

Modification of the Physical, Mechanical, and Thermal Properties of Poly(vinyl chloride) by Blending with Poly(ethyl methacrylate)

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) with different ratio of poly(ethyl methacrylate) were characterized with respect to their physical, mechanical, thermal, and morphological properties. The blends indicated a gradual rise in the modulus and ultimate tensile strength values followed by a reduction in the percent elongation at break and toughness values after an initial rise compared to the base reference compound PVC. The effect of composition of the PVC–PEMA blends on the thermal stability was investigated. Differential scanning calorimetric curves of the blends showed an inward shift of the PVC glass transition temperature and an upward shift in the degradation temperature. The thermomechanical analysis results also indicated thermal stabil-

ity over unmodified base reference compound PVC from the softening characteristics of the different samples under study. The biphasic cocontinuous systems as explicit from the scanning electron and optical micrographs supported phase-mixing at the initial stages with subsequent phasing out tendency with increasing percentage of PEMA incorporation. The thermomechanical parameters are in conformity to their mechanicals, which have been further supported by their morphological studies. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1377–1384, 2007

Key words: blends; mechanical properties; poly(vinyl chloride); thermal properties; differential scanning calorimetry

INTRODUCTION

Poly(vinyl chloride) (PVC) belongs to a major class of engineering plastics that possess many unique properties that are suitable for a wide variety of technical and industrial products. It is available at a relatively low cost, is nonflammable, and has good chemical and corrosion resistances.^{1,2} This study aims at the synthesis and characterization of poly(vinyl chloride) (PVC)/poly(ethyl methacrylate) (PEMA) blends in varying composition ratio and a comparative study of them with respect to the base reference unmodified PVC compound. It has been shown previously that the carbonyl group of the methacrylate ester moieties of PEMA acts as an electron donor and the α -hydrogen of PVC as an electron acceptor that facilitates dipole–dipole interaction between the two thus resulting in close packing of the molecules.² This is expected to produce a measurable effect on the various mechanical properties such as Young's modulus, ultimate tensile strength, toughness, and on the physical properties such as hardness and specific gravity.^{3,4}

Homopolymer PVC has a rather poor thermal stability. It starts degrading above glass transition temperature by initiation (random at normal repeat units and structural defects) followed by fast zip elimination of HCl and at the same time, formation of conjugated double bonds (polyenes) in the backbone of the polymer. PEMA is supposed to produce thermal stability when present within the system by scavenging the chloride radicals immediately as they are formed.^{5,6} Thus, the thermal analysis of the system under consideration is expected to modify influences over unmodified PVC, which also reveals some significant features in interpreting the morphology.^{7,8}

EXPERIMENTAL

Materials

PVC (Reon, *K* value 67) from M/s Reliance Industries, Mumbai, India, was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulfate (TBLS) from M/s Kalpana Industries (Daman, India) were used as suitable plasticizers and stabilizers, respectively. EMA from Berger Paints of India (India) was purified by washing first with 2% aqueous sodium hydroxide (NaOH) solution and then by thorough and repeated washing with distilled water (to make alkali free as

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tested by litmus paper) and dried over fused calcium chloride (CaCl_2). It was finally vacuum-distilled. Benzoyl peroxide (Bz_2O_2) from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as an initiator for acrylic polymerization.

Synthesis of blends

A weighed amount of purified EMA was taken in a test tube and thoroughly mixed with 2 wt % (based on EMA) of recrystallized Bz_2O_2 . PVC resin was weighed such that a predetermined ratio with respect to the monomer as weighed earlier was just made. The resin was taken in an air tight dry blender and mixed with 30 parts of DOP and 2 parts of TBLS with respect to the amount of PVC resin taken. The initiator-containing monomer was then added to the premix of PVC along with plasticizer and stabilizer. Dry mixing was further continued unless a thoroughly mixed blend of PVC and monomer was obtained. The mix was then compression molded into sheet by subjecting a three-piece mold under pressure and heat in two stages.

Initially, the mold was compressed under a pressure of 15 ton cm^{-2} at temperature 80°C to initiate and propagate the acrylic polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160°C while the pressure was maintained at the same level. This condition was maintained for 5 min to ensure complete and homogeneous sintering of PVC and acrylic polymerization as well. The whole combination was kept in an oven at 100°C for further 20 min to ensure complete polymerization of residual EMA if any. The mold was then allowed to cool down to room temperature and the molded sheet ejected.

Measurements

Tensile properties

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties such as ultimate tensile strength (UTS), percent elongation at break (% EB), modulus, and toughness. ASTM D638 method was followed. A crosshead speed of 3 mm min^{-1} was maintained. All testings were carried out at room temperature. Toughness of the blend samples was determined from the area under the load versus elongation plot. The samples were visually inspected before measurements and were found to be free from pores or nicks. The data reported were averages of at least six measurements and typical scattering range of the results was $\pm 5\%$.

Fourier transform infrared spectroscopy

The FTIR spectra in the study were recorded on a spectrophotometer from Jasco, Japan, model no.

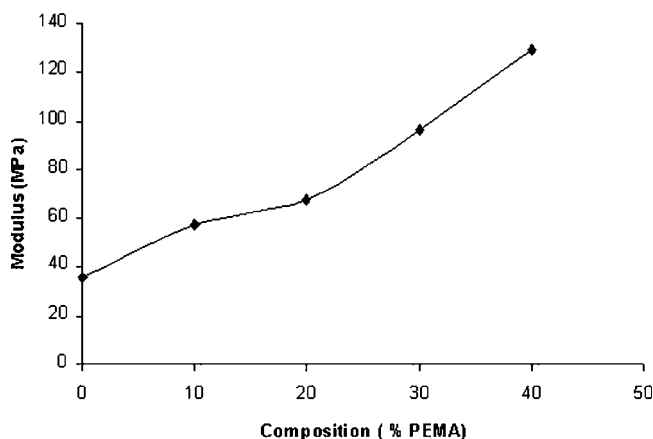


Figure 1 Variation of modulus with blend composition.

FTIR-460 plus. The experiment was carried out under 4 cm^{-1} resolution and scanning speed of 2 mm s^{-1} .

Physical properties

The two physical parameters of the blends namely hardness and specific gravity of the various blends were determined by following the Shore D scale and Archimedes' principle, respectively.

Thermal properties

The thermomechanical analysis of the various samples of PVC (containing plasticizers and stabilizers in proportion in which they are present in all the blends) and its blends with *in situ* formed PEMA were carried out in a TMA apparatus from Shimadzu (model TMA 50) in the presence of oxygen. The thermo-oxidative characteristics were studied under a constant load of 0.008 kg throughout the experiment using a compressive mode of probe up to a temperature limit of 180°C following a temperature program in which a heating rate of $10^\circ\text{C min}^{-1}$ was maintained right from the ambient temperature.

The differential scanning calorimetry (Mettler 822e) of the samples was carried out up to a limit of 350°C at a heating rate of $10^\circ\text{C min}^{-1}$ right from the ambient temperature. The transition behavior above ambient temperature and the temperature ranges of degradation were only studied. The weights of the samples were maintained between 5×10^{-6} and 8×10^{-6} kg.

Morphology

Morphology studies were undertaken in a scanning electron microscope (Model Hitachi S415A) after suitable gold coating on the samples. The fractured surface of a tensile fracture specimen was inspected for bulk morphology. The magnification of the samples was about $500\times$.

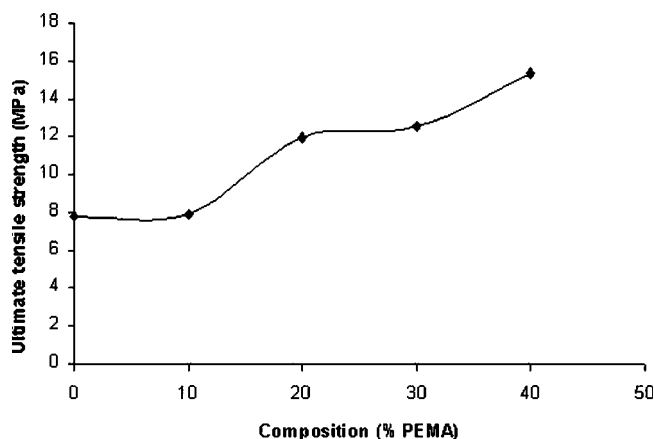


Figure 2 Variation of ultimate tensile strength with blend composition.

The surface morphology for macrophase investigation was however done in a trinocular optical microscope from Kruss (Optromic), Germany, with a magnification of 200 \times . The samples were about 0.5 mm in thickness.

RESULTS AND DISCUSSION

Mechanical properties

Both the modulus and the ultimate tensile strength of the PVC-PEMA blend systems exhibit an increasing trend with increase in the proportions of PEMA in composition as shown in Figures 1 and 2. The modifying influences of the polymethacrylate resin with increase in its content are quite well evidenced from the rise in the mechanical parameters. The improved property of such blends may be attributed to specific interactions like H-bonding and dipole-dipole interactions between molecules of the constituent polymers. It has been suggested that the α -hydrogen of vinyl chloride unit of chain segments

can interact with the ester carboxylate group (H-bond acceptor of the acrylic polymer) to form a hydrogen bond, which is assumed to play a key factor in achieving miscibility and enhanced mechanicals.⁹ The close value of the solubility parameters of PVC and PEMA might also be expected to account for the compatibility and hence enhancement of the properties ($\delta_{\text{PVC}} = 21.46 \text{ MPa}^{1/2}$, $\delta_{\text{PEMA}} = 22.69 \text{ MPa}^{1/2}$).¹⁰ It is interesting to note that both moduli and UTS increase at a steady rate with the increase in PEMA content. The breakdown in chain regularity because of PEMA incorporation appears to be possibly more than compensated by the already mentioned H-bond formation.

A short shift in frequency characteristic of C—Cl dipole can be observed in the IR spectra of our base PVC compound and its blends with PEMA as shown in Figure 3. The typical absorbance because of C—Cl in the base compound at 704 cm^{-1} undergoes a decrease in frequency (693 cm^{-1}) in the blend in presence of methacrylate esters, which may possibly be attributed to a feeble interaction between the C—Cl dipole and the β -hydrogen of the methacrylate esters.

The PVC-PEMA blends exhibit a decrease in the elongation at break and toughness values after an initial rise up to about 10% of PEMA incorporation as explicit from Figures 4 and 5. However, both these mechanicals always lie much above the corresponding values of unmodified plasticized resin (base compound). The inclusion of rigid, hard, and dispersed phase of PEMA provides a number of stress concentrators within the matrix of PVC. PVC undergoes deformation by shear mechanism and therefore produces a ductile response to tensile loading but the degree of ductility depends upon its resistance to crazing, which is much less in PEMA when compared with PVC.^{11,12} In contrast to the mechanism of rubber toughening (rubber itself being

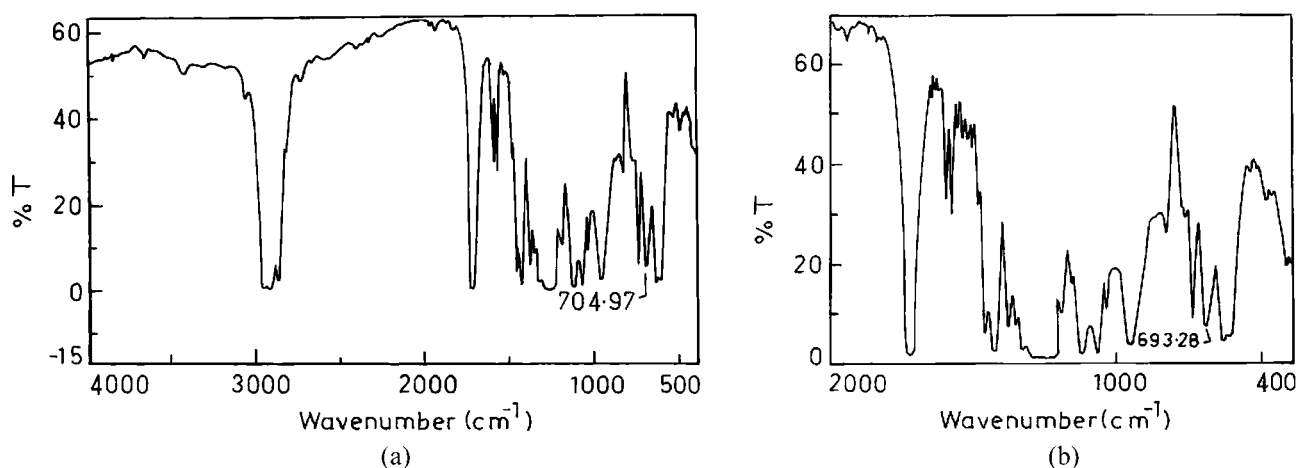


Figure 3 (a) FTIR spectra of base reference compound PVC and (b) FTIR spectra of PVC:PEMA 80:20 blend composition.

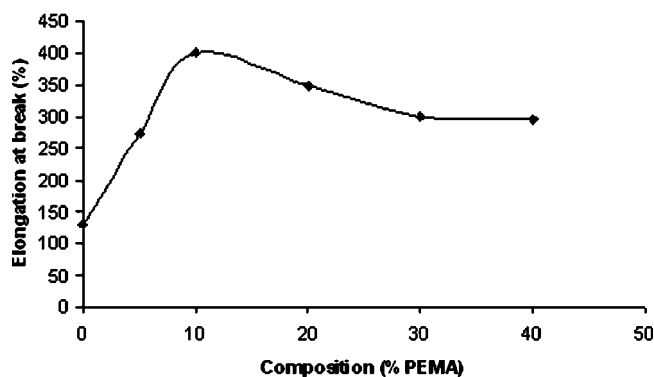


Figure 4 Variation of percent elongation at break with blend composition.

stretchable and capable of absorbing the energy for crack propagation), the *in situ* generated rigid domains of PEMA provide not only a greater path length (path around the periphery of large number of dispersed particles) for the cracks to cover before rupture but also the stress fields to dissipate the energy to propagate.¹³ Thus, more energy is required for propagating the crack and high toughness develops. Moreover, as the path length traversed by a crack increases, the elongation also increases.^{14,15}

Beyond 10% of PEMA incorporation, the elongation at break and toughness results are in conformity to our expectations. The decreasing cocontinuity (a phenomenon, which was observed up to 10% of PEMA incorporation and the coalescing tendency of the stress fields along with the increasing concentration of PEMA decreases the path length for the cracks to propagate and hence the elongation at break and toughness decrease. The decrease in the number of cracks attributed to the increasing sizes of domains because of coalescence coupled with the intrinsic rigidity of the dispersed PEMA phase may be assumed to offset the large increase in toughness of PVC observed at the initial stages of PEMA incorporation.

Physical properties

The indentation hardness, which reflects the resistance to local deformation, is a complex property related to the modulus, strength, elasticity, and plasticity. An inverse relationship between the depth of penetration (the lower the depth, the higher is the hardness) of the indenter and the modulus was suggested by Nielsen.¹⁶

$$h = \left[\frac{3}{4} (1 - \nu^2/E) \right]^{2/3} F^{2/3} R^{-1/3} \quad (1)$$

where E is the modulus, ν , the Poisson's ratio, F , the total force on the spherical indenter of radius R , and h is the depth of penetration.

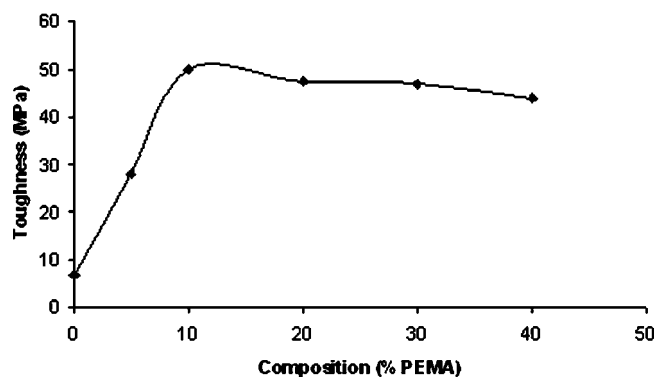


Figure 5 Variation of toughness with blend composition.

The hardness of PVC-PEMA blends remains almost invariant with increasing PEMA concentration in composition as shown in Figure 6. The rigidity imparted by the molecular interaction appears to be compensated by the effect of PEMA domains and thereby affects the hardness of the original PVC base compound only marginally.

Both the theoretical and experimental curves as indicated in Figure 7 exhibit a decreasing trend of specific gravities with increasing proportion of *in situ* formed PEMA of relatively lower specific gravities. The remarkable feature of this graph lies in very sluggish decreasing pattern of actual curve compared to the ideal theoretical one, and second, the experimental specific gravities of the various blends are always higher than the theoretically predicted values.

This positive deviation of the specific gravities can be attributed to the specific interactions like H-bonding and dipole-dipole interactions between molecules of the constituent polymers. Blaga and Feldman¹⁷ and Barlow and Paul and others¹⁸ have suggested that α -hydrogen of vinyl chloride can interact with the ester

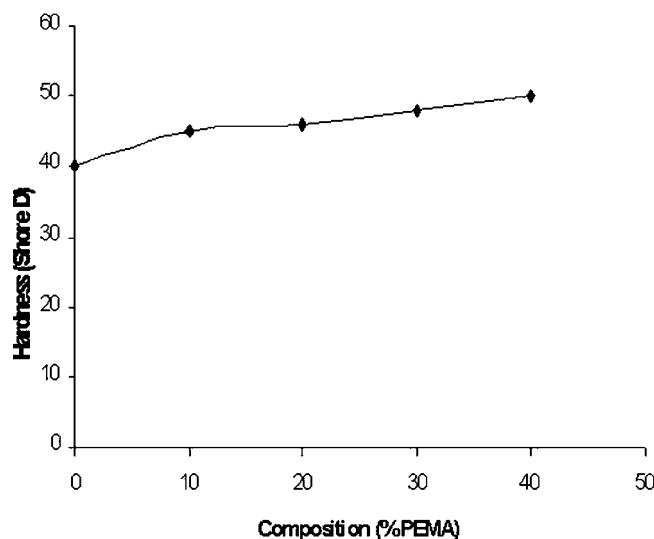


Figure 6 Variation of hardness with blend composition.

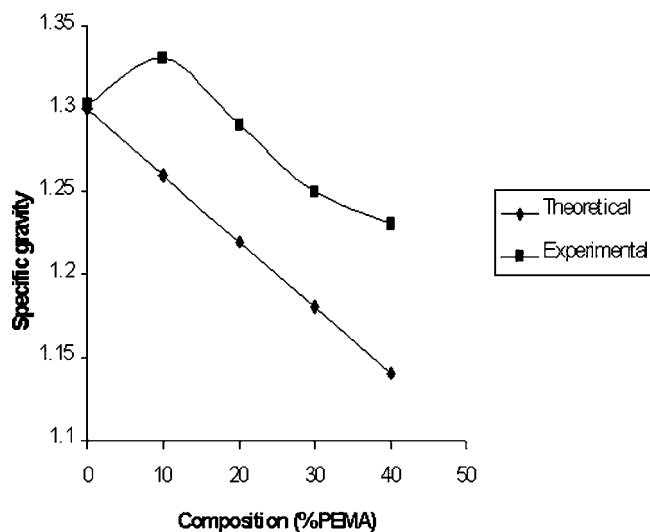


Figure 7 Variation of specific gravity with blend composition.

carboxyl group to form a H-bond leading to more compactness and the rise in specific gravity. The extent of such interaction is expected to increase with increasing proportion of PEMA up to a certain optimum limit beyond which it changes very little.

Thermal properties

The thermomechanical curves of the base reference compound PVC and the PVC-PEMA blend samples under study shown in Figure 8(a,b) respectively, indicate that, in all cases, the probe is slightly pushed up by the expansion of the samples up to a temperature around 50°C. Once the sample starts softening, the loaded probe penetrates the sample at a rate inversely related to the moduli of the various samples. The relatively sharper penetration of the probe as is encountered with pure PVC base compound is flattened to some extent and appears to

take place over a much wider span of temperature in case of its various blends with PEMA. Moreover, the peak softening temperature of the blends is somewhat lower as can be expected from the breakdown in regular chain structure of PVC. At the initial stages, the rigidity imparted by the linear chain structure of PVC (along with plasticizer DOP) is somewhat disrupted by the entry of the PEMA moieties into the system, which results in softness, but at the later stages, the increased molecular interaction coupled with the agglomeration of the dispersed PEMA phases accounts for increasing strength, which resists penetration. On the other hand, the samples undergo swelling and expansion, the extent of which increases with increasing proportion of PEMA.¹⁹

The blends, however, also exhibit stabilization over unmodified PVC, which is exhibited at the upper limiting test temperature where the molten blend samples undergo tendency of expansion while PVC shows breakdown and exhibits a sharp fall.²⁰ This is again supported by the observation of differential scanning calorimetric analysis.

The DSC thermograms of the representative samples of the blends of PVC-PEMA system have been depicted in Figure 9. The intersect of the tangents drawn on two portions of the inflection at the endothermic enthalpy change in each DSC curve has been considered as the glass transition temperature of the corresponding blends.^{21,22} The T_g s of the blends generally fall below the T_g s predicted by the law of mixture given as follows:

$$T_g(\text{av}) = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (3)$$

where w represents the weight fraction of any component in the blend and suffix 1 and 2 are used for PVC and PEMA, respectively. However, the progres-

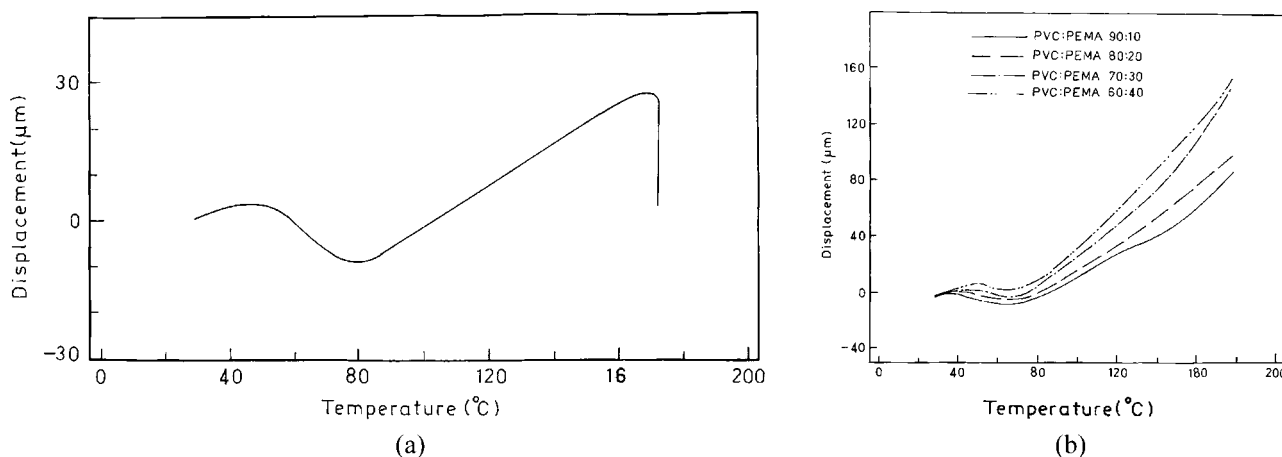


Figure 8 (a) TMA plot of base reference compound PVC and (b) TMA plot of the PVC-PEMA blends.

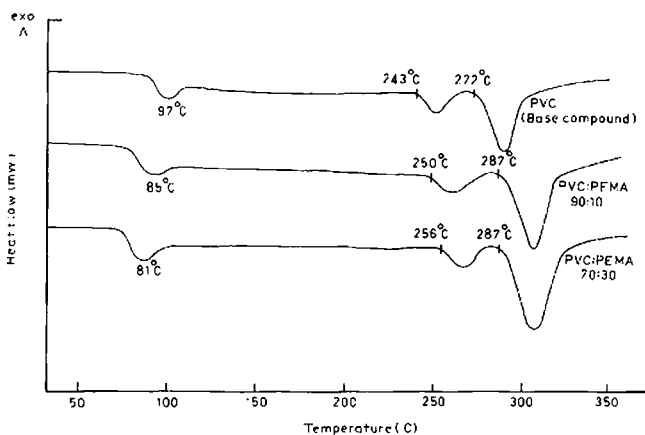


Figure 9 DSC tracings of base PVC compound and PVC-PEMA blends.

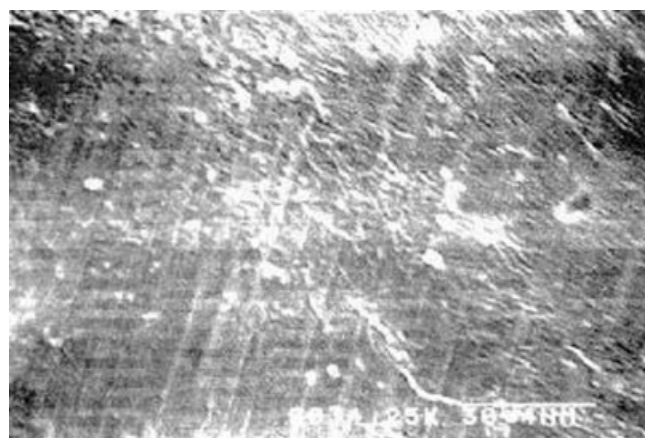
sively increasing plasticizing influence of PEMA phase on the continuous PVC resin matrix is evidenced from the DSC tracings. The T_g decreases with increase in proportion of PEMA. This may be

ascribed to the fact that the entry of PEMA molecules into the major matrix PVC pushes the chains apart thus increasing the free volume and plasticizing the already plasticized matrix. The inward shifting of T_g is also indicative of some phase mixing.

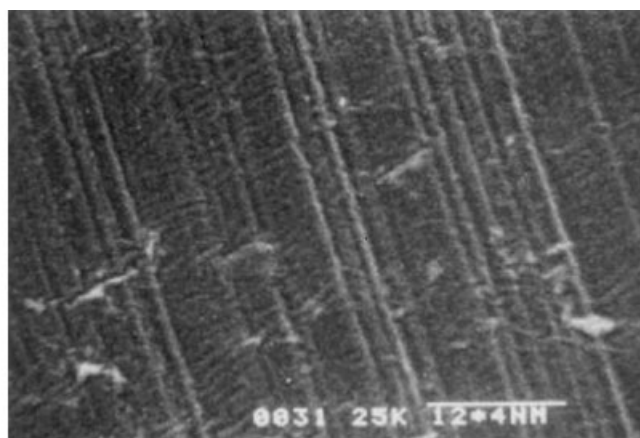
At the higher temperature, PVC and its blends undergo degradation in two stages with the blends exhibiting the onset at a higher temperature compared to that of pure PVC base compound.²³ This indicates some stabilization imparted by PEMA on PVC possibly by scavenging the chloride radicals as soon as they are formed *in situ*. The onset gradually rises with increasing proportion of PEMA as more moieties are available to absorb the chloride free radicals.

Morphology

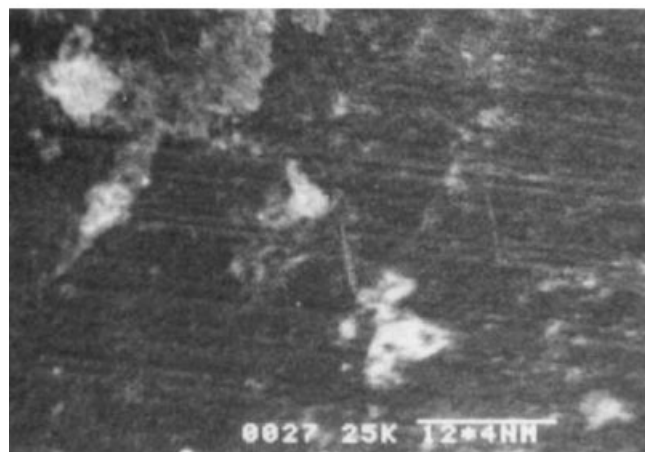
The scanning electron micrographs as shown in Figure 10 clearly indicate remarkably changed morphologies of the various blends when compared



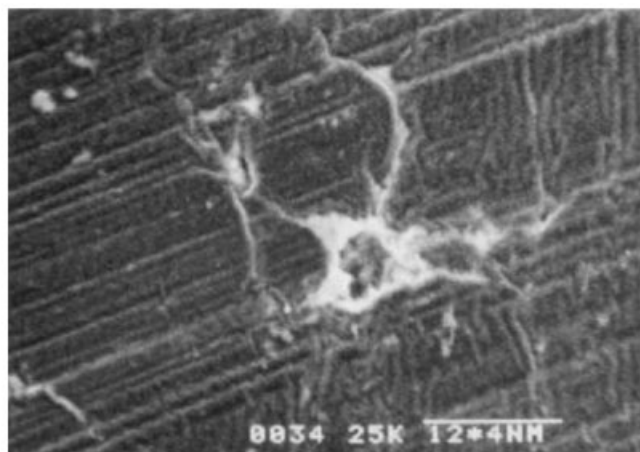
(a)



(b)



(c)



(d)

Figure 10 Scanning electron micrographs of PVC-PEMA blends: (a) base reference compound PVC, (b) PVC : PEMA 90 : 10, (c) PVC : PEMA 80 : 20, and (d) PVC : PEMA 70 : 30.

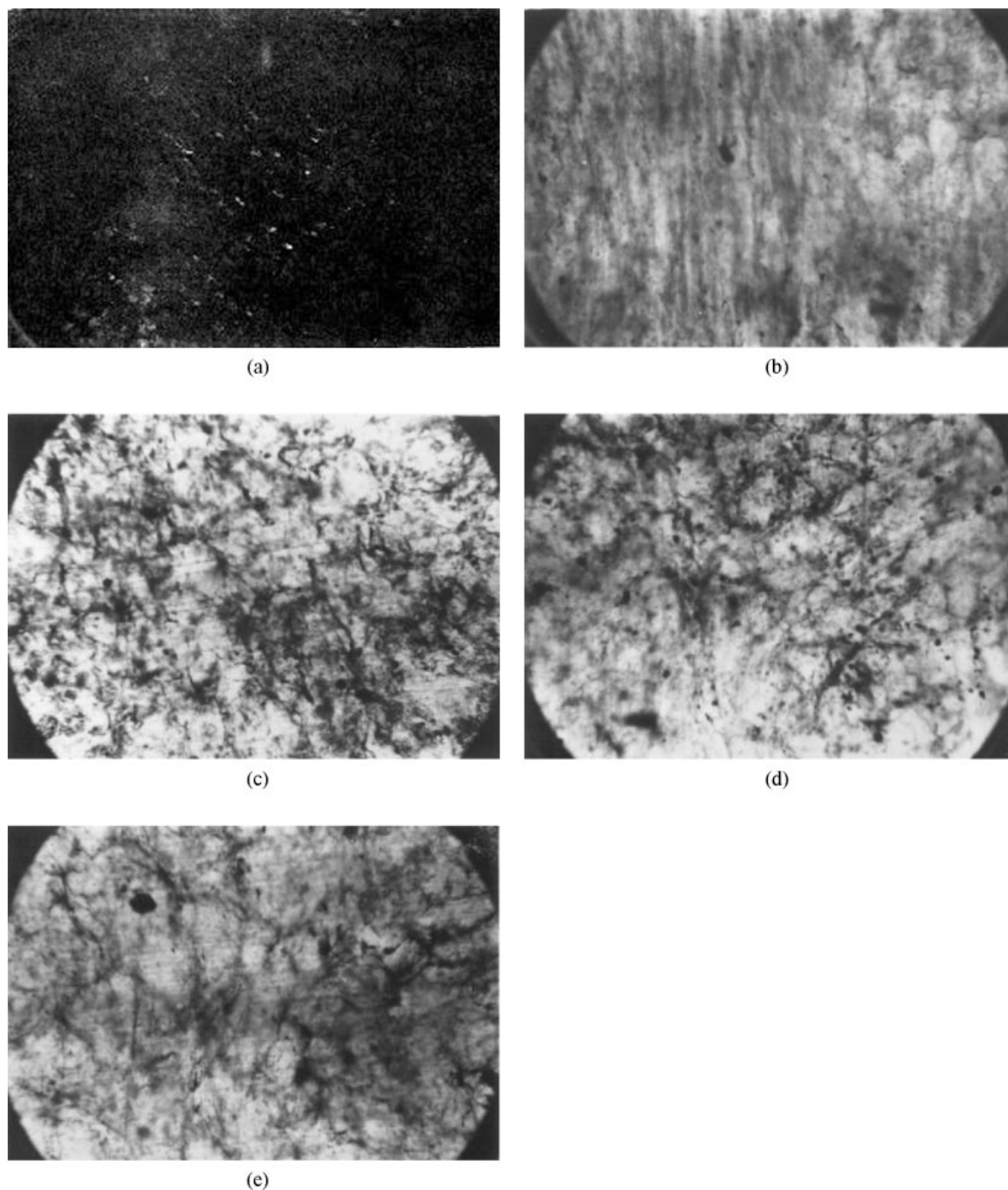


Figure 11 Optical micrographs of PVC-PEMA blends: (a) base reference compound PVC, (b) PVC : PEMA 90 : 10, (c) PVC : PEMA 80 : 20, (d) PVC : PEMA 70 : 30, and (e) PVC : PEMA 60 : 40.

with that of the pure standard compound PVC as used in this study. PVC appears to exhibit micro-characteristics somewhat resembling a rigid and glassy surface exhibiting stress whitening and micro-cavitation. The blends exhibit two phase morpholo-

gies although the boundary region of the phases are not very sharp and there appears to be some phase mixing at the interfacial regions as can be predicted and expected from the proximity of their respective solubility parameters. The homogeneity in phase

mixing as can be encountered at the lower level of PEMA incorporation is however absent in higher doses within the range of concentration studied. The dispersed PEMA phase appears to be distributed in the form of fibrils in more or less orderly manner. This type of disposition of the dispersed phase eliminates the problems of microcavitation leading to a ductile blend with improved toughness. At the higher level of PEMA incorporation, the system exhibits increased coalescence of the various stress fields, which are indicative of gradually receding ductility.²⁴

In conformity to our observation in SEM studies, the PVC sample shows white specks and microvoids as structural defects, which are expected with rigid glassy chain structures from the optical micrographs (Fig. 11). The formation of PVC resin matrix is preceded by the *in situ* formation of PEMA particles. Thus, while the PVC resin particles undergo fusion and subsequent crystallization on cooling and the neighboring chains exert dipole–dipole interaction through the C–Cl bonds, the already formed PEMA particles inhibit such interaction and plasticize the resin matrix beyond the extent to which it was plasticized by the DOP already present in the master formulation. At the initial stages of PEMA incorporation, some phase mixing between the phases appears to develop by the tendency to cocontinuous formation of the matrices; while at the later stages, the PEMA moieties undergo agglomeration tending to the development of phase separation. The association of the molecules of the dispersed phase rises with rising methacrylate content thus exhibiting the formation of self-assembled entities of the modifying resin into the continuous matrix of PVC.²⁵

CONCLUSIONS

The systems under study revealed the impact of blend formation of PVC with the poly(alkyl methacrylate) ester. The introduction of PEMA moieties within the matrix of PVC produced a rise in the mechanical and thermal stability. The combination of the two polymers also created a directing influence one over the other, which was explicit from the micrographs. The degree of PEMA incorporation

had a measurable increasing effect on the modulus and ultimate tensile strength and an overall rise in the toughness values as well. Thus, blends with increased strength and toughness have been simultaneously achieved at as the toughness values though exhibiting a gradual fall along with composition, always lie above that of unmodified PVC. The thermomechanical properties have also been modified, which produces an overall increasing stability.

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