\text{C}$
2.5	125 - 128
5.0	126 - 129
10.0	126 - 129
15.0	126 - 129
20.0	126 - 129
30.0	130 - 132
50.0	170 - 190
80.0	220 - 250
100.0	267 - 270

From table 3.4, the m.pt range of 100% PEMA is higher at about 267 - 270 $^{\circ}\text{C}$ than that of 100% PVAc which is about 122 - 126 $^{\circ}\text{C}$. With increase in the concentration of the PEMA in the PVAc/PEMA blend, the m.pt range increased slightly to a constant value of 126 - 129 $^{\circ}\text{C}$ for blends of 5% PEMA to 20% PEMA. Beyond this PEMA concentration, a slight increase was observed at 30% PEMA, before a sudden increase in the m.pt range for 50% PEMA. This above observation is expected since the presence of the PEMA in the blend will tend to increase the m.pt range towards that of the pure PEMA.

3.3.2 Dependence of Melt flow index (MFI) of the blend on composition.

Figure 3.5 shows an initial increase in MFI of PVAc up to a maximum at about 23% weight PEMA in the blend for PEMA of $(\bar{M}_v)$ of 1.514×10^6 . About 5% by weight PEMA of $(\bar{M}_v)$ of 3.816×10^6 was needed to produce a blend with the highest peak value of MFI with the PVAc sample used. Beyond the concentration there is a rapid decrease in MFI tending to that of pure PEMA.

It can also be observed from figure 3.5 that the straight line joining the $(MFI)_{PVAc}$ to $(MFI)_{PEMA}$ in each case cuts the curve only in one region indicating that only one type of interaction existed between PVAc and PEMA in their melt form. In figure 3.5, the point at which the straight line joining $(MFI)_{PVAc}$ with $(MFI)_{PEMA}$ touches the curve at a point which shifts towards 100% PVAc as $(\bar{M}_v)_{PEMA}$ is increased. Thus in theory when $(\bar{M}_v)$ or $(\bar{M}_v)_{PEMA}/(\bar{M}_v)_{PVAc}$ is sufficiently large, the (%) PEMA required in the blend of PVAc/PEMA to give very high (MFI) would be minimised) (check figure 3.6). This suggests that the interaction between PVAc and PEMA in the melt form always leads to an improvement in the melt flow characteristics of either of the two polymers. Apparently poly(ethylmethacrylate)

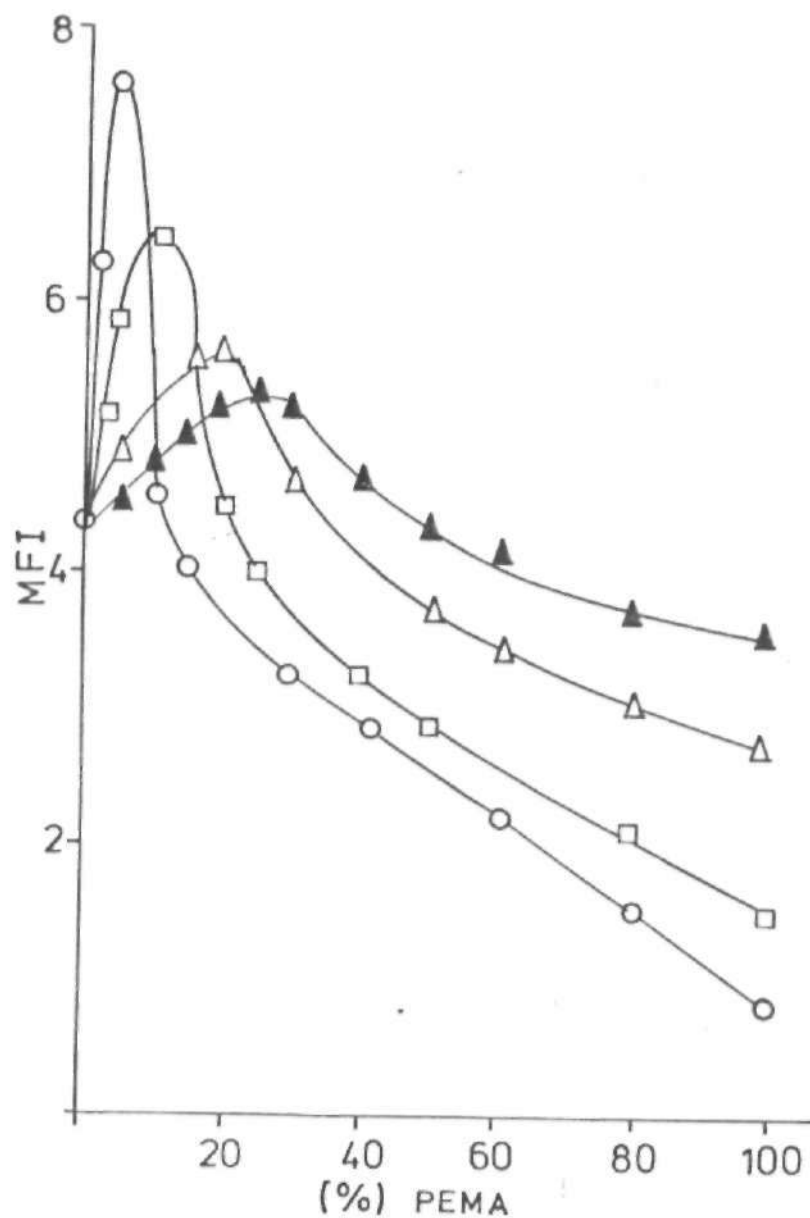


Fig 35 Plots of MFI versus (%) PEMA composition in the blend of PVAc and PEMA

PVAc ($\bar{M}_v, 0.450 \times 10^6$) (o) PEMA ($\bar{M}_v, 3.816 \times 10^6$)
 (□) PEMA ($\bar{M}_v, 3.008 \times 10^6$) (Δ) PEMA ($\bar{M}_v, 2.212 \times 10^6$)
 (▲) PEMA ($\bar{M}_v, 1.514 \times 10^6$)

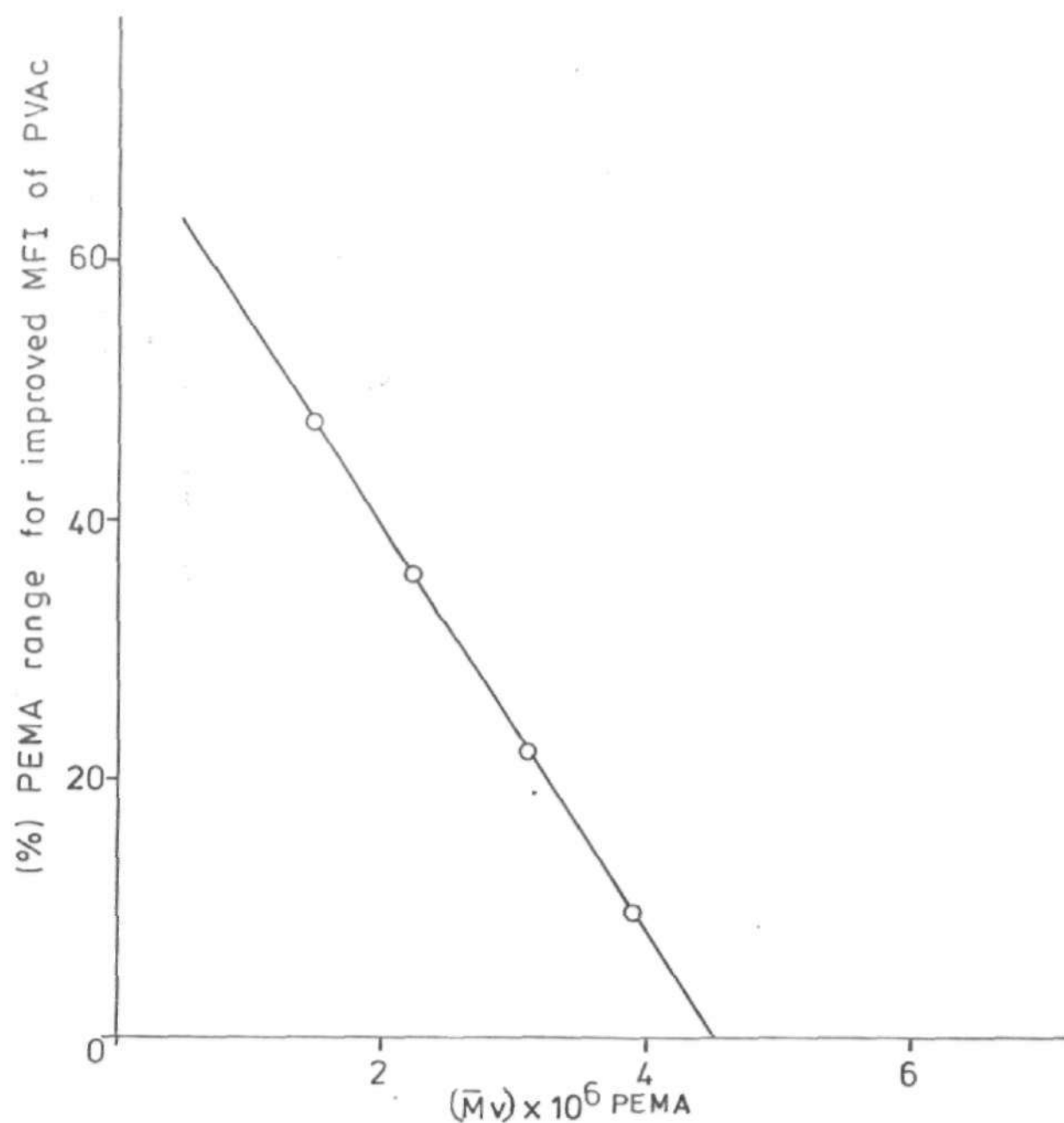


Fig. 3.6 The dependence of (%) PEMA range for improved MFI of PVAc on $(\bar{M}_n)$ of PEMA

samples of very high ($\bar{M}_v$) gives blends with . . .
 PVAc with (MFI) showing no superiority to those expected
 on the basis of the ideal equation given as:-

$$(\text{MFI})_{\text{PVAc}} \times W_{\text{PVAc}} + (\text{MFI})_{\text{PEMA}} \times W_{\text{PEMA}} = (\text{MFI})_{\text{Blend}}$$

...(3-2)

where W = weight (%) composition of component
 in blend.

The above equation can be referred to as the sum of
 free mixing of the polymers with the interfacial
 interaction contribution of the polymers, while the
 energy of interfacial interaction is counter to energy
 of mixing

TABLE 3.5

PEMA range for rubbery behavior

$(\bar{M}_v)$ PEMA $\times 10^6$	(%) PEMA range
1.514	up to 48
2.212	up to 36
3.008	up to 22
3.816	up to 10

From figure 3.6, the % PEMA range for improved η (MFI), which corresponds to interfacial interaction, decreases as $(\bar{M}_v)_{\text{PEMA}}$ increases for $(\bar{M}_v)_{\text{PVAc}}$ of 0.45×10^6 . Range of % PEMA for interfacial interaction reduces to zero when

$$(\bar{M}_v)_{\text{PEMA}} / (\bar{M}_v)_{\text{PVAc}} = 9.78.$$

However, if η (MFI)_{PVAc} is taken as a measure of the strength of the interfacial interaction, this increases with $(\bar{M}_v)_{\text{PEMA}}$, suggesting a mode of interaction through PEMA acting as a surface on which PVAc is arranged. This idea would be similar to the grafting of oligomers of PVAc on to polyethylmethacrylate.

Also since a linear mode of variation in melt viscosity with composition is typical of miscible polymers in which the interactions are additive (9), in the present study, the maximum point or rather the area above the ideal line may therefore be associated with the composition at which the two polymers i.e. PEMA and PVAc fully interact intermolecularly and strongly on a molecular level. The appearance of a peak in fig. 3.5 is in agreement with Chaffey's work (47) who reported that no linear behavior of property-composition plot occurs in a two-phase solution or in mixture of polymers without solvent i.e. in the melt form. The maximum point is also expected, since at that composition

of the blend, a fluctuation network formed by entanglement of macromolecules of the different polymers forms at the interface. Disintegration of the network by flow of the PEMA - PVAc does not cause a linear or Newtonian behavior. Entanglement between molecular chains in a non-Newtonian flow character is an indication of strong interactions between the polymers.

Masuda et al (48) reported that a factor which causes non-Newtonian behavior is concerned with deformation and orientation of the molecules themselves though it is masked by larger effects by the entanglements. In other words, the flow properties of polymer melts are concerned, not only with the relative movements between the molecules such as translational or rotational movements against viscous resistance between the surrounding molecules which is affected mainly by the entanglements, but also with deformation of the molecules themselves or intramolecular motion of chain segments. Masuda et al (48) also referred to a straight line plot of property-composition as a transition region. A peak following a transition region as observed in this present study of PEMA/PVAc blends implies a blend with rubbery behavior, and the higher the molecular weight of PEMA in this study, the more pronounced the peak.

Table 3.6 indicates that the peak at the point of maximum (MFI) increases with the molecular weight ratio of PEMA and PVAc.

TABLE 3.6

$$(\bar{M}_v)_{PVAc} = 450,000$$

$(\bar{M})_{PEMA}$ $(\bar{M})_{PVAc}$	Composition at peak MFI (%) PEMA	MFI at peak (MFI peak)	Area above ideal line
3.364	21.0	5.20	0.165
4.916	18.0	5.65	0.170
6.683	13.1	6.65	0.140
8.480	10.1	7.60	0.092

The (%) weight of PEMA in the blend at the MFI peak decreased with increase in the molecular weight ratio of PEMA and PVAc (table 3.6). This is expected since as the molecular weight of PEMA increases with a constant molecular weight PVAc, the concentration at which the two polymers interact intramolecularly tends to lower concentration of the PEMA. Figure 3.7 represents the plot of area above the curve in figure 3.5 versus the PEMA/PVAc molecular weight ratio. The plot shows a decrease in the area above the straight line joining

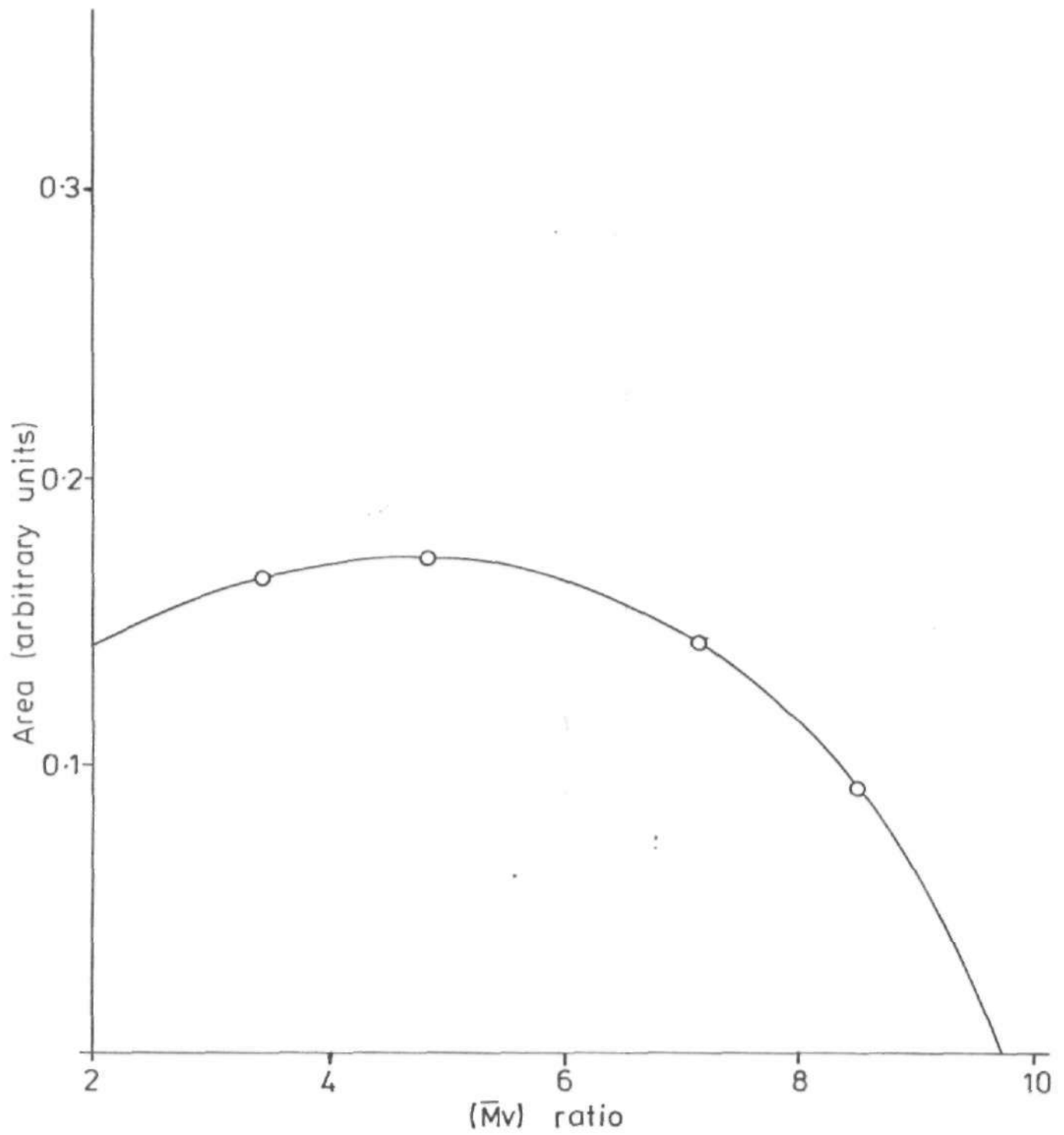


Fig. 3.7 Dependence of area above the tie-lines in figure 3.5 on $(\bar{M}_v)$ ratio of PEMA and PVAc

$(MFI)_{PVAc}$ and $(MFI)_{PEMA}$ with increase in $(PEMA)/(PVAc)$ molecular weight ratio cutting the x-axis at $(\bar{M}_v)_r = 9.80$. This decrease may be in agreement with the fact that as the molecular weight of one of the polymers in a blend increases, the allowable concentration (area) for strong intermolecular interactions before the formation of independent intramolecular interaction decreases (16), but the interaction becomes stronger with increase in molecular weight of the PEMA.

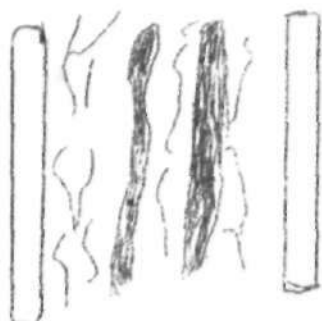
The melt viscosity of a polymer is related to the internal structure of the polymer in blend and their molecular weights. Also since melt viscosity is inversely proportional to the $(\bar{M}_v)$ of polymers (49) then PEMA of the higher $(\bar{M}_v)$ value will have the lower melt viscosity and the higher intramolecular interactions. The maximum point in MFI versus (%) PEMA composition (figure 3.5) can be explained as due to the formation of entanglements between the molecules of PEMA and PVAc. Beyond the concentration corresponding to the maximum MFI, the decrease in the MFI of blend with increase in the percent of PEMA in the blend could be due to the change in the mode of molecular motion during the flow than to reduction in entanglements or to increase in the degradation of the chains subjected to the shear. The decrease in the MFI may probably be due to formation of PVAc or PEMA intermolecular interactions as a result of the PVAc being no longer interacting

intermolecularly with PEMA, which leads to an increasing microheterogeneity. The maximum also corresponds to a good reinforcement of PVAc with PEMA.

From the above discussion, it can thus be concluded that PEMA with the highest ($\bar{M}_v$) value is more effective in providing reinforcement for PVAc, but the point for independent flow of the polymers is towards the smaller concentration of PEMA than that of the low($\bar{M}_v$)PEMA.

Also interaction that leads to increase in MFI-effectively leads to structures that allow for increasing toughness and rigidity (not brittleness) with possible increase in flexibility, hence elongation.

In sketch (1), PEMA which is larger and essentially linear, more rigid and less flexible molecule, aligns the smaller PVAc molecules thus causing an increase in MFI. With increase in % PEMA in the blend, effect described i.e. alignment of PVAc by PEMA reduces and blend flow pattern becomes more diffused.



PVAc behaves as a
lubricant for PEMA.

Sketch (1)

The MFI corresponding to peak should increase with (PEMA/PVAc) $\bar{M}_v$ ratio and probably reach a maximum limit for a paste of PEMA in VAc monomer where $(\bar{M}_v)$ ratio tends to infinity.

3.4 TENSILE MECHANICAL PROPERTIES.

3.4.1 Stress-strain behavior of PVAc/PEMA blends.

The stress-strain behavior of heterogeneous polyblends depend on their chemical composition.

Those consisting of a soft rubbery component and a hard glassy component may either be rubber-like or plastic-like respectively. (50)

In this present work, the stress-strain behavior of PVAc/PEMA blends will be discussed. The stress-strain curves for some of the PVAc sample are shown in figure 3.8. The curves exhibit very high elasticity of about 800%, depending on the molecular weight of PVAc. The higher elasticity is due to the rubbery property of the PVAc.

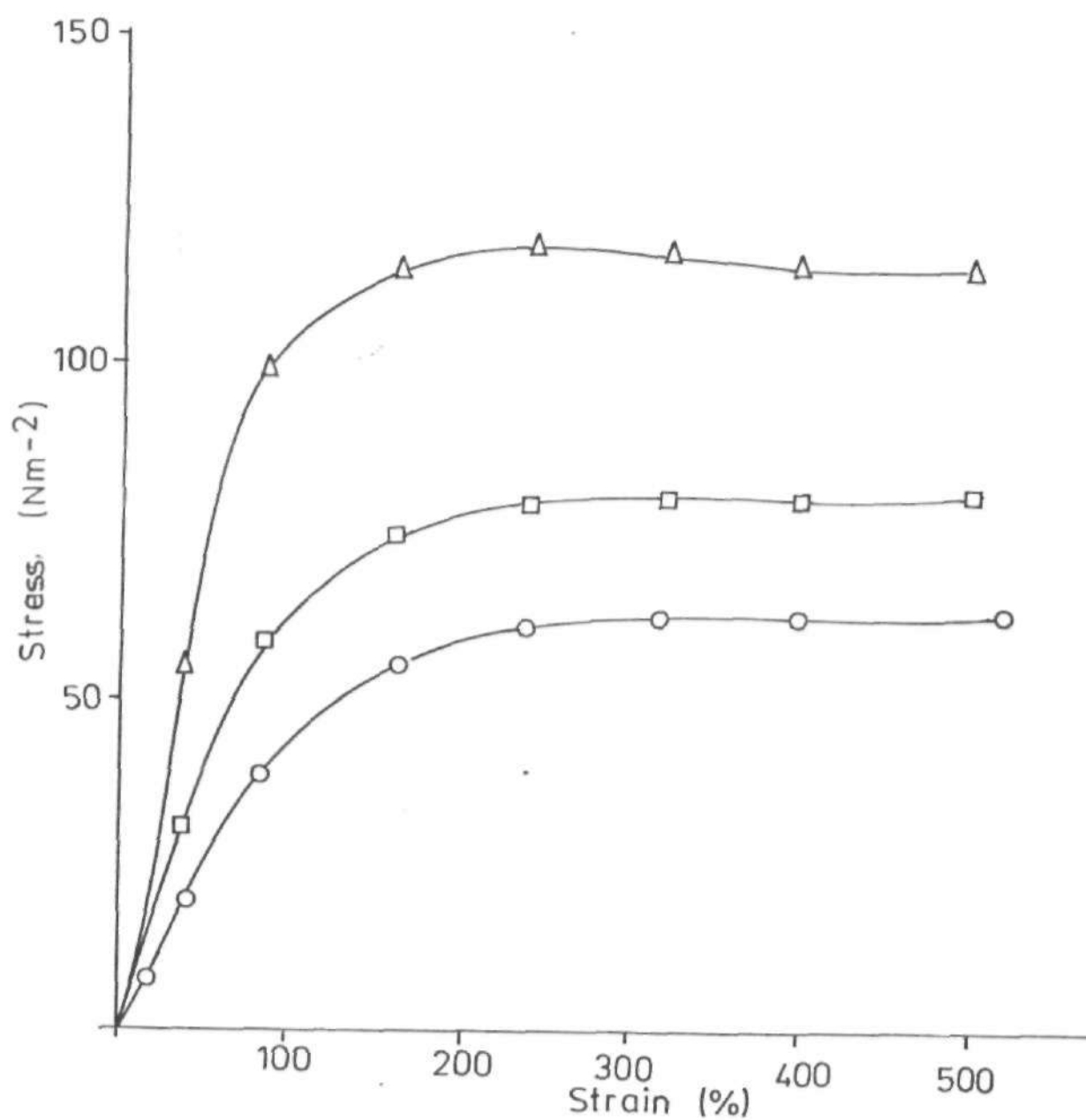


Fig. 3-8 Stress/Strain curve for 100% PVAc
(○) ($\bar{M}_v$, 0.532×10^6), (□) ($\bar{M}_v$, 0.721×10^6)
(Δ) ($\bar{M}_v$, 0.745×10^6)

Also the stress-strain behavior of some of the PEMA samples exhibit a very low elasticity of about 60%, depending on the molecular weight of PEMA before fracture figure 3.9. This low elasticity is due to the brittleness of PEMA which increases with the molecular weight of the PEMA. Hence higher molecular weight PEMA samples are more brittle than low molecular weight PEMA.

The stress-strain curves for the different blends of PVAc/PEMA using same PVAc with different PEMA samples are shown in figures 3.10 to 3.12. In the case of the blend with 15% by weight PEMA composition, the rubber like elasticity may still arise from the fact that, the plastic domains . . . "anchor" the rubbery network chains as pseudo crosslinks thereby forming a blend of the two polymers which act as a rubbery material. However, tendency of plastic behaviour might set in at higher (%) PEMA. For example, in the case of the 80% by weight PEMA in the blend, the plastic like behavior which causes low elasticity is evident and may be due to the brittle PEMA forming the continuous phase thereby breaking after a slight elongation. As can be seen from figures 3.10 to 3.12, the yield stress increased and the elongation at rupture decreased with increasing PEMA content. The blend with 15% by weight PEMA shows very pronounced ductile behavior, the elongation at rupture of this specimen is remarkably high at about 400% (Figure 3.10).

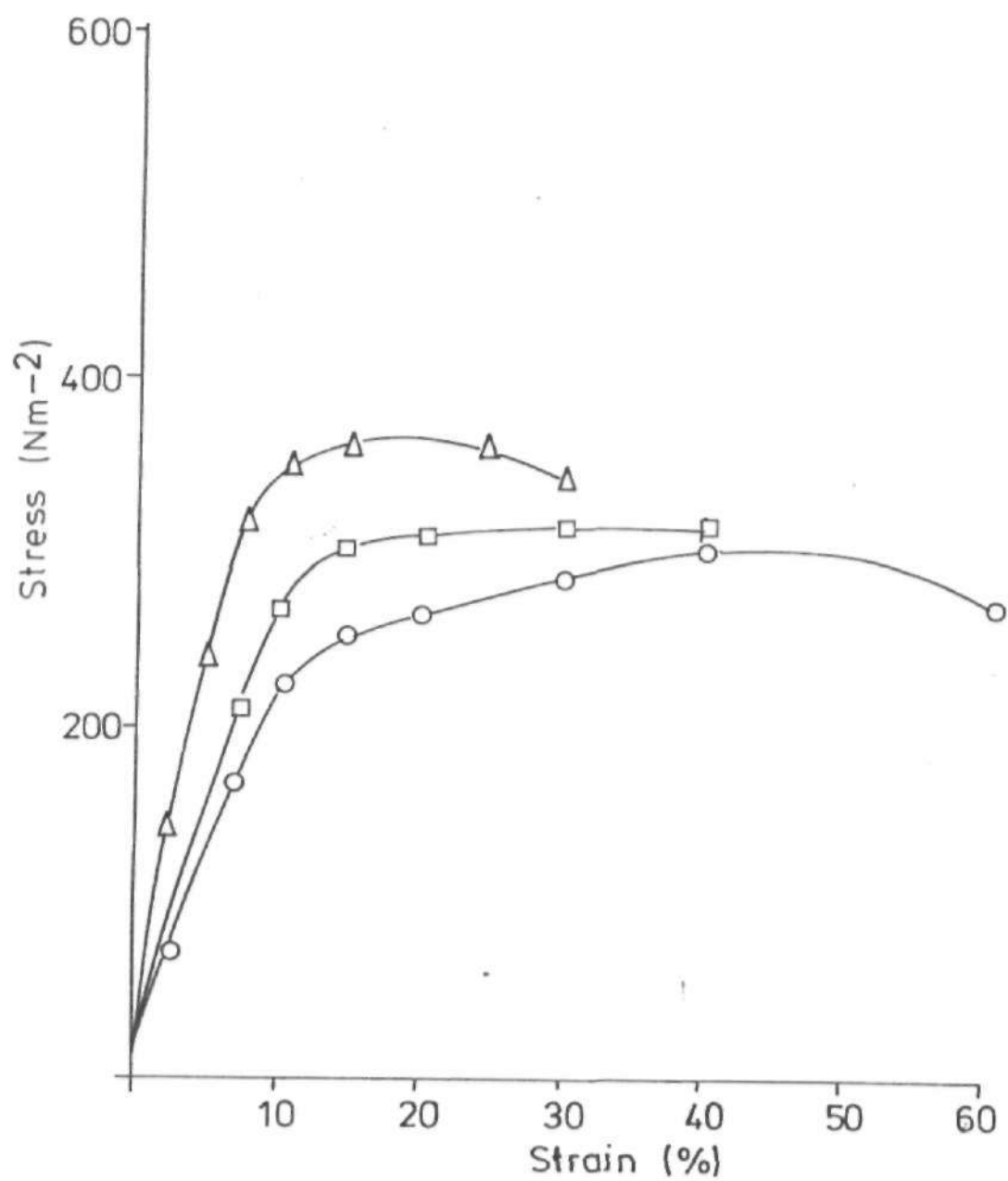


Fig. 3.9 Stress/Strain Curves for 100 % PEMA
($\circ$) ($\bar{M}_v$, 1.513×10^6) ($\square$) ($\bar{M}_v$, 3.008×10^6)
(Δ) ($\bar{M}_v$, 3.816×10^6)

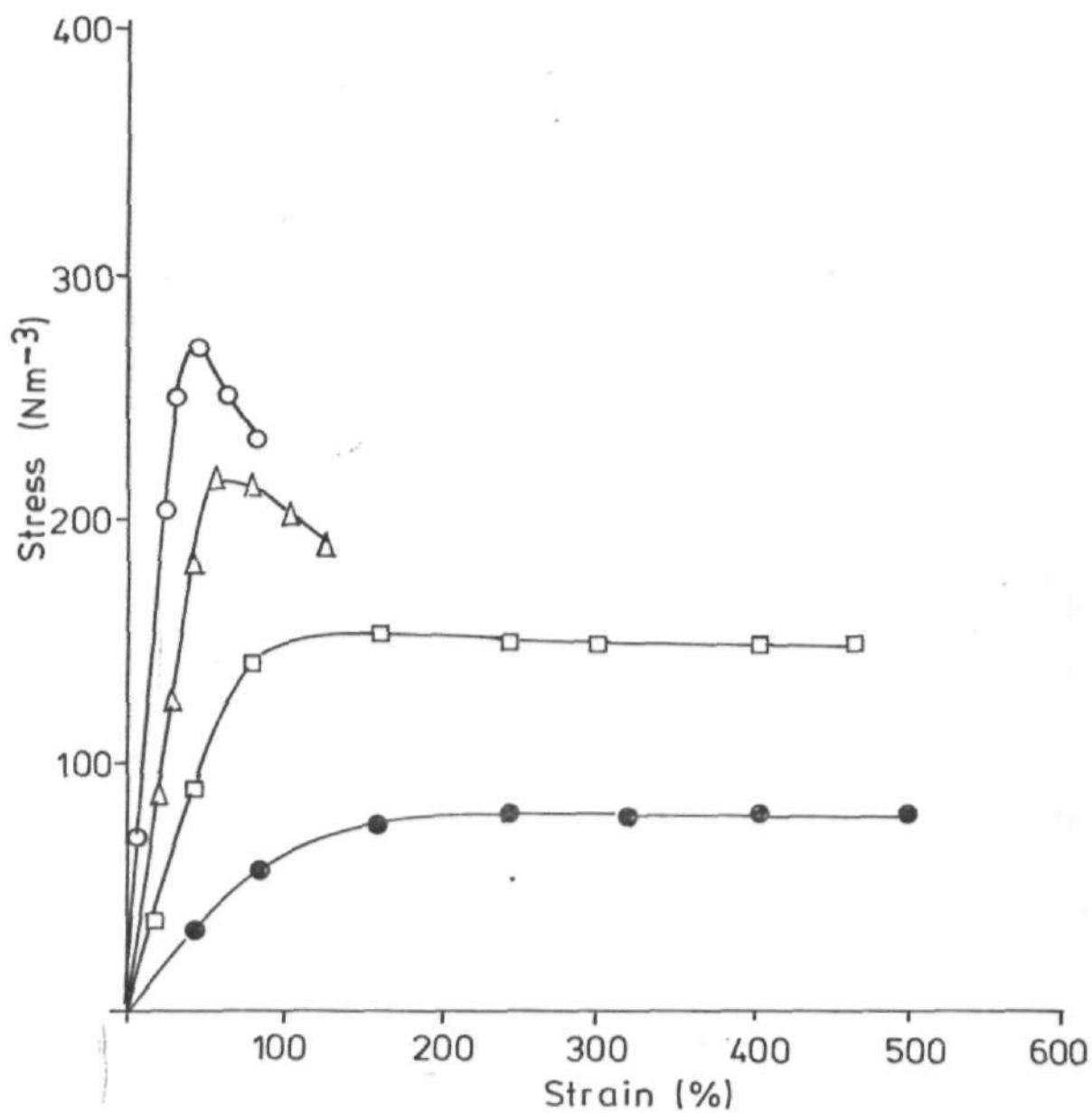


Fig. 3-10 Stress/Strain Curve for PVAc/PEMA blend
 $(\bar{M}_v)$ PEMA 1.513×10^6 $(\bar{M}_v)$ PVAc 0.726×10^6
 (●) 100% PVAc (□) 15% PEMA (Δ) 80% PEMA
 (○) 100% PEMA

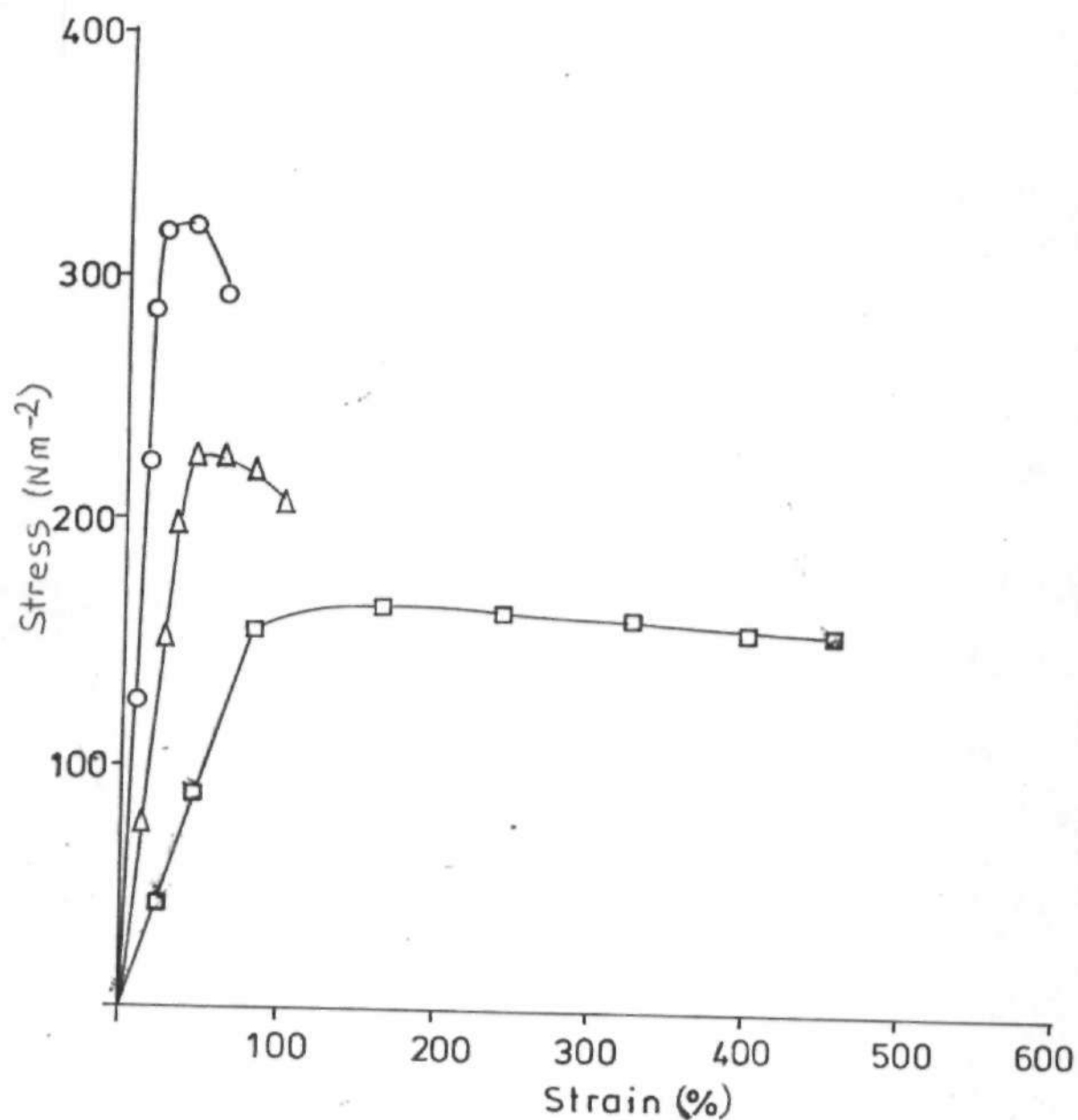


Fig 3.11 Stress/Strain Curves for PVAc/PEMA blends

($\bar{M}_v$), PEMA 3.008×10^6 ($\bar{M}_v$), PVAc 0.721×10^6
 (○) 100% PEMA (Δ) 80% PEMA (□) 15% PEMA

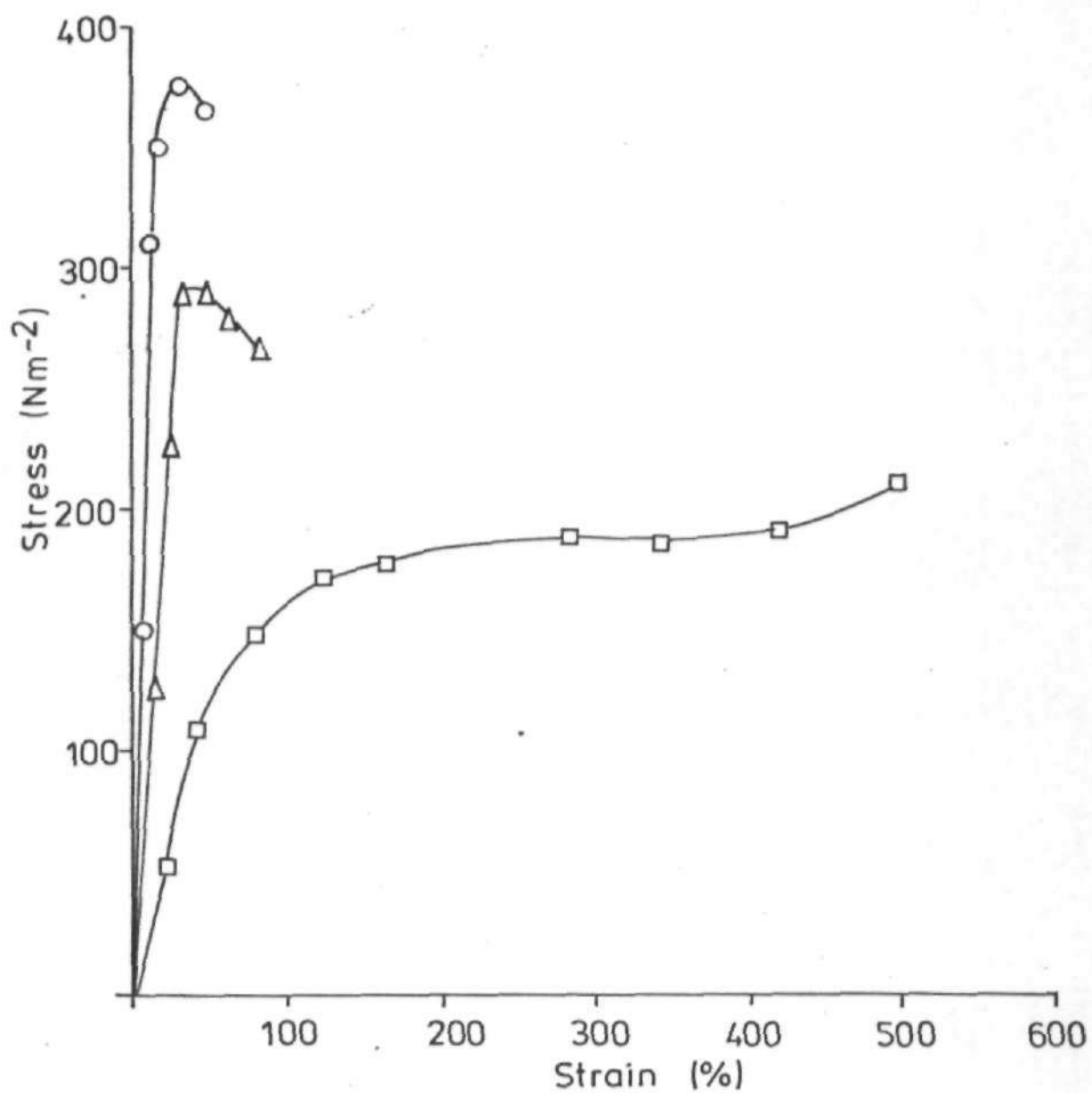


Fig. 3.12 Stress/Strain Curves for PVAc/PEMA blend
 $(\bar{M}_v)$ PEMA 3.816×10^6 $(\bar{M}_v)$ PVAc 0.721×10^6
 (○) 100% PEMA (Δ) 80% PEMA (□) 15% PEMA

The toughness, which is defined as the amount of energy stored in a sample during deformation prior to failure, can be deduced from the area under the stress-strain curve. For the blends studied, it can be observed from figures 3.10 to 3.12 that the toughness decreases markedly with increasing PEMA content.

The mechanisms of plastic deformation of the blend with 80% by weight FEMA will now be explained. In glassy polymers, two different toughening mechanisms have been identified: crazing and shear deformation (51). Crazing is a tensile yielding process accompanied by molecular orientation in the stretching direction and extensive formation of microvoids. Crazes occur in a direction perpendicular to the tensile-stress axis and cause an increase in the sample volume. Shear yielding involves elongation by shearing at a certain angle with regard to the tensile-stress direction, with no change in sample direction. It is well known that the impact strength and the toughness of glassy polymers can be improved by the incorporation of finely dispersed elastomer particles. When such a composite material is stretched, the stress concentration around the rubber particles cause the glassy matrix to yield locally by allowing crazing and shear mechanism to operate (51).

In the present work, when the applied stress exceeded the yield point, it was observed that the samples first showed homogeneous whitening throughout their whole length, indicating that crazing occurred. It then underwent a localized deformation in the form of a neck. For the blend of 15% by weight of PEMA for all the different PEMA samples, the initiated neck subsequently grew until the whole sample was covered. Fracture then occurred for this sample. A very high fracture strain was obtained. Whereas for the 80% by weight of PEMA, the neck only propagated over a certain length of the samples and early fracture resulted. Consequently for this blend, the elongation at break was much smaller than that for the blend with 15% by weight of PEMA.

The observation that the different blends exhibited stress whitening, necking, and cold drawing during a tensile test indicates that crazing and shear processes contributed to the tensile strain.

3.4.2 Mechanical properties of polyethyl methacrylate and polyvinyl acetate samples.

The values determined for the tensile strength, percentage elongation at break and initial modulus of elasticity, for the PEMA and PVAc samples are shown in tables 3.7 and 3.8 respectively.

TABLE 3.7

Dependence of some tensile mechanical properties
of PEMA films on ($\bar{M}_v$) of the polymer.

Polymer sample	$(\bar{M}_v) \times 10^6$	Tensile strength $\times 10^{-4} \text{Nm}^{-2}$	Initial modulus Nm^{-2}	Elongation (%)
A	1.513	4.134	70.00	104.00
B	2.212	4.221	82.50	90.10
C	3.008	4.383	95.01	75.00
D	3.816	4.651	105.0	48.00

TABLE 3.8

Dependence of some tensile mechanical properties
of PVAc films on ($\bar{M}_v$) of the polymer.

Polymer sample	$(\bar{M}_v) \times 10^6$	Tensile strength $\times 10^{-4} \text{Nm}^{-2}$	Initial modulus Nm^{-2}	Elongation (%)
I	0.531	3.385	34.10	520.00
F	0.570	3.412	36.30	516.00
H	0.638	3.460	38.21	506.00
G	0.721	3.500	40.90	500.00
E	0.745	3.889	43.01	466.96

The tensile strength in general, has been observed to increase with molecular weight. This increase is expected since with increase in molecular weight, the curled PEMA and PVAc can stretch out and straighten. During this stretching operation the groups responsible for the secondary valence forces may become aligned thus increasing the tensile strength of the macromolecule (52) i.e the PEMA and PVAc samples. Also from tables 3.7 and 3.8, the (%) elongation at break of the PEMA and PVAc samples decreased with increasing viscosity average molecular weight. This can be attributed to the fact that increasing the molecular weight of the polymers increases the strong secondary valence forces thereby reducing the extensibility of the macromolecule (3). As with tensile strength, the initial modulus increased with molecular weight of PEMA and PVAc. Since initial modulus is a measure of the stiffness or resistance to deformation of the polymer, the higher the tensile strength i.e. strength of the polymer, the higher the polymer's stiffness to any applied stress. So since tensile strength, increases with molecular weight of the polymer, initial modulus will also increase with molecular weight of the polymer.

3.4.3 Effect of PEMA concentration on tensile strength, initial modulus and (%) elongation at break of films of PEMA/PVAc blend.

As indicated in figures 3.13 to 3.15, the tensile strength of the polymer blends increased slightly up to a maximum corresponding to a certain percent composition of PEMA, then decreased to a minimum before increasing gradually, approaching the tensile strength for the pure PEMA sample used. Only three out of the four PEMA samples and three out of the five PVAc samples used are represented in figures 3.13 to 3.15, for clarity.

The maximum point or rather the peak value of tensile strength increased with increase in molecular weight of the PEMA as in Figure 3.16. The observed peak value or maximum in tensile strength may be explained in terms of a strong specific interaction between the polymers PEMA and PVAc at the particular blend composition. This strong interaction led to a better molecular packing, that is greater densities and therefore an increased tensile strength as observed in figures 3.13 to 3.15. These observations agree with the results of Shur et al (53) who also observed a peak in the tensile strength versus composition plot for PMMA and PVAc blend system.

Thus it was claimed that their result demonstrated synergism in tensile strength of the two polymers in the blends.

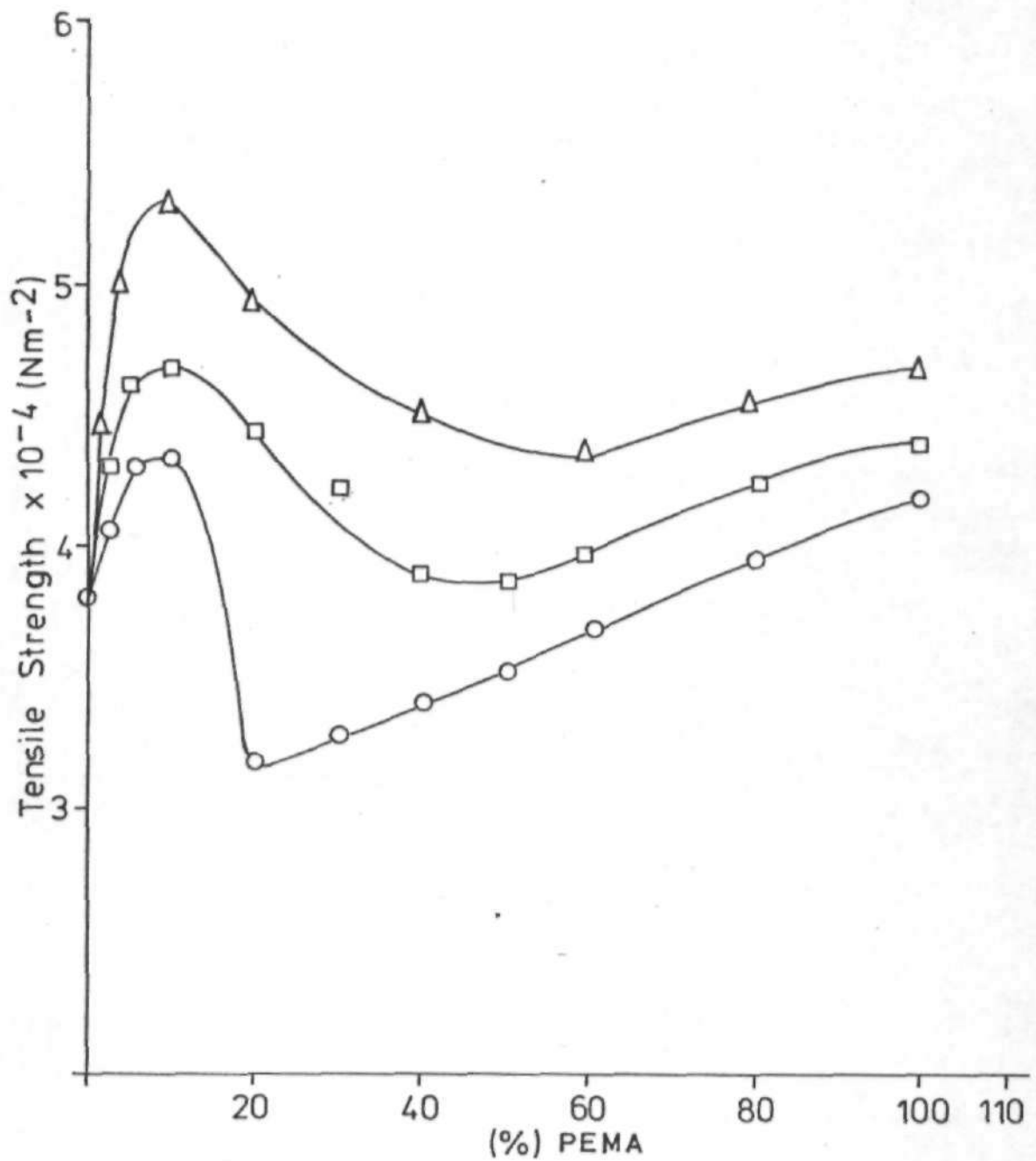


Fig. 3.13 Variation of T.S. of PVAc/PEMA blend with (%) composition of PEMA
 PVAc ($\bar{M}_v$, 0.745×10^6) (o) PEMA ($\bar{M}_v$, 1.513×10^6)
 (□) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

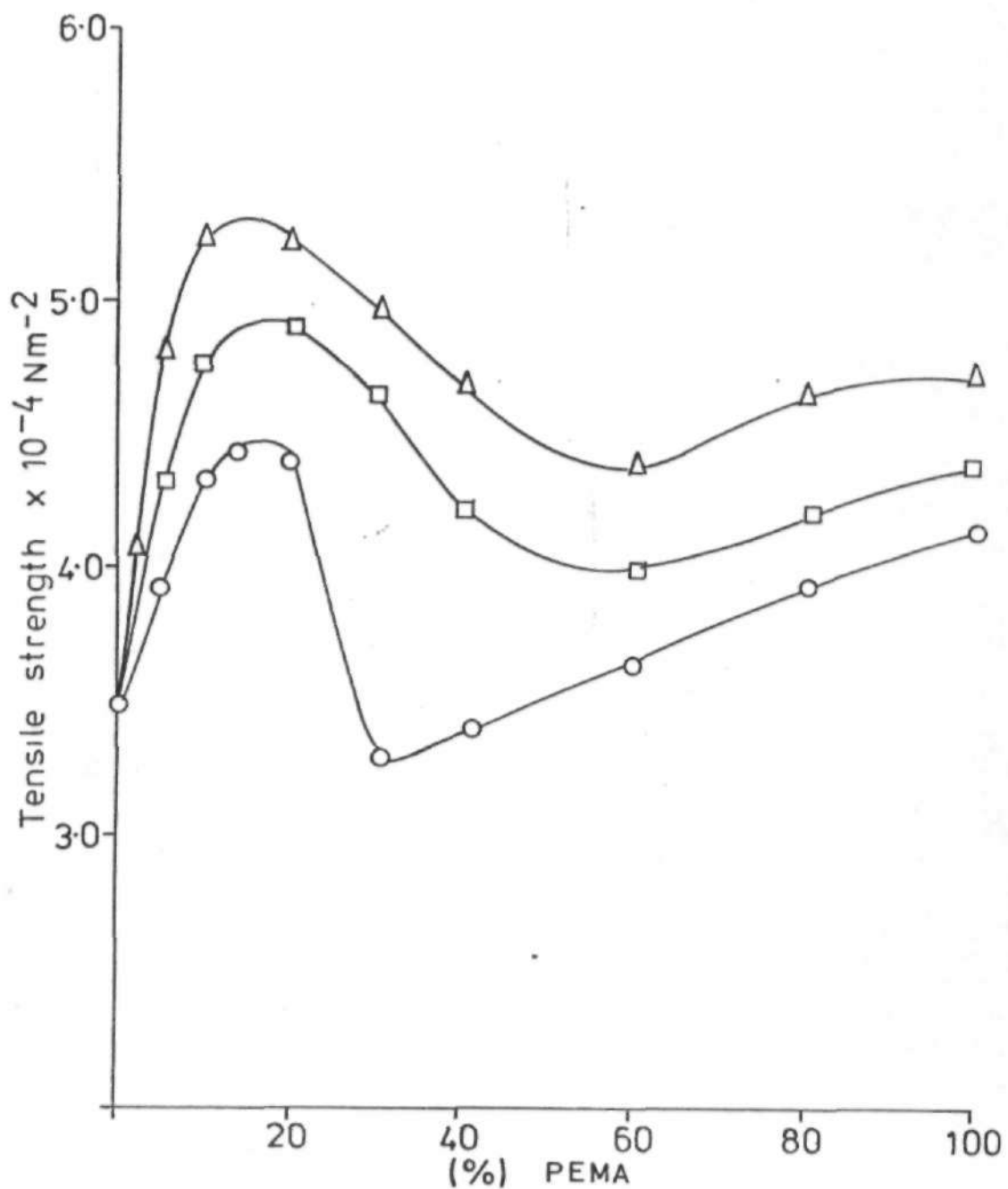


Fig. 3.14 Variation of T. S. of PVAc/PEMA blend with (%) composition of PEMA

PVAc ($\bar{M}_v$, 0.7205×10^6), ($\circ$) PEMA ($\bar{M}_v$, 1.5130×10^6)
 ($\square$) PEMA ($\bar{M}_v$, 3.0080×10^6), (Δ) PEMA ($\bar{M}_v$, 3.8160×10^6)

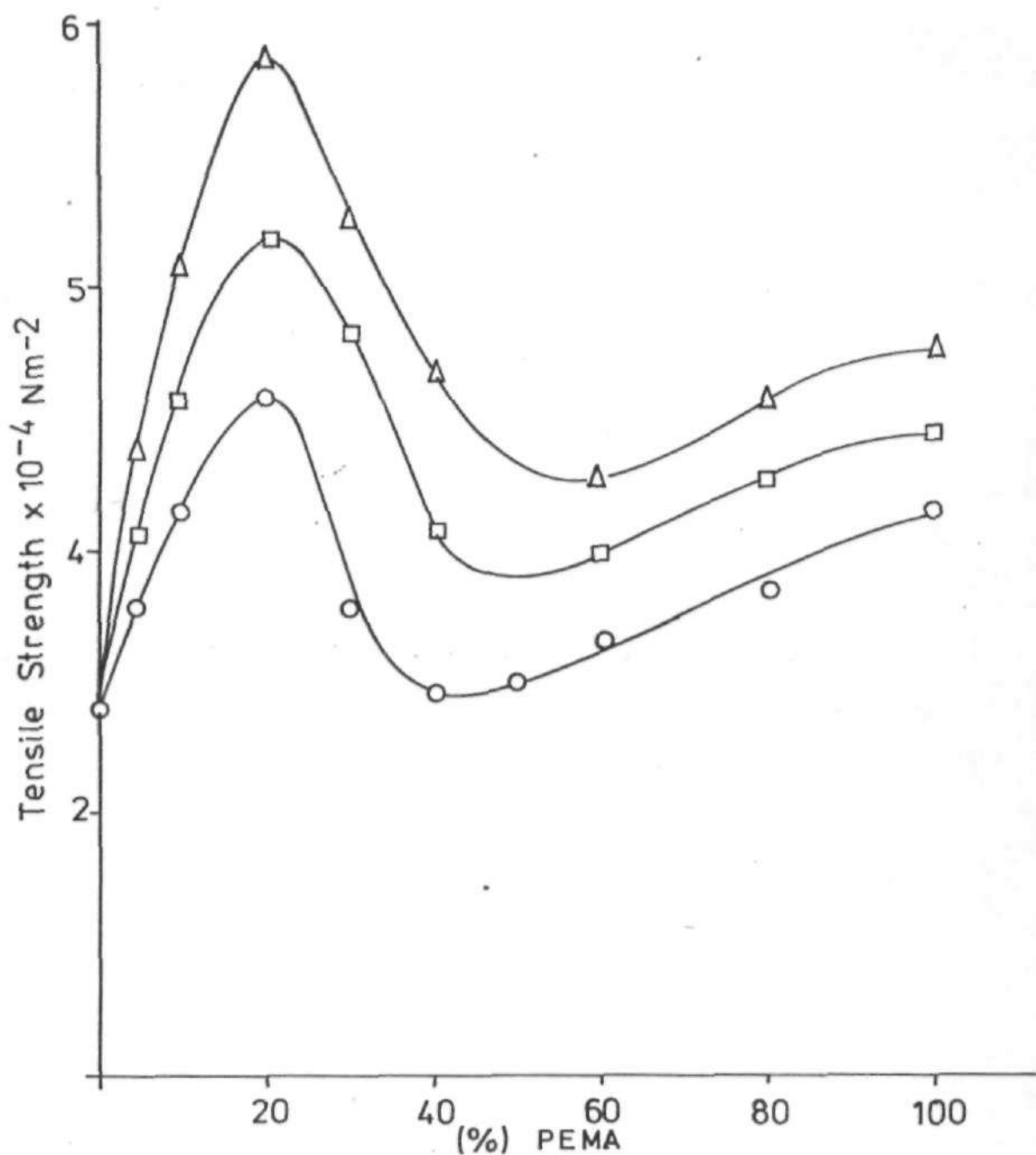


Fig. 3.15 Variation of (T.S) of PVAc/PEMA blend with (%) composition of PEMA

PVAc ($\bar{M}_v$, 0.570×10^6) (○) PEMA ($\bar{M}_v$, 1.513×10^6)
 (□) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

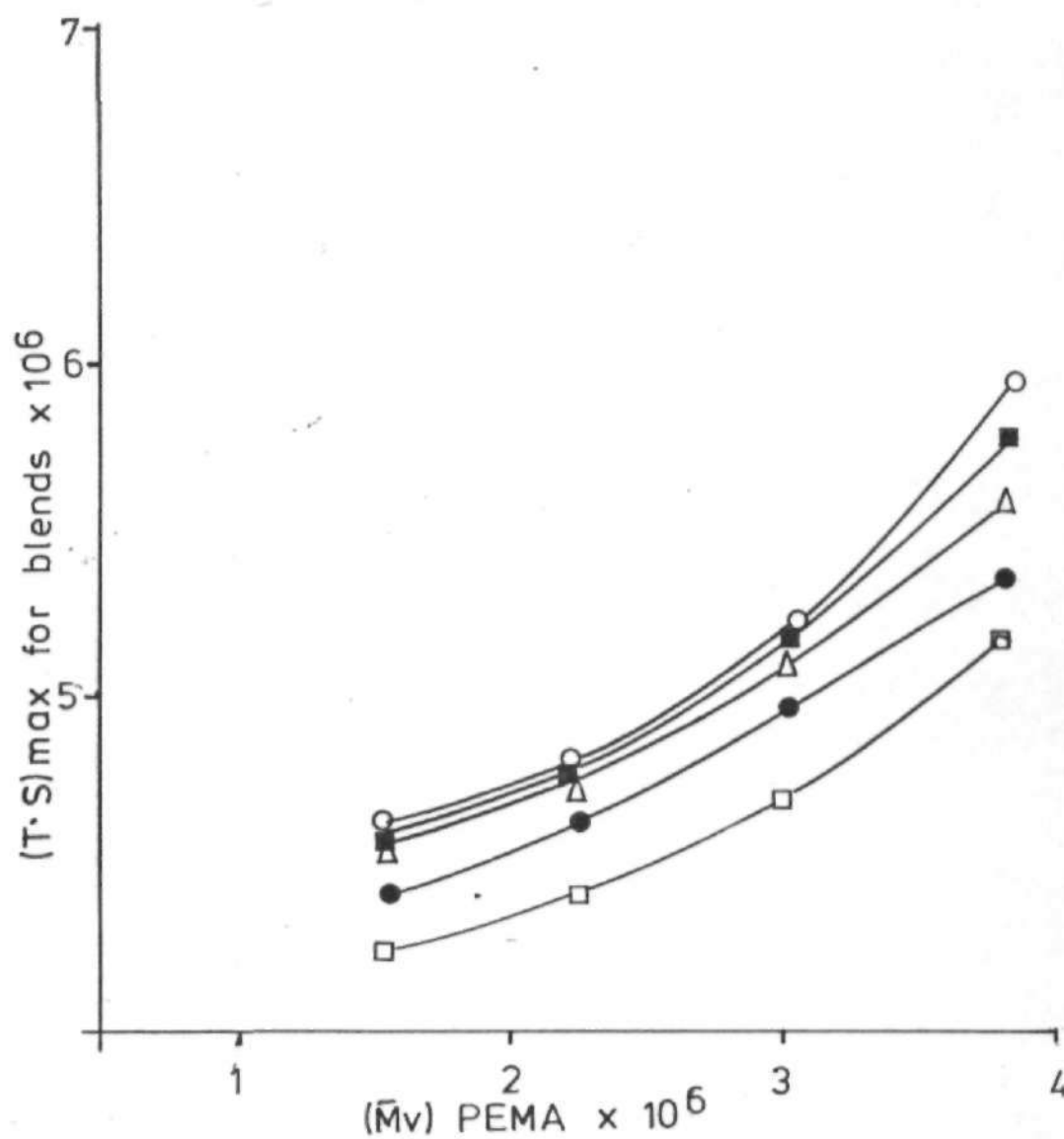


Fig. 3.16 Variation of $(T.S)_{\max}$ with M_v of PEMA for different $(\bar{M}_v)$ PVAc of:
 (o) PVAc $(\bar{M}_v, 0.531 \times 10^6)$ ($\square$) PVAc $(\bar{M}_v, 0.570 \times 10^6)$
 (Δ) PVAc $(\bar{M}_v, 0.638 \times 10^6)$ ($\bullet$) PVAc $(\bar{M}_v, 0.721 \times 10^6)$
 ($\blacksquare$) PVAc $(\bar{M}_v, 0.745 \times 10^6)$

Also Kuleznev et al (9) in their study on polystyrene and polybutadiene blends, reported that a total linear plot of tensile strength versus blend composition denotes total compatibility between the polymers, but the presence of a maximum or peak in the plot denotes specific interactions between the two types of macromolecules.

Since a large number of polar groups is present in both PEMA and PVAc namely: the methacrylate and acetate, there could exist strong interactions between the molecules of the polymers in their blends. This would lead to low chain mobility and an increase in tensile strength. It is also important to note that as the amount of PEMA increases in the blends up to the point of maximum tensile strength, its swelling capacity would decrease as a result of an increase in intermolecular interaction mainly of the type PEMA-PVAc, and possibly due to the formation of a network structure as suggested from Reznikova's work on Polyvinylchloride/Butadiene nitrile copolymer (54).

It is also interesting that for each of the PVAc sample, the tensile strength composition curve show a maximum at the same (%) PEMA in the blend. The maximum becomes more pronounced with increase in the molecular weight of PEMA. This can be explained probably by saying that as the molecular weight of PEMA increases with constant

molecular weight of PVAc, the solid state arrangement of the polar groups of PEMA available for specific interaction with PVAc at the maximum for tensile strength for a particular blend becomes more favorable and therefore the PEMA-PVAc interaction becomes stronger. Due to this stronger interaction and better molecular packing, tensile strength also increases. Beyond this composition of PEMA corresponding to the peak of tensile strength, decrease in tensile strength is observed, and may be due to the fact that after the mode of interaction that led to maximum tensile strength, other forms of interactions like free mixing with and without entanglement have set in. These effects might be less than the specific interaction and may serve in diluting the specific interaction effect that produced tensile strength maximum.

From Keznikova's work (55), the presence of the maximum in results of the present study may be due to the change in the nature of the PEMA and PVAc. As the content of PEMA in the blend increases, the elastic rupture of PVAc passes into a brittle break. Increase of the breaking load in these conditions is due to orientation of the molecular chains and a more uniform distribution of the load between the molecules. On further increase of the PEMA content, the tensile strength decreases before increasing again tending towards that of PEMA as a result of the flow of the polymer i.e. a dispersion of the stronger and longer PEMA molecules.

in a continuous matrix of the PVAc (55). This implies some independent behavior of the two polymers in the blend.

It can thus be concluded from all the above explanations that, the higher the molecular weight of PEMA, the greater the number of points of attraction and entanglement between the molecules.

From figure 3.17, the (%) PEMA at maximum tensile strength of the PEMA/PVAc blend decreased with increase in the viscosity average molecular weight of PVAc. Also figure 3.16 shows an increase in the maximum tensile strength of the blend with increased viscosity average molecular weight of PEMA. These observations imply that lower molecular weight PVAc samples accommodate PEMA more than the higher molecular weight samples. Also blending of PEMA with PVAc produces improved properties in the two composite polymers, the size of which increases as $(\bar{M}_v)$ of PVAc decreases, figure 3.18.

Two regions can be recognised from the tensile strength-composition plots if a straight line is drawn to join $(T.S.)_{PVAc}^0$ with $(T.S.)_{PEMA}^0$. For the lower molecular weight PEMA samples:-

- (1) region of synergism i.e. where $(T.S.)_{blend}$ is greater than that of the pure polymers, and

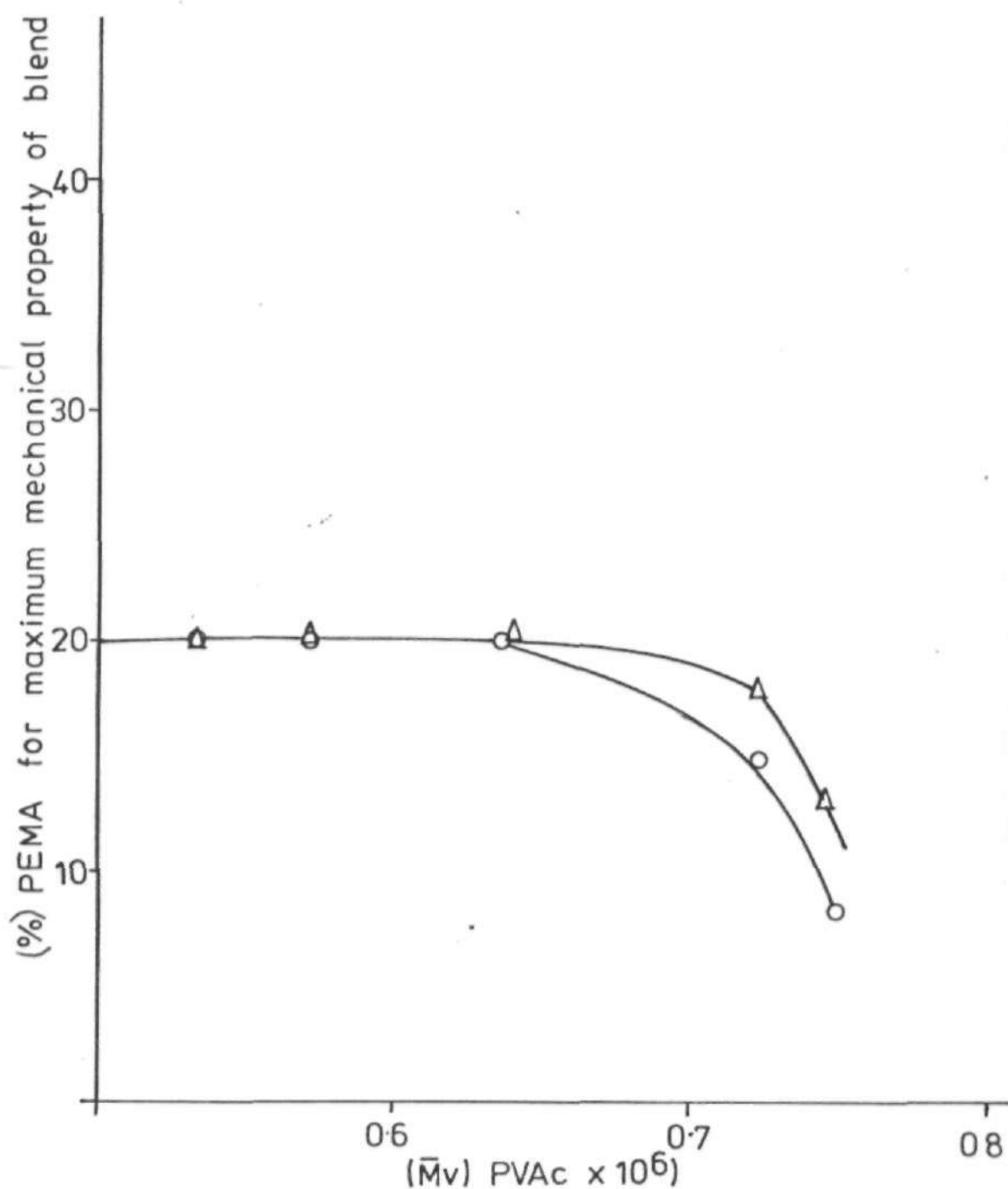


Fig. 3.17 Variation of (%) PEMA at maximum mechanical property of blend with ($\bar{M}_v$) of PVAc
 (O) Tensile Strength (Δ) Initial modulus
 while T.S = elongation (%)

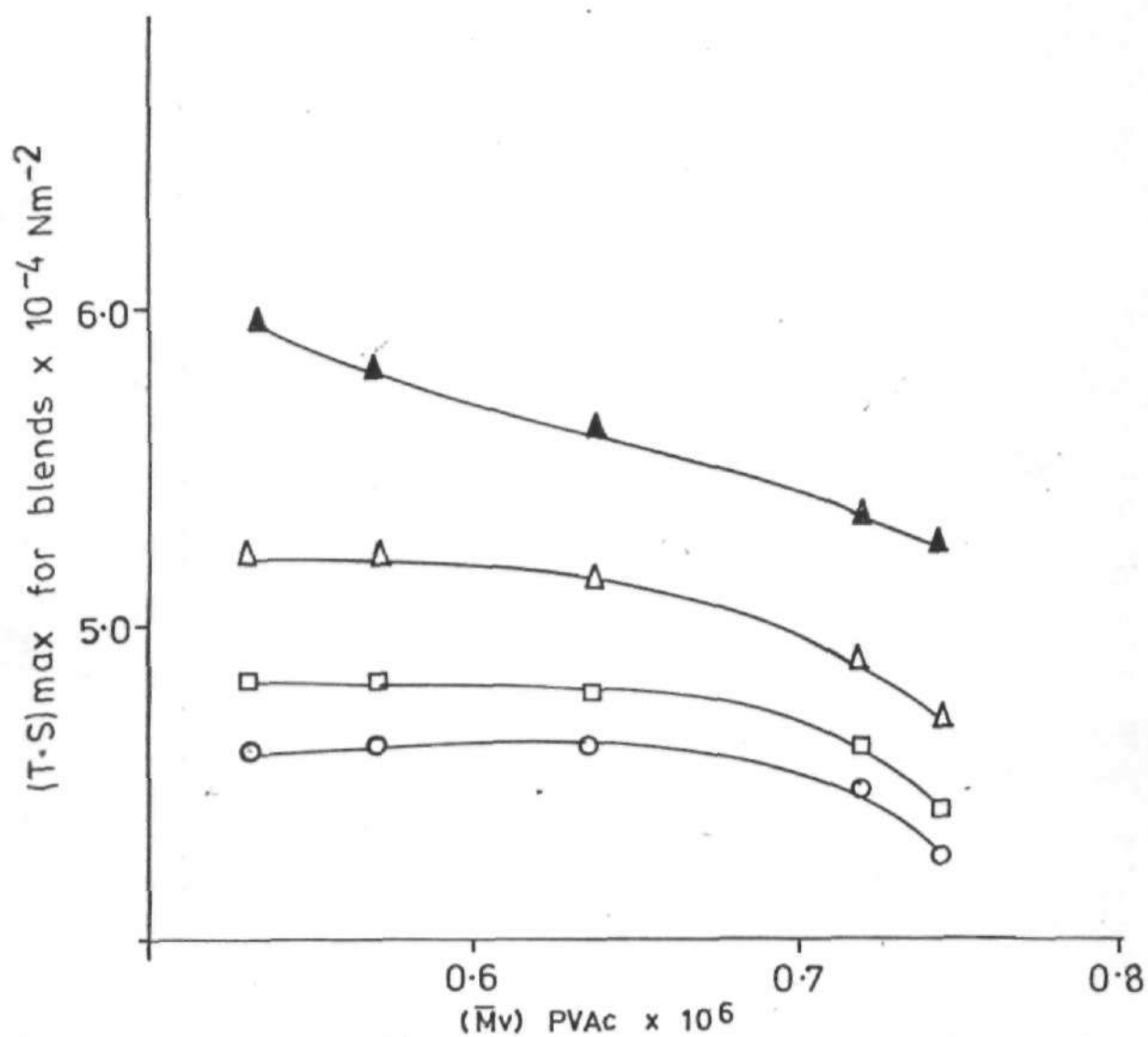


Fig. 3-18 Variation of $(T-S)_{\max}$ with $(\bar{M}_v)$ of PVAc for different $(\bar{M}_v)$ PEMA of:
 (o) PEMA $(\bar{M}_v, 1.513 \times 10^6)$ ($\square$) PEMA $(\bar{M}_v, 2.212 \times 10^6)$
 (Δ) PEMA $(\bar{M}_v, 3.008 \times 10^6)$ ($\blacktriangle$) PEMA $(\bar{M}_v, 3.816 \times 10^6)$

- (ii) region of antagonism, where (T.S) lower than that expected are often noted.

The region of synergism grows with $(\bar{M}_v)_{\text{PEMA}}$ while that of antagonism reduces, and does not occur with PEMA of a sufficiently high molecular weight. Also, the region of synergism is larger covering wider range of (%) PEMA in blend while that of antagonism decreases for PVAc of lower molecular weight, i.e. as $(\bar{M}_v)_{\text{PEMA}} / (\bar{M}_v)_{\text{PVAc}}$ increases.

This suggests that blending of PEMA with PVAc would be fully synergistic if the molecular weight ratio $(\bar{M}_v)_r$ is sufficiently large, provided that the polymers remain compatible. It is noteworthy that a second peak, at very high $(\bar{M}_v)_{\text{PEMA}}$ might develop in the property-composition plot at higher (%) PEMA composition, figure 3.13 to 3.15. While synergism in the (T.S) behavior has been explained as due to favourable and specific PEMA - PVAc interaction leading to improved molecular packing, antagonism might be regarded as developing as a result of incompatibility of the polymers. Phase separation as a result of incompatibility or poor mixing of the polymer molecules could not assume a higher molecular order (in their conformation) than those of the PVAc except if the former are more in number than the latter. Thus as observed, antagonism is expected to decrease with increase in (%) PEMA in the blend.

As with tensile strength, the initial modulus increases initially up to a maximum point at a certain composition of PEMA figures 3.19 to 3.21. Beyond this concentration of PEMA, the initial modulus decreases to a minimum before increasing again, approaching that of pure PEMA, as shown in figures 3.19 to 3.21. The same trend was obtained for all the PEMA samples, the only difference being that the peak value of (I.M) increases with the molecular weight of PEMA as shown in figure 3.22. The increase in (I.M) may be due to the rearrangement of the molecules of PEMA and PVAc at that blend composition corresponding to the peak or maximum.

The rearrangement of the molecules leads to a very stiff blend of higher initial modulus than those of the pure polymers.

Figure 3.23 also shows decrease in the initial modulus at maximum with increase in the ($\bar{M}_v$) of PVAc. It is observed also from the figure that at lower ($\bar{M}_v$) of PVAc the change in property of the blend is constant for different ($\bar{M}_v$) PEMA but differs as the ($\bar{M}_v$) of PVAc increases. This effect may be due to the blends of lower ($\bar{M}_v$) of polymers having similar initial modulus whereas at high ($\bar{M}_v$) of polymers the effect of the stiffness of their blends become very pronounced.

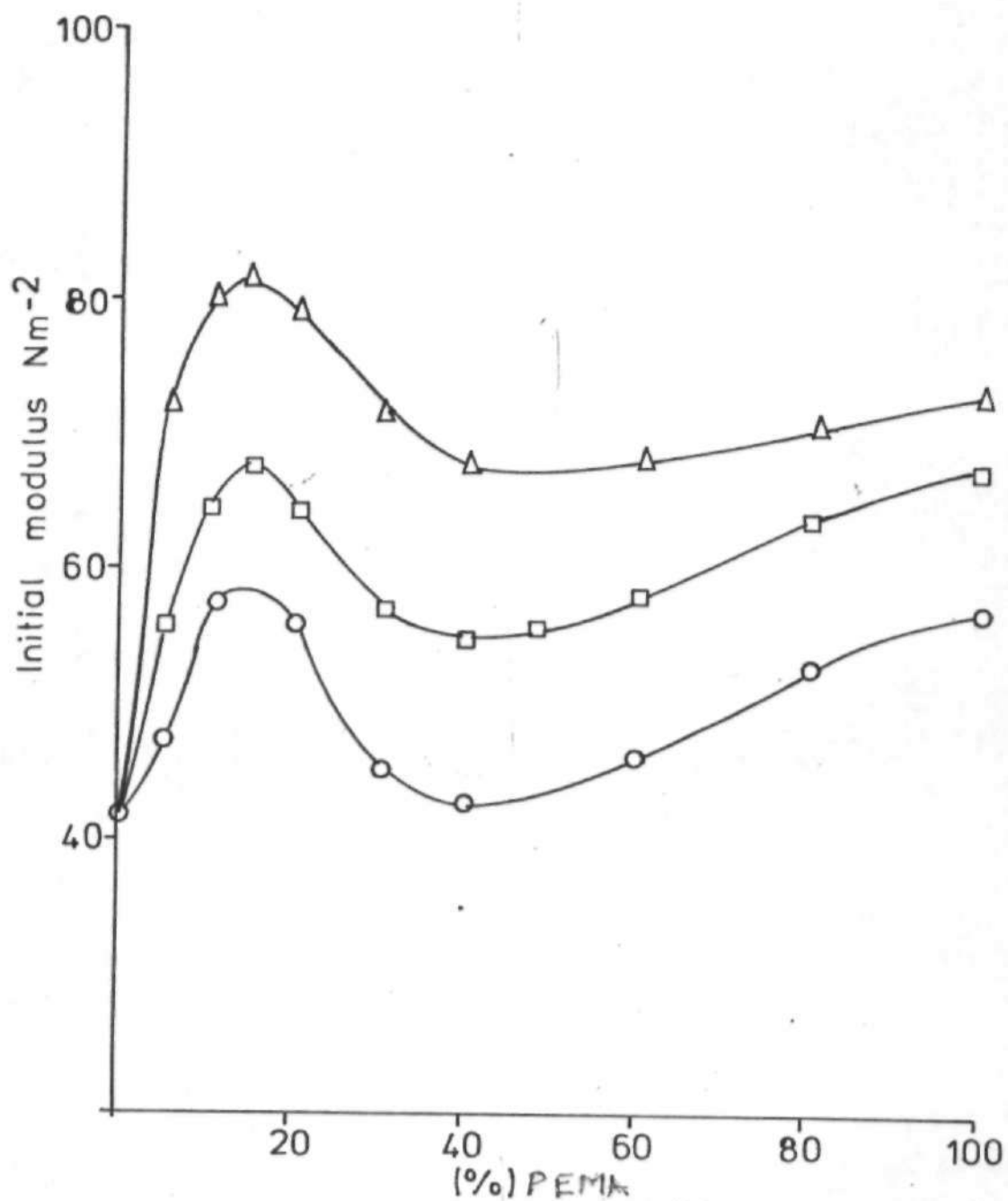


Fig. 3-19 Variation of initial modulus of PVAc/PEMA blend with (%) composition of PEMA

PVAc ($\bar{M}_v$, 0.745×10^6) (○) PEMA ($\bar{M}_v$, 1.513×10^6)
 (□) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

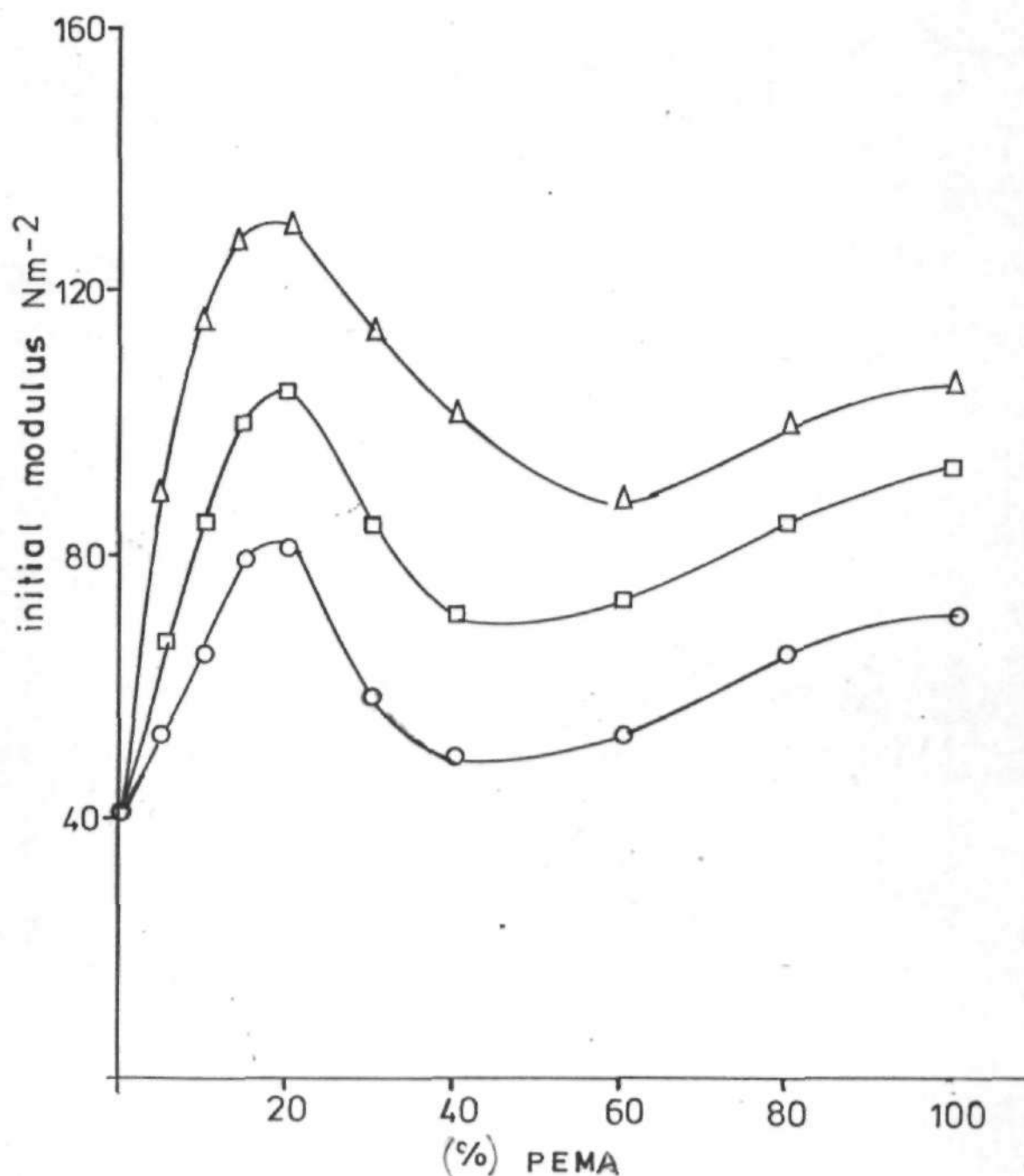


Fig. 3-20 Variation of initial modulus of PVAc/PEMA blend with (%) composition of PEMA

PVAc ($\bar{M}_v, 0.721 \times 10^6$) (○) PEMA ($\bar{M}_v, 1.513 \times 10^6$)
 (□) PEMA ($\bar{M}_v, 3.008 \times 10^6$) (Δ) PEMA ($\bar{M}_v, 3.816 \times 10^6$)

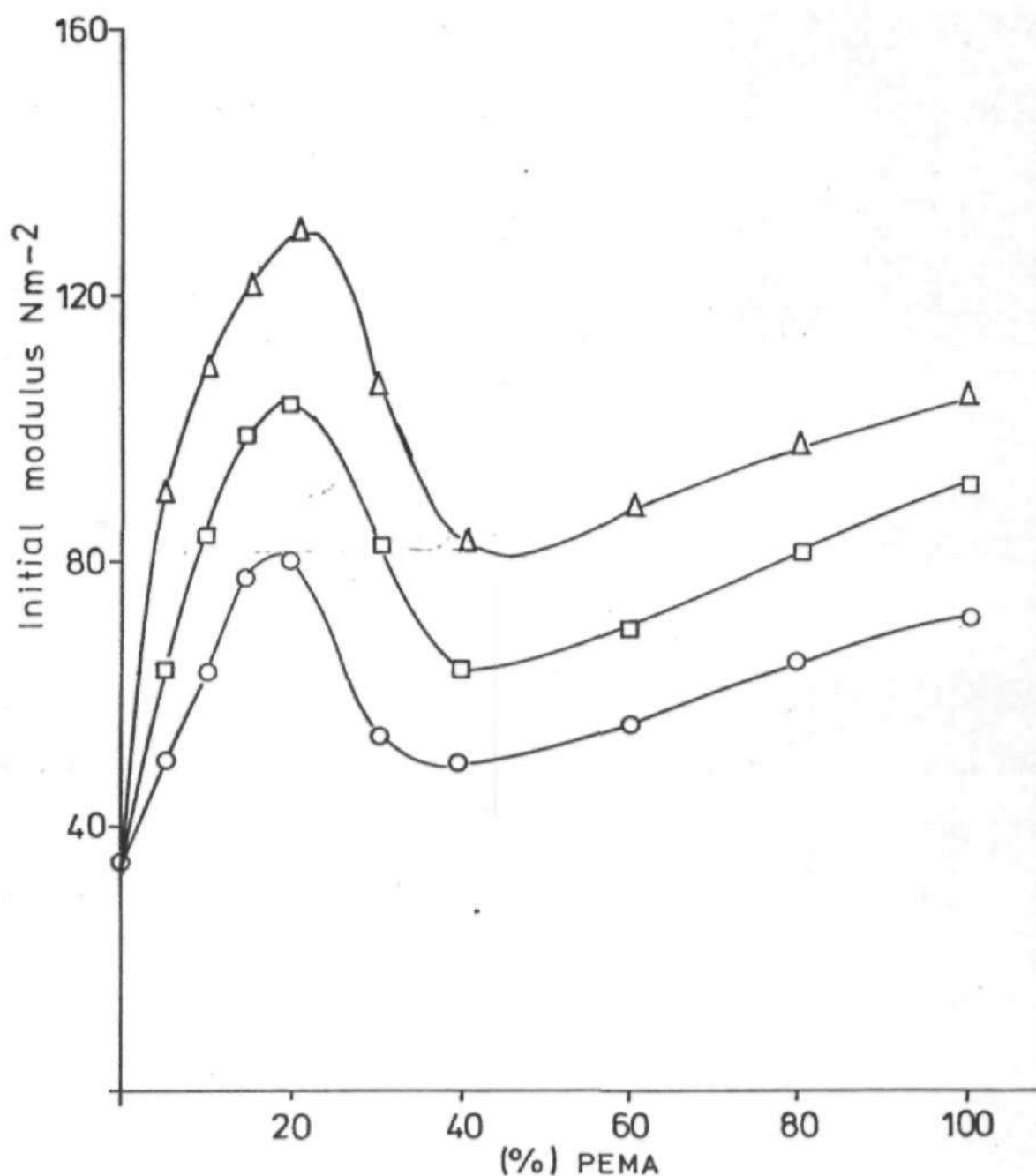


Fig. 3-21 Variation of Initial modulus of PVAc/PEMA blend with (%) composition of PEMA
 PVAc ($\bar{M}_v$, 0.570×10^6) (o) PEMA ($\bar{M}_v$, 1.513×10^6)
 (□) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

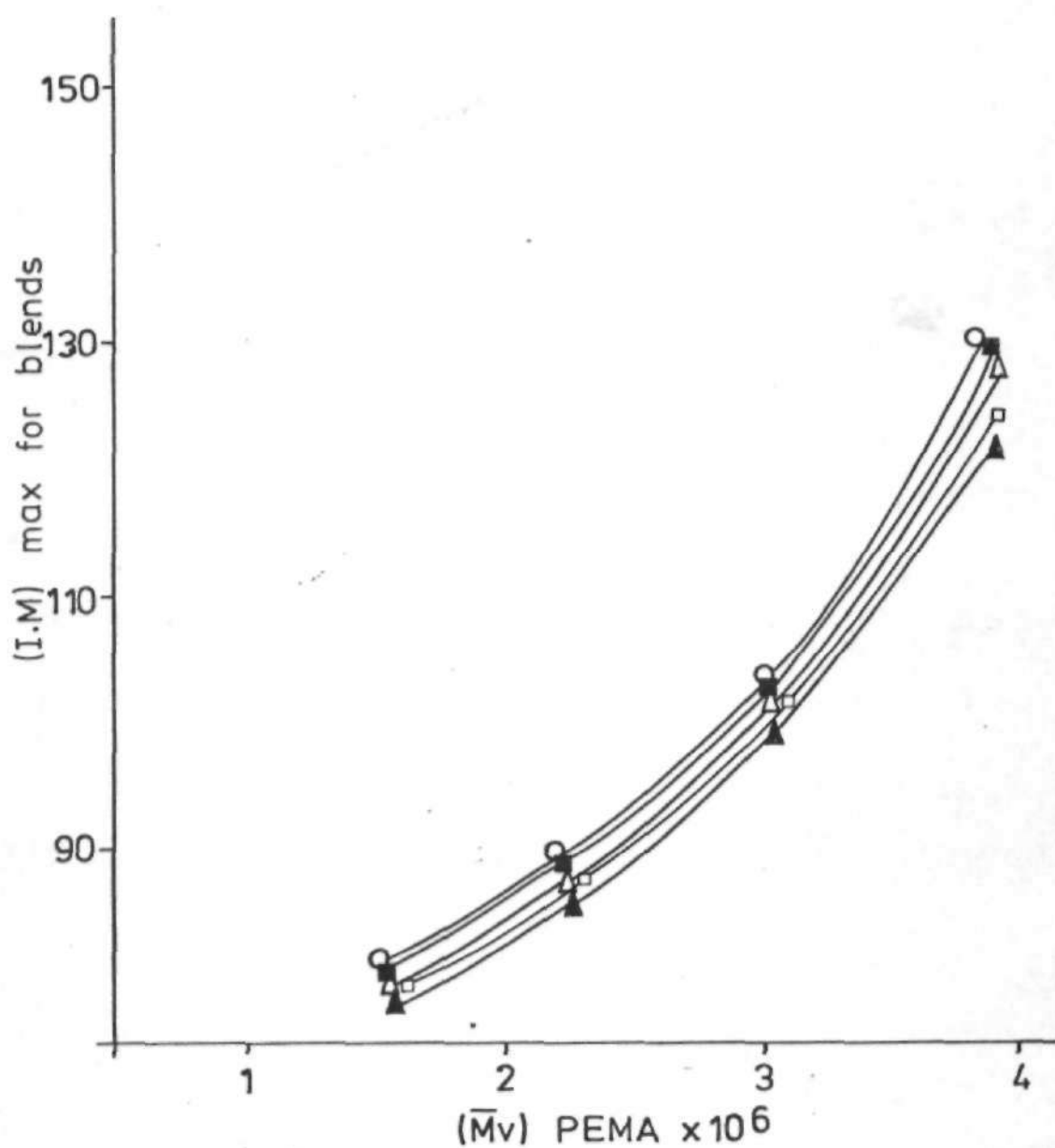


Fig. 3-22 Variation of (I.M) max with ($\bar{M}_v$) of PEMA for different ($\bar{M}_v$) PEMA of
 (o) PVAc ($\bar{M}_v$, 0.531×10^6) (■) PVAc ($\bar{M}_v$, 0.570×10^6)
 (Δ) PVAc ($\bar{M}_v$, 0.638×10^6) (□) PVAc ($\bar{M}_v$, 0.721×10^6)
 (▲) PVAc ($\bar{M}_v$, 0.745×10^6)

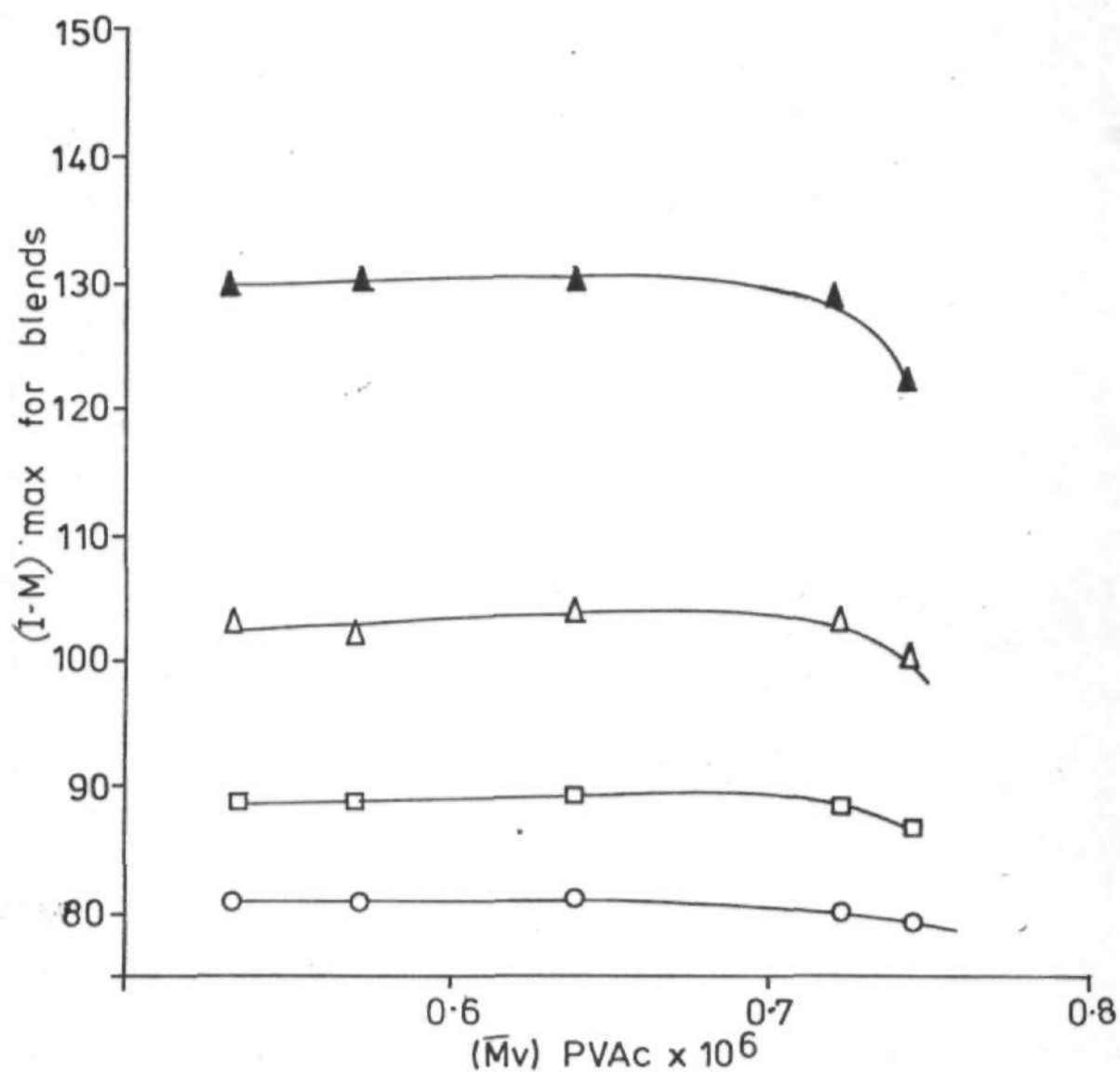


Fig. 3-23 Variation of $(I-M)_{\text{max}}$ with $(\bar{M}_v)$ of PVAc for different $(\bar{M}_v)$ PEMA of:
 (o) PEMA ($\bar{M}_v, 1.513 \times 10^6$) ($\square$) PEMA ($\bar{M}_v, 2.212 \times 10^6$)
 ($\triangle$) PEMA ($\bar{M}_v, 3.008 \times 10^6$) ($\blacktriangle$) PEMA ($\bar{M}_v, 3.816 \times 10^6$)

Figure 3.17 shows some differences at high $\bar{M}_v$ of PVAc for tensile strength and initial modulus when compared while (%) elongation agrees with tensile strength results. This implies that the specific interactions between the polymers are affected by only those properties which affect only (%) elongation and tensile strength. As shown in figures 3.24 to 3.26, the percentage elongation at break increased slightly up to a maximum corresponding to a certain blend composition of the polymers. Beyond this concentration the value decreased tending towards that of the pure PMAA. Similar trend was observed for all the other PEMA samples. Largest elongation was observed for the lowest molecular weight PEMA as would be anticipated from the reasoning that PEMA has lower elongation than PVAc. This was also expected since it was in this sample that greatest reduction of tensile strength also occurred. Also the maximum point may probably be due to some kind of strong interaction between the molecules of the polymers thus leading to better alignment of molecules as explained for tensile strength above. This is also expected since due to the strong interactions between the molecules, structural changes between the molecules of the polymers can take place. Application of a stress will therefore not break the sample easily but stretch it up to a higher value thereby increasing the elongation to the maximum point.

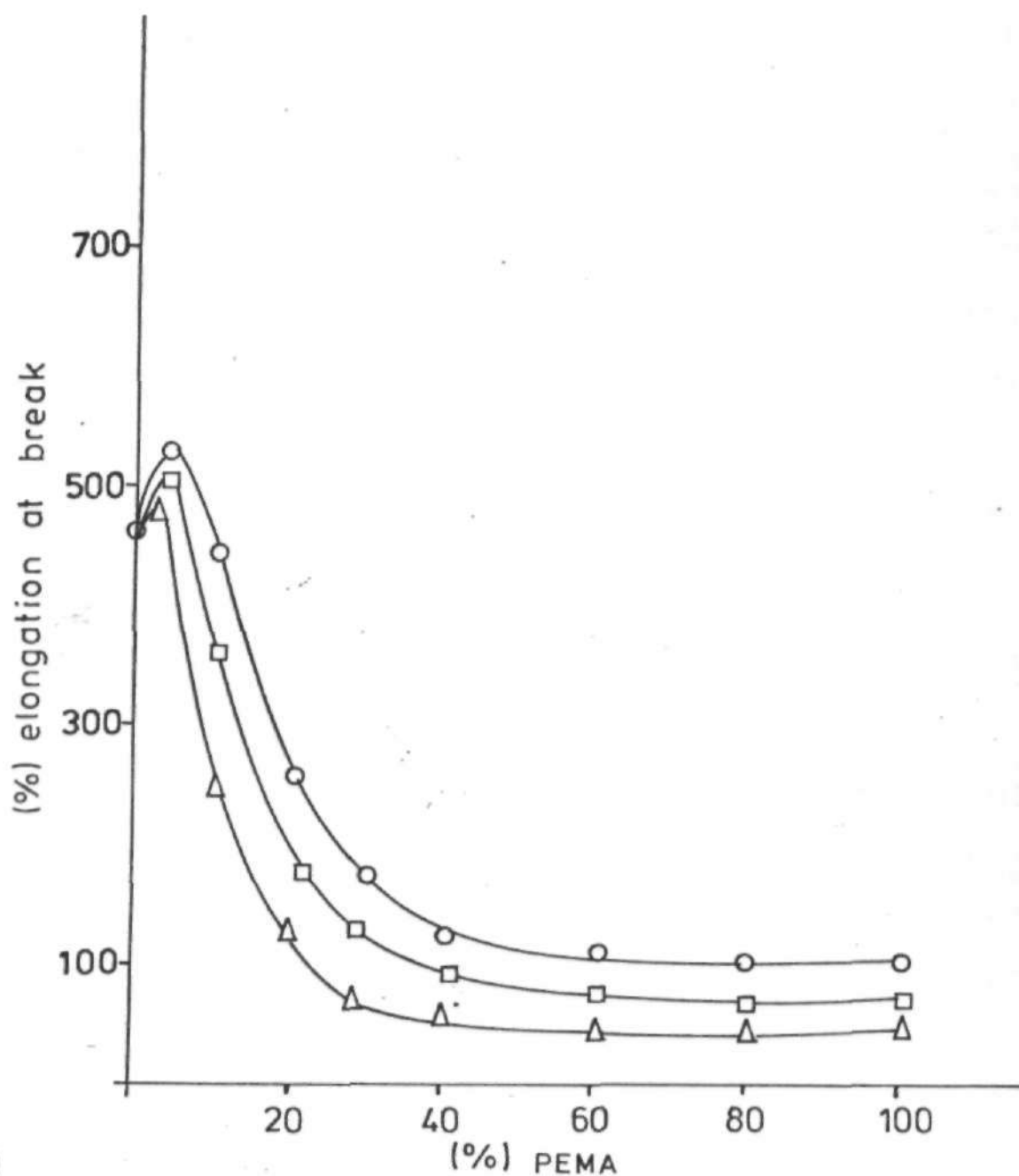


Fig. 3-24 Variation of (%) elongation at break of PVAc/PEMA blend with (%) composition of PEMA
 PVAc ($\bar{M}_v, 0.745 \times 10^6$) (o) PEMA ($\bar{M}_v, 1.513 \times 10^6$)
 (□) PEMA ($\bar{M}_v, 3.008 \times 10^6$) (Δ) PEMA ($\bar{M}_v, 3.816 \times 10^6$)

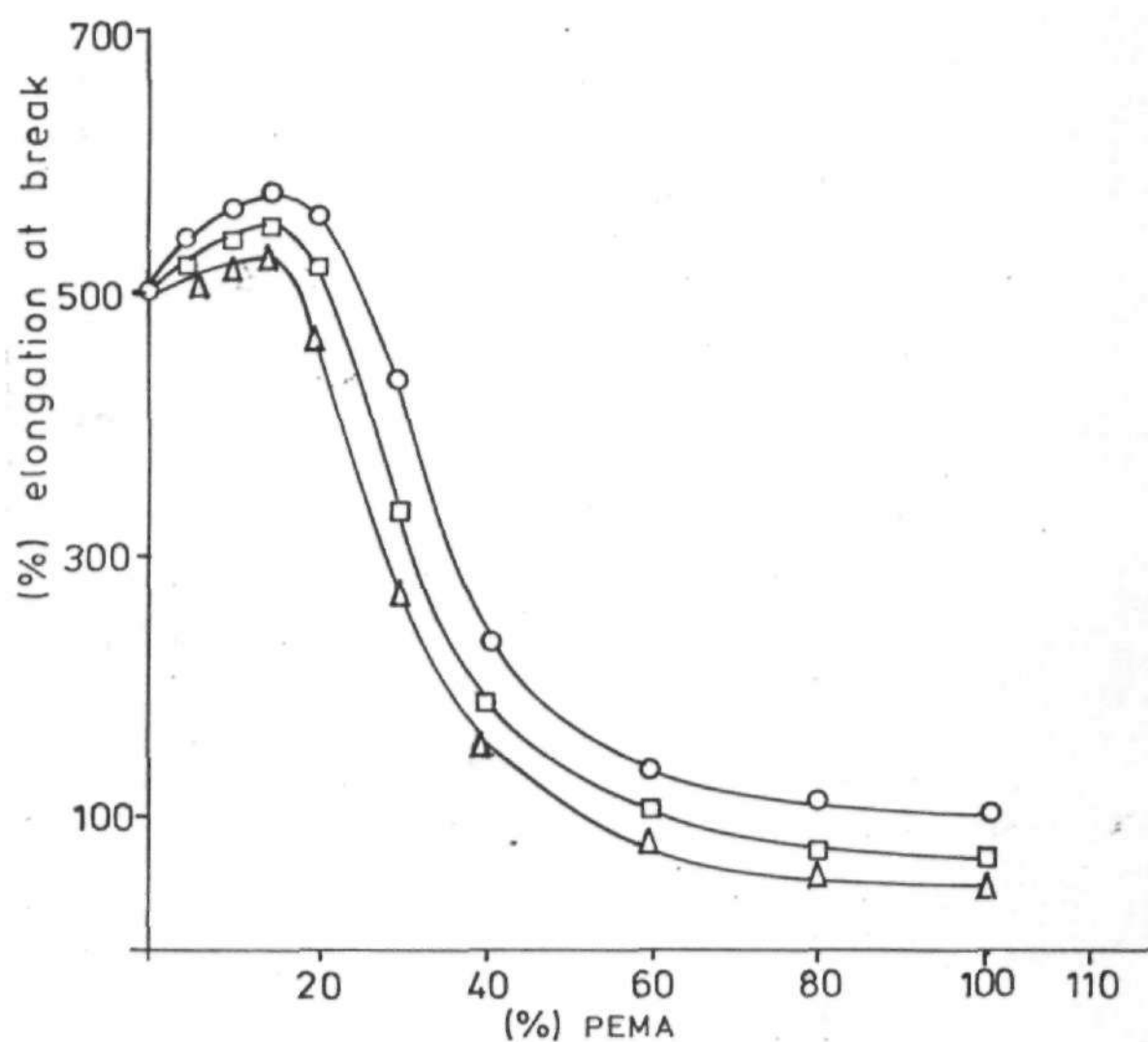


Fig. 3-25 Variation of (%) elongation at break of PVAc/PEMA blend with (%) composition of PEMA
 PVAc ($\bar{M}_v$, 0.721×10^6) (O) PEMA ($\bar{M}_v$, 1.513×10^6)
 (□) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

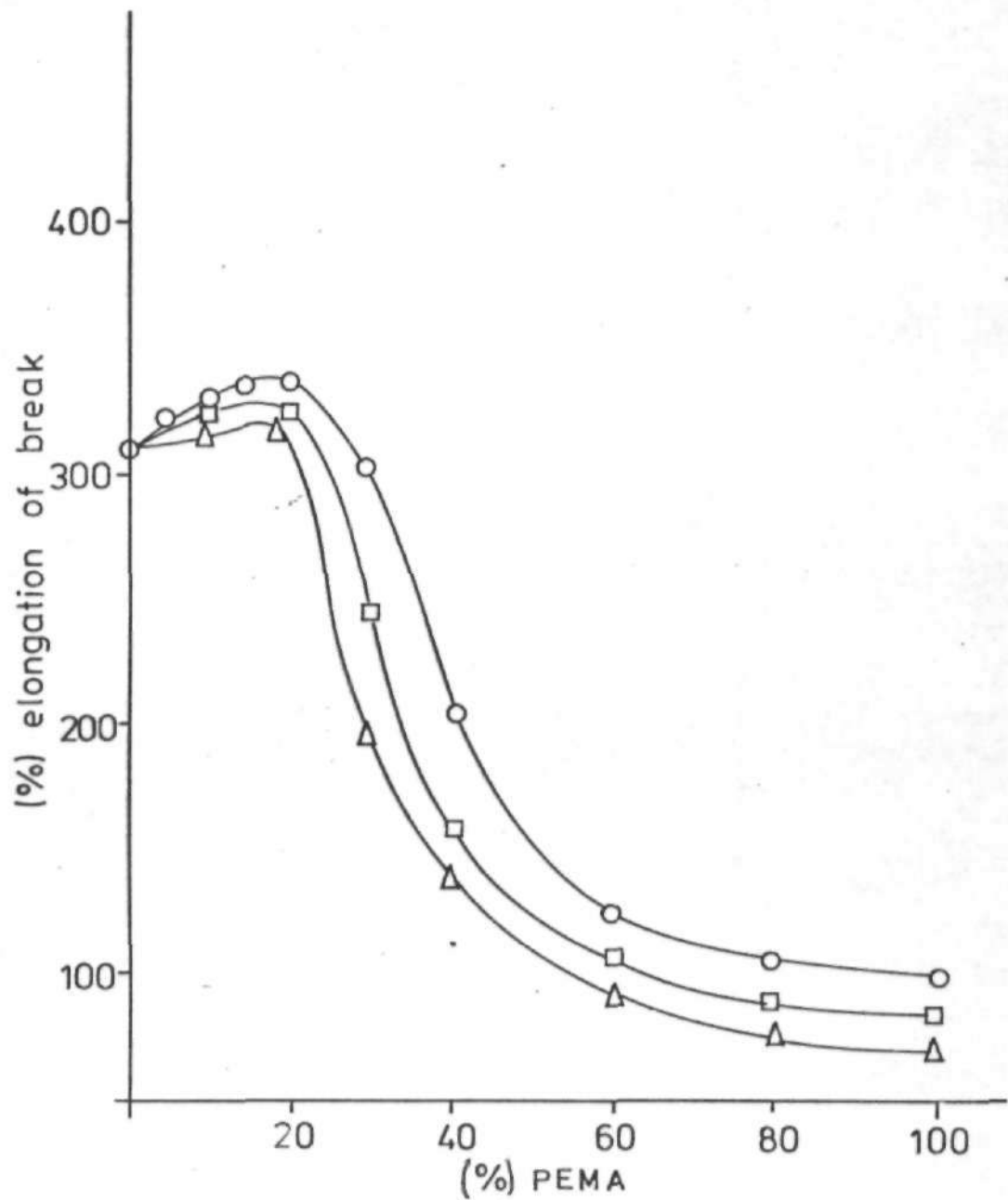


Fig. 3.26 Variation of (%) elongation at break of PVAc/PEMA blend with (%) composition of PEMA
 PVAc ($\bar{M}_v$, 0.570×10^6) (○) PEMA ($\bar{M}_v$, 1.513×10^6)
 (◻) PEMA ($\bar{M}_v$, 3.008×10^6) (Δ) PEMA ($\bar{M}_v$, 3.816×10^6)

Beyond the concentration of PEMA required for peak elongation, the decrease in elongation can be attributed to the fact that there is an increase in the stiffness induced by PEMA on the PVAc. Elongation of a polymer is influenced by the morphology of the polymer (37). Polymers with finer-textured spherulites tend to fail at high elongation after drawing, while those with large, co-ar-se spherulites often fail by brittle fracture at low elongation. Also the decrease in (%) elongation could be due to the fact that straightening of the flexible chains of the polymer could develop rubbery/ brittle strain. This causes a decrease in the stress needed for any deformation (37). From the above explanation, it can thus be concluded that the (%) elongation of a PVAc/PEMA blend decreases with increase in the molecular weight of the PEMA and PVAc present in the blend figures 3.27 and 3.28.

3.4.4 Effect of molecular weight of PVAc and molecular weight ratio (PEMA/PVAc) on the tensile strength, initial modulus and (%) elongation of the PEMA/PVAc blend.

From figure 3.17, the (%)PEMA for maximum mechanical property of blend decreased slightly over a very small range with increase in molecular weight of PVAc, this denotes a shift in maximum or peak in figures 3.13 to 3.25

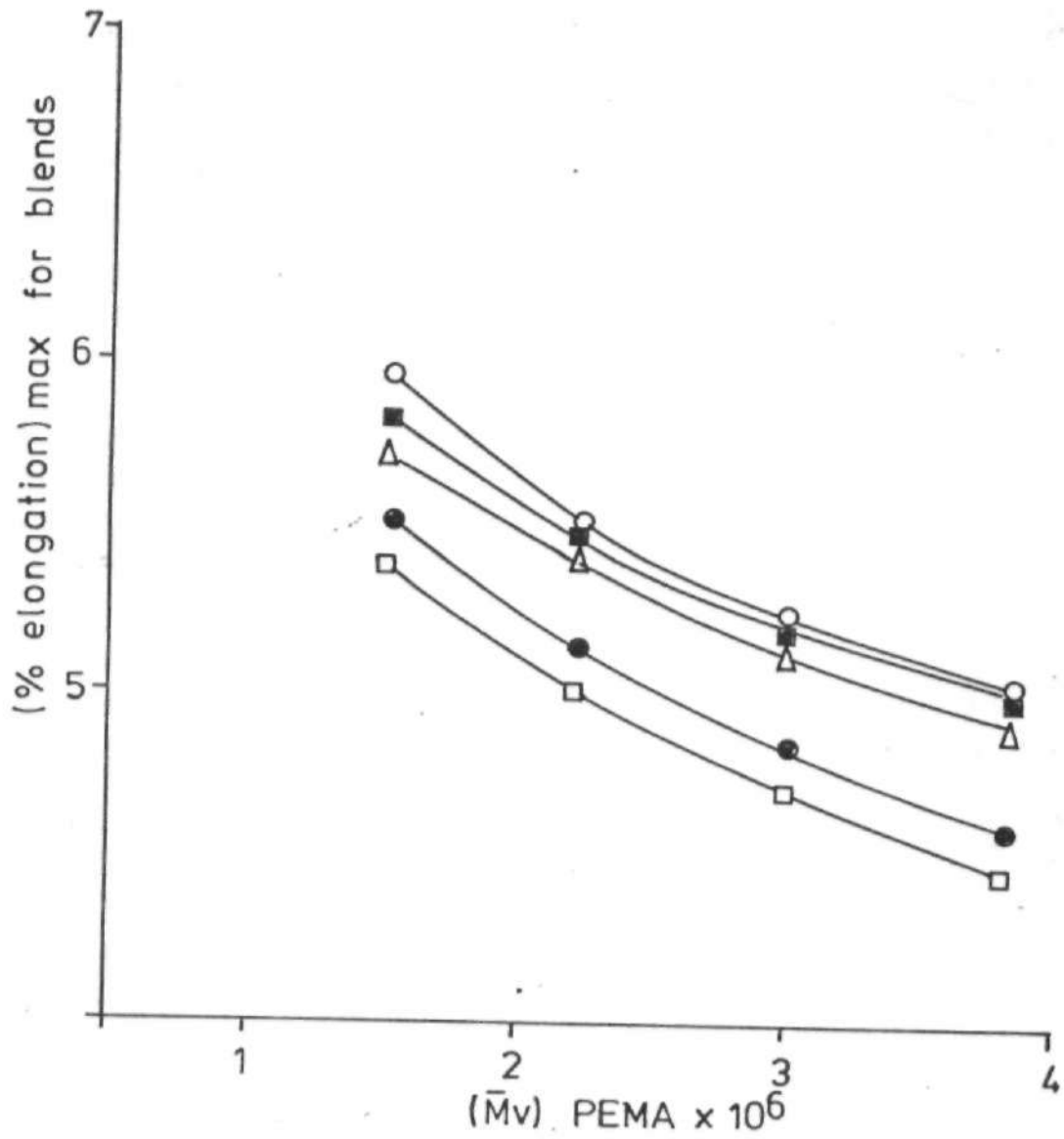


Fig. 3-27 Variation of (% elongation) max with ($\bar{M}_v$) for different ($\bar{M}_v$) of PVAc of
 (o) PVAc ($\bar{M}_v, 0.531 \times 10^6$) (□) PVAc ($\bar{M}_v, 0.570 \times 10^6$)
 (Δ) PVAc ($\bar{M}_v, 0.638 \times 10^6$) (●) PVAc ($\bar{M}_v, 0.721 \times 10^6$)
 (■) PVAc ($\bar{M}_v, 0.745 \times 10^6$)

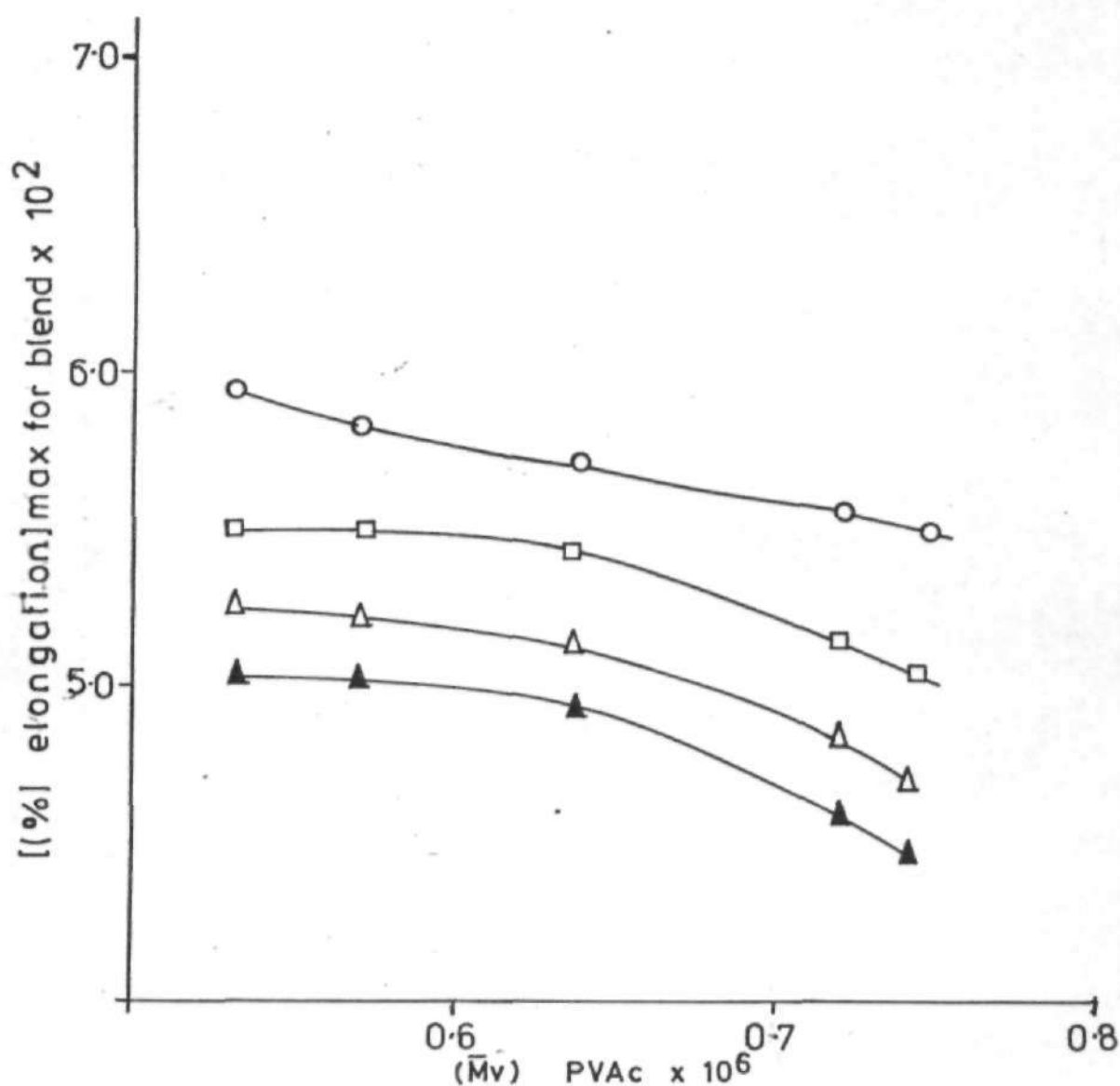


Fig. 3.28 Variation of [(%) elongation] max with ($\bar{M}_v$ of PVAc for different ($\bar{M}_v$) PEMA of:
 (o) PEMA ($\bar{M}_v$, 1.513×10^6) (□) PEMA ($\bar{M}_v$, 2.212×10^6)
 (Δ) PEMA ($\bar{M}_v$, 3.008×10^6) (▲) PEMA ($\bar{M}_v$, 3.816×10^6)

to higher concentration of added PEMA with decrease in the molecular weight of PVAc. This is expected since from Dobry et al's (16), the higher the molecular weight of the polymers, the less compatible, the polymers become and the more the (%) composition of added polymer shifts to lower concentration of PEMA. Kraus and Rollman (56) have also suggested in their work on the effect of block copolymer molecular weight on compatibility that as the block lengths are decreased, transition temperatures of the two polymers become closer, suggesting greater molecular mixing at the interphase.

In the limit of very low molecular weight, homogeneity and the mechanical behavior of random copolymers is approached.

These shifts in maximum or peak point have been observed for all the properties i.e., tensile strength, initial modulus, and (%) elongation. The curves in figure 3.17 shows some differences at big molecular weight of PVAc for tensile strength and initial modulus when compared, while (%) elongation at break agrees with tensile strength results. This difference in tensile strength and initial modulus at high molecular weight PVAc may be explained as due to some molecular interactions which is not common to both properties at higher ($\bar{M}_v$).

From the above explanations, it can thus be concluded that lower molecular weight PVAc accommodates PEMA better than the higher molecular weight samples. Also blending of PEMA with PVAc produces improved properties in the two composite polymers, the size of which increases as $(\bar{M}_v)$ of PVAc decreases.

The molecular weight ratio of the PEMA and PVAc samples play an important role in the limit of phase separation between the polymers.

From figures 3.29, 3.30 and 3.31, the plot of mechanical properties corresponding to peak versus the molecular weight ratios of PEMA to PVAc, $(\bar{M}_v)r$, it was observed that the curves for PEMA samples with $(\bar{M}_v)$ of 1.513×10^6 , 2.212×10^6 and 3.008×10^6 have the same tangent which meets the straight line for PEMA with $(\bar{M}_v)$ of 3.816×10^6 at $(\bar{M}_v)r$ of about 4.85. This 4.85 molecular weight ratio may therefore be taken as a critical molecular weight ratio of PEMA/PVAc after which the mechanical properties increase linearly with increase in the molecular weight ratio of the polymers.

The two straight lines that intersect at $(\bar{M}_v)r$ of 4.85 can be described by the two corresponding calculated equations:-

$$(T.S)_{\max} = (TS)_1^* + L_1 (\bar{M}_v)r \quad \dots(3-3)$$

$$\text{and } (T.S)_{\max} = (TS)_2^* + L_2 (\bar{M}_v)r \quad \dots(3.4)$$

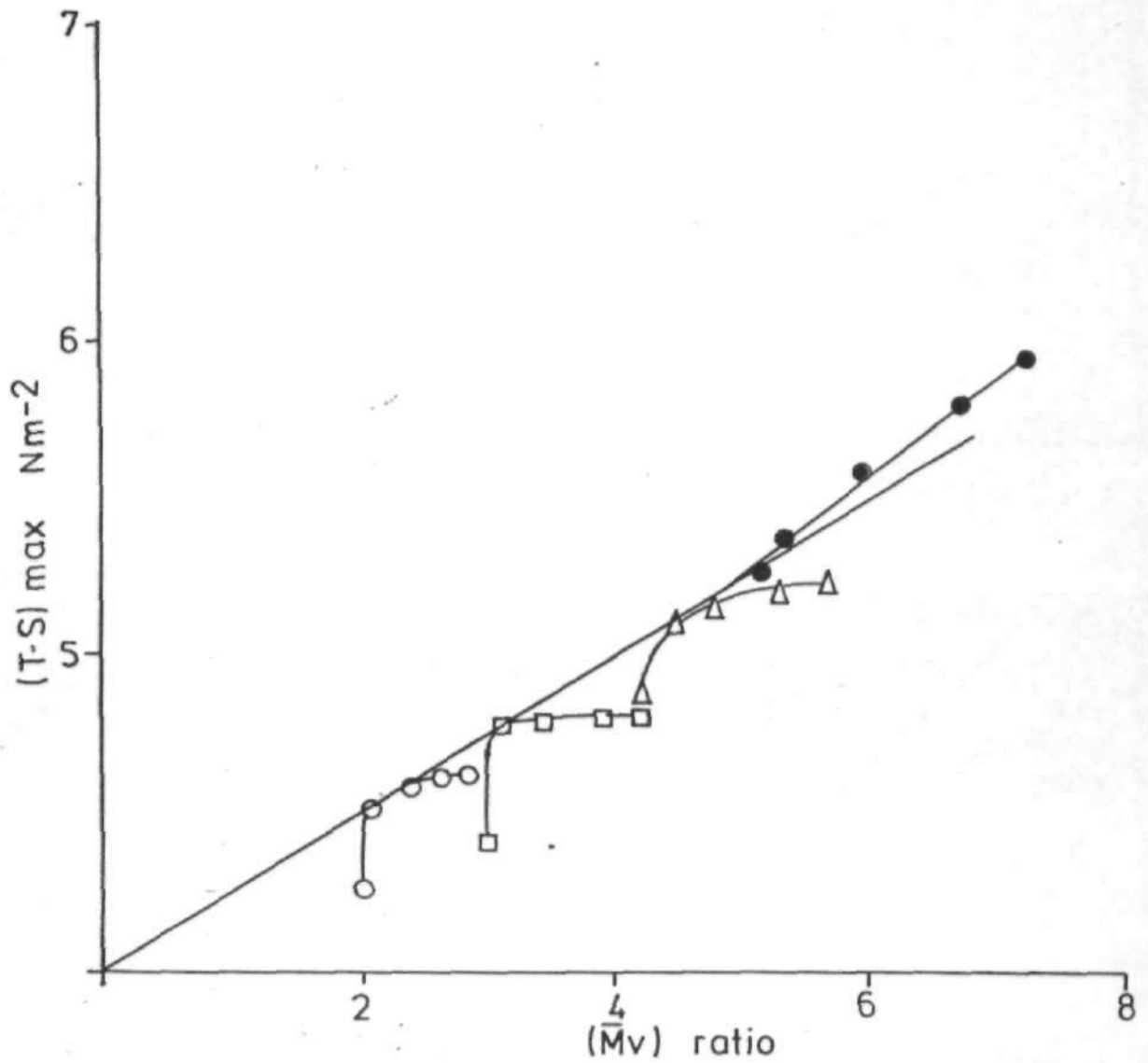


Fig 3.29 The dependence of $(T.S)_{\max}$ of PEMA/PVAc blends on $(\bar{M}_v)$ ratio

(○) PEMA $(\bar{M}_v, 1.513 \times 10^6)$ (□) PEMA $(\bar{M}_v, 2.212 \times 10^6)$
 (△) PEMA $(\bar{M}_v, 3.008 \times 10^6)$ (●) PEMA $(\bar{M}_v, 3.816 \times 10^6)$

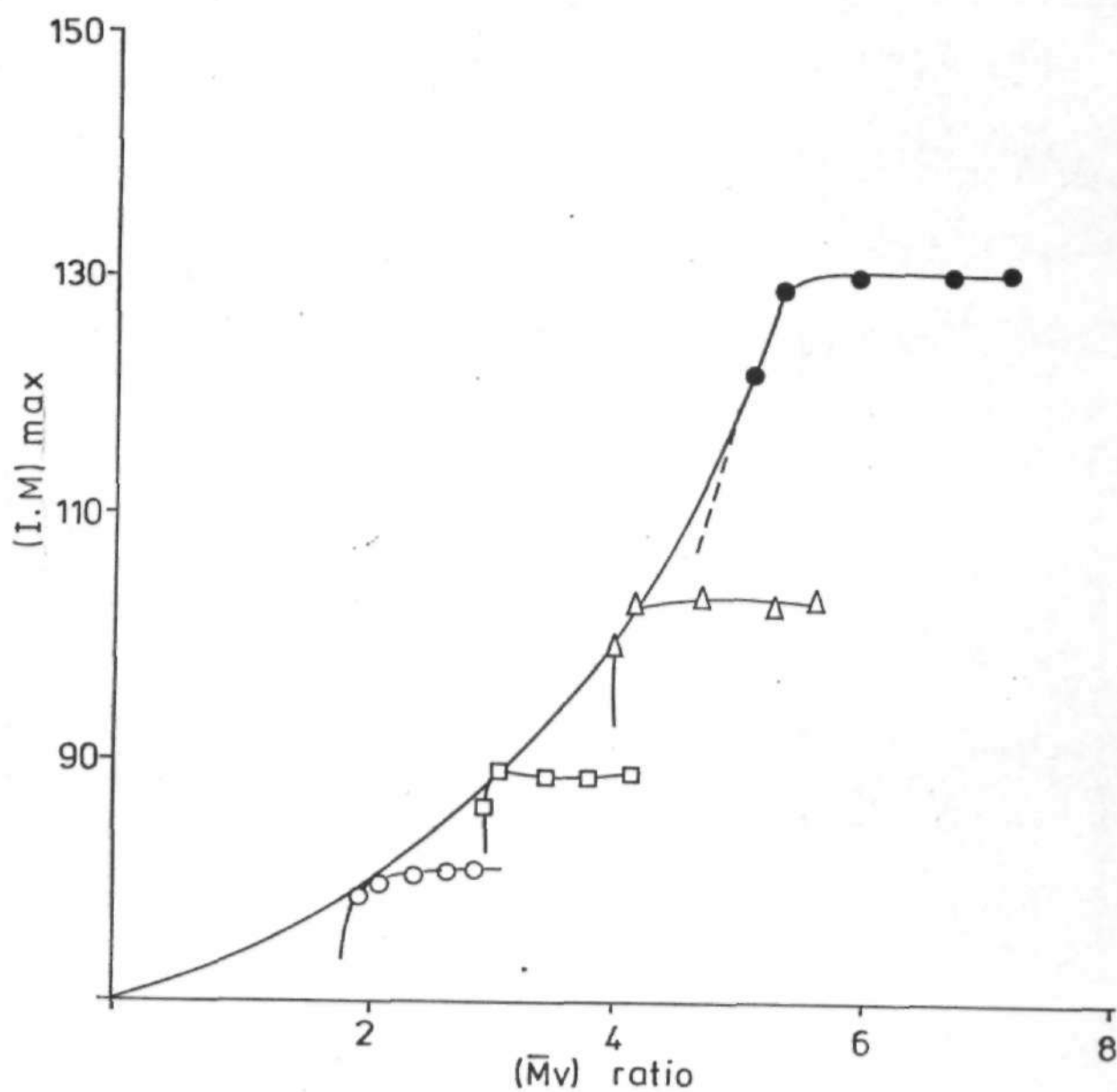


Fig. 3.30 The dependence of (I.M) max of PEMA/PVAc blends on ($\bar{M}_v$) ratio:
 (○) PEMA ($\bar{M}_v$ 1.512×10^6) (□) PEMA ($\bar{M}_v$ 2.212×10^6)
 (△) PEMA ($\bar{M}_v$ 3.008×10^6) (●) PEMA ($\bar{M}_v$ 3.816×10^6)

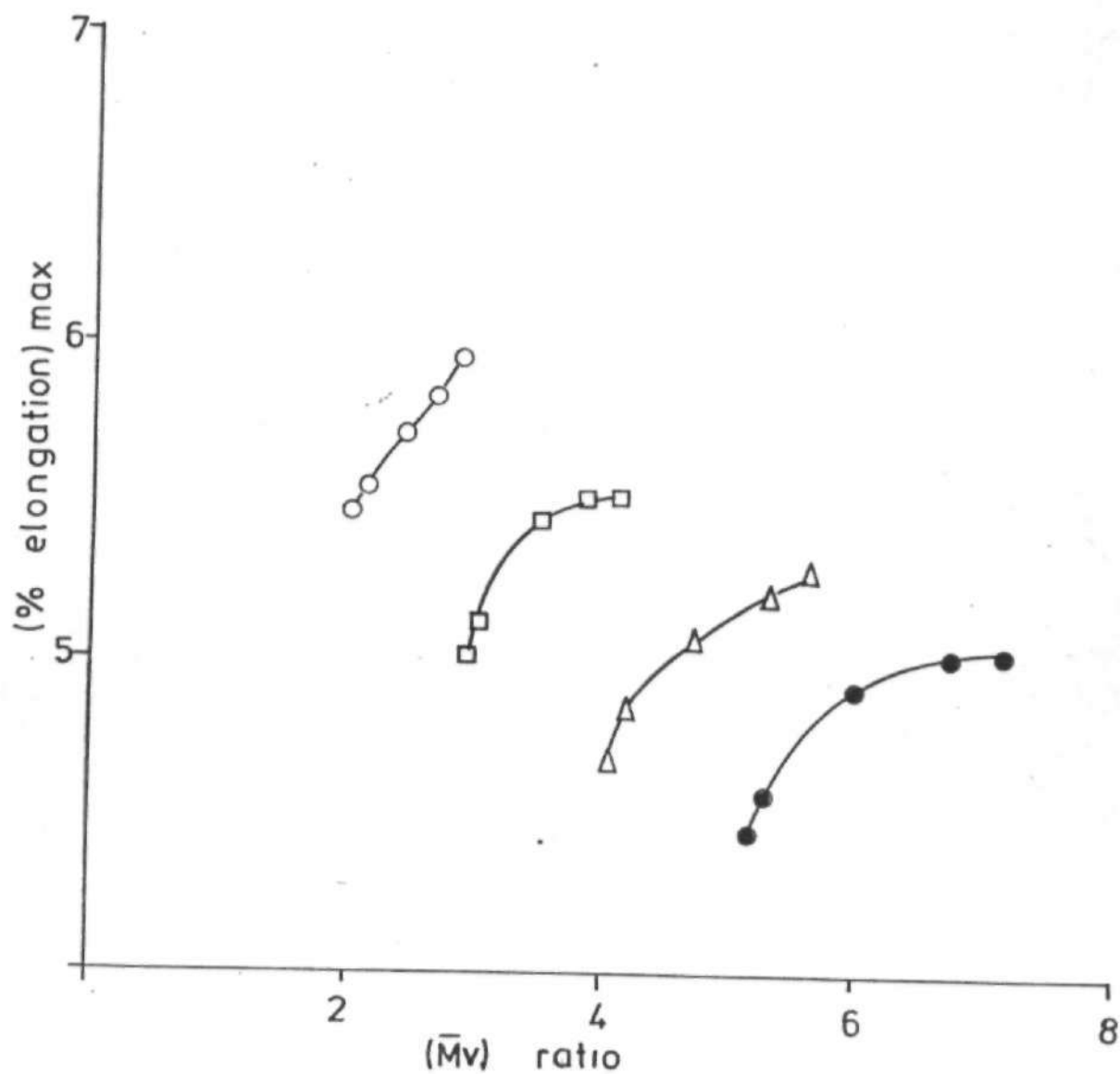


Fig. 3.31 The dependence of (% elongation) max of PVAc/PEMA blends on ($\bar{M}_v$) ratio

(O) PEMA ($\bar{M}_v$, 1.513×10^6) (□) PEMA ($\bar{M}_v$, 2.212×10^6)
 (Δ) PEMA ($\bar{M}_v$, 3.008×10^6) (●) PEMA ($\bar{M}_v$, 3.816×10^6)

where the (3-3) describes the line that is a common tangent to the three curves at the lower $(\bar{M}_v)_{\text{PEMA}}$ values, and (3-4) represents the straight line for the highest $(\bar{M}_v)_{\text{PEMA}}$ sample. In equations (3-3) and (3-4), $(TS)_{\text{max}}$ is the tensile strength at peak, while $(TS)^*$, and $(TS)_2^*$ are the maximum tensile strength values for $(\bar{M}_v)_r$ equals zero, for the two lines respectively and are 4.011 and $3.720 \times 10^4 \text{ Nm}^{-2}$ respectively, while L_1 and L_2 are the slopes of the two straight lines and are 0.255 and 0.312 respectively.

At the point where the two lines meet,

$$(TS)_1^* + L_1(\bar{M}_v)_{rc} = (TS)_2^* + L_2(\bar{M}_v)_{rc} \quad \dots(3-5)$$

Here $(\bar{M})_{rc}$ is therefore the point of intersection and by calculation from (3-5) is equal to 4.91 .

Figure 3.29 can be seen to contain a range of $(\bar{M}_v)_r$ values showing an anomalous behavior, corresponding to equation (3-4), up to $(\bar{M}_v)_r = (\bar{M}_v)_{rc}$, revealing much bigger improvement to (TS) of the PVAc/PEMA blend than anticipated, at least on the basis of equation (3-4).

Whether equation (3-4) would continue to be applicable at very high values of $(\bar{M}_v)_r$ is not known. Results of MFI study however suggest that at about $(\bar{M}_v)_r < 10$ there might not be any improvement to the MFI of FVAc on blending with PEMA.

It can thus be concluded from the above discussions that to obtain blends of PEMA and PVAc of excellent mechanical properties the molecular weight ratio $(\bar{M}_v)_r$ must be as large as possible with molecular weight of PVAc as small as possible. Thus at very high molecular weight ratio, it may be possible for one of the polymers to dissolve in the other, thereby forming a completely miscible polymer mixture. Also a situation could be reached where PEMA dissolves in oligomers, dimers etc of vinylacetate. Actually PEMA dissolves in VAc, so does PVAc in EMA. However, dissolution of PEMA in VAc is assessed to be faster than PVAc in EMA. Hence it is better to consider high molecular weight PEMA blending with low molecular weight PVAc, the latter acting as a dispersant for the former.

TABLE 3.9

The dependence of $(T.S)_{\max}$ of PEMA/IVAc blends
on $(\bar{M}_v)_r$.

$\frac{PVAc}{(\bar{M}_v) \times 10^6}$	0.531	0.570	0.638	0.721	0.745
$(\bar{M}_v)_{PEMA} = 1.513 \times 10^6$					
$(\bar{M}_v)_r$	2.85	2.65	2.40	2.12	2.06
$(T.S)_{\max}$	4.60	4.60	4.59	4.48	4.25
$(\bar{M}_v)_{PEMA} = 2.212 \times 10^6$					
$(\bar{M}_v)_r$	4.17	3.83	3.49	3.07	2.97
$(T.S)_{\max}$	4.81	4.82	4.78	4.72	4.41
$(\bar{M}_v)_{PEMA} = 3.008 \times 10^6$					
$(\bar{M}_v)_r$	5.67	5.28	4.72	4.17	4.04
$(T.S)_{\max}$	5.22	5.20	5.12	4.88	4.70
$(\bar{M}_v)_{PEMA} = 3.816 \times 10^6$					
$(\bar{M}_v)_r$	7.19	6.70	5.98	5.29	5.12
$(T.S)_{\max}$	5.94	5.80	5.60	5.35	5.25

TABLE 3.10

The dependence of $(I.M)_{\max}$ of PEMA/PVAc blends
on $(\bar{M}_v)_r$ ratio.

PVAc $(\bar{M}_v) \times 10^6$	0.531	0.570	0.638	0.721	0.745
$(\bar{M}_v)_{\text{PEMA}} = 1.513 \times 10^6$					
$(\bar{M}_v)_r$	2.85	2.65	2.40	2.12	2.06
$(I.M)_{\max}$	81.00	80.00	80.70	80.00	79.00
$(\bar{M}_v)_{\text{PEMA}} = 1.212 \times 10^6$					
$(\bar{M}_v)_r$	4.17	3.83	3.49	3.07	2.97
$(I.M)_{\max}$	89.50	88.50	88.50	89.00	86.50
$(\bar{M}_v)_{\text{PEMA}} = 3.008 \times 10^6$					
$(\bar{M}_v)_r$	5.67	5.28	4.72	4.17	4.04
$(I.M)_{\max}$	103.00	102.00	103.50	103.00	99.0
$(\bar{M}_v)_{\text{PEMA}} = 3.816 \times 10^6$					
$(\bar{M}_v)_r$	7.19	6.70	5.98	5.29	5.12
$(I.M)_{\max}$	130.00	130.00	130.00	129.00	122.00

TABLE 3.11

The dependence of (%) elongation maximum of
PEMA/FVAc blends on $(\bar{M}_v)_r$.

	PVAc $(\bar{M}_v) \times 10^{-6}$				
	0.531	0.570	0.638	0.721	0
$(\bar{M}_v)_{PEMA} = 1.513 \times 10^6$					
$(\bar{M}_v)_r$	2.85	2.65	2.40	2.12	2.06
$((\%) \text{ elongation})_{\max} \times 10^2$	5.95	5.83	5.70	5.54	5.48
$(\bar{M}_v)_{PEMA} = 2.212 \times 10^6$					
$(\bar{M}_v)_r$	4.17	3.83	3.49	3.07	2.97
$((\%) \text{ elongation})_{\max} \times 10^2$	5.50	5.50	5.43	5.12	5.05
$(\bar{M}_v)_{PEMA} = 3.008 \times 10^6$					
$(\bar{M}_v)_t$	5.67	5.28	4.72	4.17	4.04
$((\%) \text{ elongation})_{\max} \times 10^2$	5.25	5.20	5.11	4.82	4.68
$(\bar{M}_v)_{\max} = 3.816 \times 10^6$					
$(\bar{M}_v)_r$	7.19	6.70	5.98	5.29	5.12
$((\%) \text{ elongation})_{\max} \times 10^2$	5.02	5.02	4.90	4.57	4.44

3.5 OPTICAL MICROSCOPY.

Optical microscopy, Electron microscopy and phase contrast microscopy have been widely used in polymer-polymer studies. Several polymer-polymer systems of reported miscibility have been shown to contain domains by using the electron microscope (21).

In the present study, Optical microscopy has been used to detect and characterise the different polymer phases present in the polymer blends.

Thin polymer films of blends were produced from solution mixtures of PVAc and PEMA at selected percentage compositions. The thickness of these films are about 0.010cm. The films were supported on a camera mounted in a microscope for optical microscopy observation.

Plates 1 to 6 show that optical micrograph of polyethylmethacrylate of ($\bar{M}_v$), 1.513×10^6 polyvinyl acetate of ($\bar{M}_v$), 0.745×10^6 and their blends.

Plates 1 to 6 indicate changes in the morphology of the polymers or their blends as the composition changed from pure PVAc to pure PEMA. The morphology of the blends is characterized at some point by a high level of phase interconnection in both the minor and major phases, a structure which could possess some rather unusual mechanical characteristics (21).

Plate 2 represents the blend containing about 17% PEMA, which gave the peak observed in the property composition curves (Fig. 3.14). The micrograph shows an almost homogeneous blend with some rigdes developing, this may be due to the strong interaction between PEMA and PVAc, i.e. the latter coating the former.

Plate 3 represents the micrograph for 30% PEMA in the blend. It shows the development of another phase which is probably the PEMA phase since the continous phase is the PVAc.

Plate 4 is the micrograph for 55% PEMA in the blend. Here the two phases are distinct with the PVAc domain having an occluded PEMA structure.

Plate 5 is the micrograph for 80% PEMA in the blend, it shows the movement of PVAc in a stream of the continous PEMA phase with independent interaction between them as observed in the tensile strength measurements.

Plate 6 represents the micrograph for the 100% PEMA.

Plate 7 shows the micrograph corresponding to 10% PEMA in the blend.

Plate 8 is the micrograph corresponding to 20% PEMA in the blend. This (%) PEMA composition gave a blend revealing antagonism in the tensile strength test

(Fig. 3.14). It shows the two polymers well separated from one another.

Plate 9 is the micrograph for blend of 50% PEMA. It shows the flow of one polymer in the continuous phase of the other. The bands might be PEMA flowing in continuous phase of PVAc.

Optical micrograph of PVAc ($\bar{M}_v$) of 0.745×10^6
PEMA ($\bar{M}_v$) 3.816×10^6 and their blends.

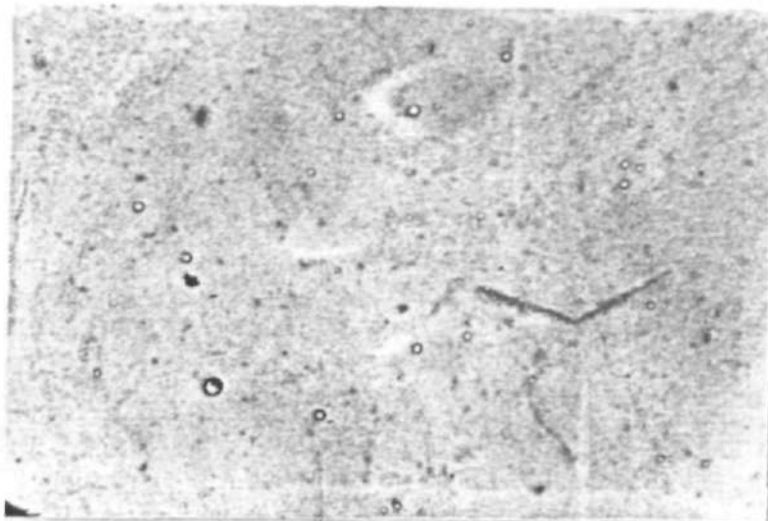


Plate 1
100% PVAc

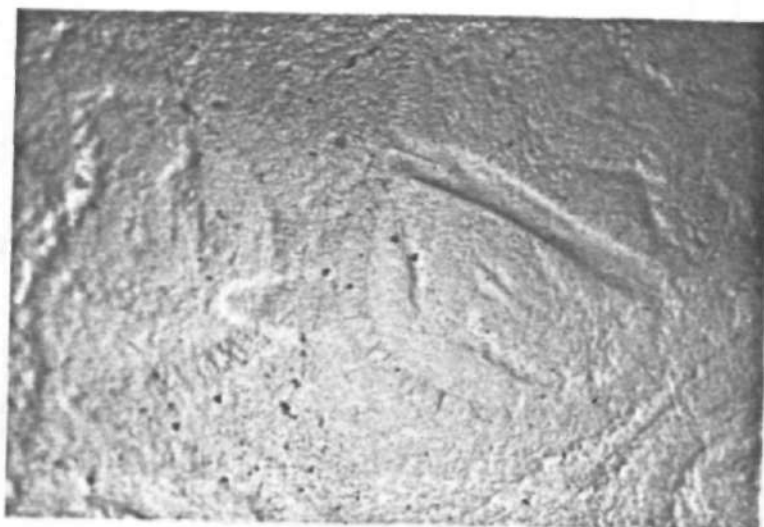


Plate 2
17% PEMA

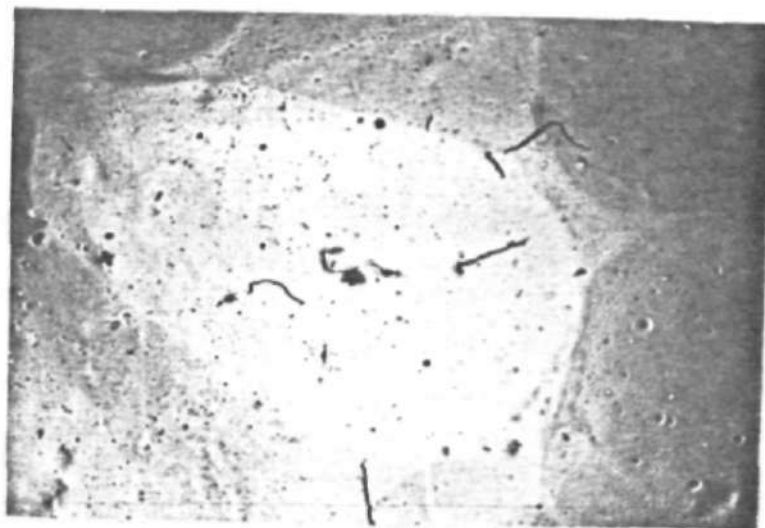


Plate 3
30% PEMA

Optical micrograph of PVAc ($\bar{M}_v$) of 0.745×10^6 ,
PEMA ($\bar{M}_v$) of 3.816×10^6 and their blends.

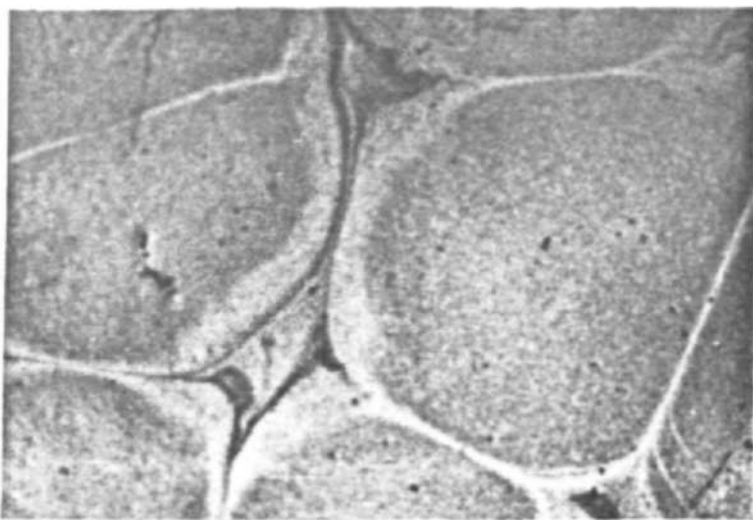


Plate 4

55% PEMA



Plate 5

80% PEMA

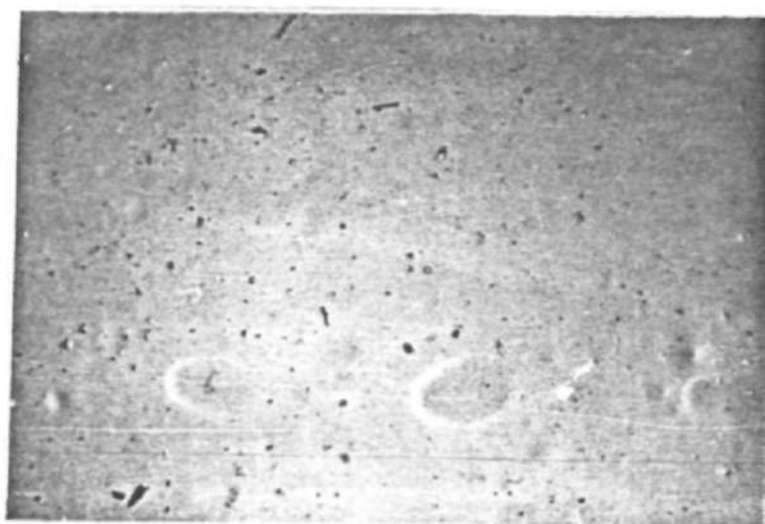


Plate 6

100% PEMA

Optical micrograph of blends of PVAc ($\bar{M}_v$) of 0.745×10^6
with PEMA ($\bar{M}_v$) of 1.513×10^6 .

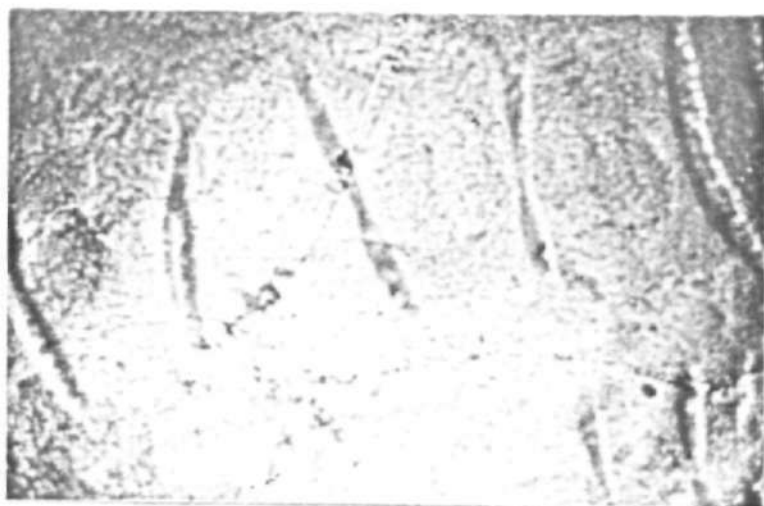


Plate 7
10% PEMA

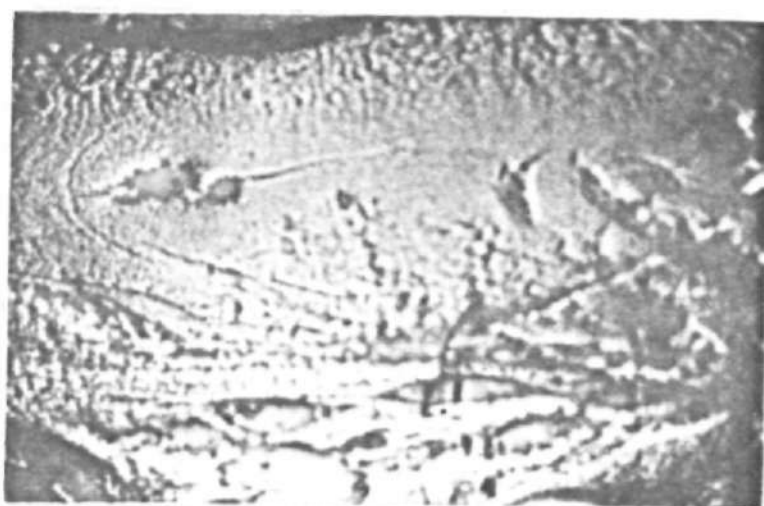


Plate 8
20% PEMA

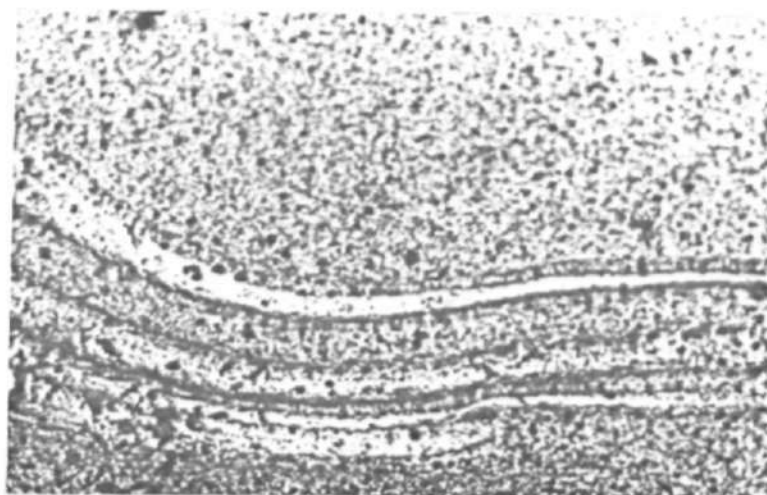


Plate 9
50% PEMA

CHAPTER FOUR

4.0

CONCLUSION AND RECOMMENDATION

The work reported in this present study proves that there is an evidence of synergistic behavior in the blends of Poly vinyl acetate and Poly ethyl methacrylate. This behavior was observed in the dilute solution viscosity study, melt flow index measurements, tensile mechanical property studies.

The range of synergistic behavior is below a certain percentage of PEMA. In all the studies considered here, there is an optimum possibility for highest value of properties when compared with the properties of the pure polymers as observed in the optical microscopy study.

There is also an evidence of antagonistic behavior between the PEMA and PVAc at very low molecular weight ratio and above about 20% PEMA composition. This effect is reflected in the optical microscopy study where the plate at 20% PEMA composition shows onset of phase separation between the polymers.

The two polymers have been found to be compatible to a reasonable extent. The extent of compatibility is determined by the molecular weight ratio. It increases with increase in the molecular weight ratio and a decrease in the (%) composition of PEMA.

There is also a tendency for a binodal as observed in the dilute solution viscosity measurement. The appearance of the binodal tends to a higher (%) composition of PEMA.

Evidence also shows that the molecular weight ratio is very important in the blending of PEMA and PVAc. From MFI measurements and the tensile mechanical property test of the blends, the range of the molecular weight ratio of PVAc and PEMA to give improved properties of PVAc by PEMA is given as

$$9.8 \geq (\bar{M}_v)_r \geq 4.8.$$

Improvement to properties of the various polymers suggests that there seems to be a specific interaction between the polymers. Self interaction may be due to PVAc with PEMA intramolecular interaction, it could also be due to PVAc and PEMA intermolecular interactions, while antagonistic behavior of the polymers will arise from intramolecular interaction of either of PEMA or PVAc thus leading to phase separation. Also the type of interaction between the polymers in the dilute solution viscosity study may be affected by the polymer-solvent interaction which competes with the polymer-polymer interaction.

Also the bulky ethyl acetate side group in PEMA play an effective role in the type of interaction it has with PVAc. Thus the higher the molecular weight of PEMA, the more the steric hindrance of the larger ethyl group in PEMA on PVAc and the smaller the concentration of PEMA for high improvement to the properties.

4.4 RECOMMENDATION

The points has been made for the possibility of of a binodal especially in the dilute solution viscosity study and tensile mechanical study of the PVAc and PEMA blends. This is worth looking into as an extension of this work and that require very high molecular weight ratio of the polymers and may involve fractionation of the two polymers so as to be able to have very high molecular weight PEMA and very low molecular weight PVAc to blend together.

The dependence of the life of blends of various compositions of PEMA and molecular weight ratio should be critically examined. It is also worth establishing the types of interactions that exist in the blends.

The technological implications of the results of these studies should also be looked into.

REFERENCES

1. Krause, S., Polyme - Polymer Compatibility in polymer blends (edited by D.R. Paul and Seymour Newman) Vol. 1 Academic Press, New York (1978).
2. Ambrose, R.J and Aggarwal, S.L., Advances in preparation and characterisation of multiphase polymer systems. An Interscience Publication. Pg. 189, 1977.
3. Brydson, J.A., "Plastic Materials" Third Edition, Newnes - Butternorths, London, 1975.
4. Krause, S. J. Macromol. Sci. 1972, C7, 251.
5. Olayemi, J.Y. and Oniyangi, M.A., J. Appl. Polym. Sci., 1981, 26, 4059.
6. Singh, Y.P. and Singh, R.P., Eur. polym. J., 1983, 19, 535.
7. Kuleznev, V.N., J. Colloid (USSR) 1965, 27, 459.
8. Kuleznev, V.N., Kolloid Zh, 1975, 37, 267.
9. Kuleznev, V.N. and Melnikova, O.L., Eur. Polym. J. 1978, 14, 455.
10. Hourston, D.J. and Hughes, I.D. Polymer, 1978, 19, 1181.
11. Shen, M. and Kawai, H., A.I. Chem. E.J., 1978, 24, 1.
12. Fettes, E.M. and Macley, W.N., Perspectives in polyblends (in polymer modification of Rubbers and Plastics) Henno Keskula (ed) Applied polymer Symposia, Interscience Publisher 1967.

13. Smith, K.L. and Winslow, A.E., Ind. Eng. Chem., 1959, 51, 1361.
14. Hsu, P., Macromolecules, 1974, 7, 320.
15. Scott, R.L., J. Chem. Phys. 1949, 17, 279.
16. Dobry, A. and Boyer Kawenoski, F., J. Poly. Sci, 1947, 2, 90.
17. Bikales, N.M., Encyclopedia of Poly. Sci. and Tech., 1968, 8, 164.
18. Angier, D.J. and Watson, W.F., J. Polym. Sci., 1955, 13, 129.
19. Kern, R.J., J. Polym. Sci., 1974, 21, 19.
20. Simril, V.M., J. Poly. Sci., 1947, 2, 142.
21. Olabisi, O., Lloyd, M.R., and Shaw, T.M. Polymer-Polymer Miscibility (1979) Acad. Press New York London.
22. Pouchly, J and Biros, J. Polym. Lett., 1969, 7, 463.
23. Olabisi, O. Macromolecules, 1975, 9, 316.
24. Nishi, T. and Wang, T.T., Macromolecules 1975, 8, 909.
25. Imken, R.L., Paul, D.R. and Barlow, J.W., Polym. Eng. Sci. 1976, 16, 593.
26. Gesner, B.D., J. Poly. Sci. 1965, A3, 3825.
27. Yuen, A. and Kisinger, P. Macromolecules, 1974, 7, 329.

28. Brage Golding, Polymers and Resins, D. Vans
Nostrand Company Inc. New York (1959).
29. Nielsen, L.E., "Mechanical Properties of polymers
and Composites Dekker, New York, 1974.
30. Jordan, E.F., Artymyshyn. B. J. Appl. Poly.
Sci. 1976, 20, 2715 - 2757.
31. Jenckel, E. and Herwing. S., Kolloid Zh.,
1956, 148, 57 - 66.
32. Van Oene, H., "Rheology of Polyblends and
dispersion" in Polymer blends (edited by
D.R. Paul and Seymour Newman) Vol. 1.
Acad. Press. New York 1978.
33. Van Oene. H.J. Colloid Interface Sci. 1972.
40, 448.
34. Galimov, E.R. and Ushakova, G. Int. Polym.
Sci. Technol. 1975, 2 T/7.
35. Vogel, I. Practical Organic Chemistry, Pg. 186.
Third Edition Longman Green and Co. Ltd.,
36. Brandrup. J. and Immergut E.H., Polymer Handbook,
second Edition, 1975.
37. Billmeyer, F.W. "Textbook of Polymer Science"
second Edition. John Wiley, New York . 1972.
38. Harkins, W.D. J. Polym. Sci. 1950, 5, 217.
39. Smith, W.V. and Ewart, R.W. J. Chem. Phys.
1948, 16, 592.
40. Bikales, N.M., "Enclopedia of Polymer Science and
Technology", 1968, see "Kinetics of polymerisation",
McGraw-Hill. Inc., New York, 1970, 161.

41. Olayemi, J.Y. and Mosuro, Y. Makromole.
Chem. (In Print) 1983.
42. Carpenter, D.K., "Viscometric Methods" in P.E.
Slade Jr. Ed., Polymer Molecular weights
Part II, Techniques and Methods of Polymer
Evaluation 4 Marcel Dekker, Inc. New York.
43. Friis, N. and Nyhagen, L. J. Appl. Poly. Sci.,
1973, 19, 2311.
44. Izumi, Z. and Hinshik, J. Polym. Sci., 1967.
5(A - 1) 455.
45. Bender, B.W., J. Appl. Poly. Sci. 1965. 9.
2887.
46. Feldman, D. and Rusu, M. Eur. Poly. J. 1974,
10, 41.
47. Chaffey, J.P., J. Colloid Interface Sci., 1967
24, 285.
48. Masuda, S., Onogi, A. and Ibaragi, T, J. Kollid
Z.Z. Poly. 19.
49. Briston J.H., "Plastics Films" Published for the
Plastic Institute, 1974.
50. Cooper, L. Strucert, "Muliphase Polymers",
Advances in Chemistry Series, 1978.
51. Kambour, R.F., J. Poly. Sci. (Macromole. Rev.),
1973, 7, 1.
52. Brage. G., Polymers and Resins. C.D. Vans.
Nostrand Company Inc.) New York. 1969.
53. Shur, Y.J. and Ranby, B. J. Appl. Poly. Sci.,
1975. 19, 1337.
54. Reznikova, V. J. Colloid (USSR), 1953, 15, 111.
55. Reznikova, J. Colloid (USSR), 1954, 16, 207.
56. Kraus. G. and Rollman, K. J. Polym. Sci.,
Polym. Phys. Edition 1976, 14, 1133.