

# Physical, Mechanical, and Thermal Properties of PVC/PMMA Blends in Relation to Their Morphologies

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**Abstract:** The effect of blending poly (methyl methacrylate) (PMMA) in various proportions with suitably stabilized and plasticized poly (vinyl chloride) (PVC) was studied with reference to their physical, mechanical, and thermal properties. The resulting morphologies of the various blends were also studied to find a suitable explanation of these properties. The physical and mechanical properties of such polyblends revealed a substantial increase in toughness accompanied with unusual increase in modulus and ultimate tensile strength after an initial drop at the initial stages of PMMA incorporation compared to pure reference compound PVC. The toughening effect, however, undergoes a

reduction with increasing proportion of PMMA but it never goes below that of pure PVC (reference compound) within the ranges of PMMA incorporation under study. The various polyblends exhibit the two-stage degradation typical of PVC and all of them possess higher thermal stability as manifested in their characteristic thermograms. The softening characteristics imparted by PMMA were also reflected in their respective TMA curves. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2721–2730, 2004

**Keywords:** mechanical; thermal; morphology; blend; poly (methyl methacrylate); Poly (vinyl chloride)

## INTRODUCTION

The inherent problems of poor impact strength and difficult processing of rigid poly (vinyl chloride) (PVC) are quite well known and are usually overcome by incorporation of suitable plasticizers and lubricants. In this process of modification, the mechanical properties such as modulus and ultimate tensile strength (UTS) are remarkably reduced. The process of blending certain other polymeric materials, which are referred to as impact modifiers and processing aids, offers a unique tool for overcoming the deficiencies of PVC as mentioned above without much loss in the mechanic.<sup>1–4</sup>

The most important types of such polymeric modifiers are the acrylates, the incorporation of which is expected to act both as processing aid as well as impact modifiers.<sup>5</sup> The incorporation of acrylates in PVC is analogous to the rubber toughening of glassy polymers, as these are well known to be rubbery in character, having glass transition temperatures close to or below room temperature. This increment in ductility of PVC is associated with a simultaneous decrease in load-bearing characteristics as manifested by modulus and UTS.

The present study involves blending of PVC with amorphous, rigid, and glassy polymer such as poly (methyl methacrylate) (PMMA) having a very high glass transition temperature ( $T_g$ ) value. PMMA, having a solubility parameter ( $\delta = 9.27 \text{ cal/mL}^{1/2}$ ) very close to that of PVC ( $\delta = 9.47 \text{ cal/mL}^{1/2}$ ), might be expected to have very good compatibility with PVC.<sup>6–8</sup> Second, the inherently stiff, rigid, and hard PMMA might be expected to counterbalance the fall in mechanic of PVC attributed to the disruption in molecular packing of stiff and rigid chains of PVC.

## EXPERIMENTAL

### Materials

PVC (Reon, K value 67) from M/s Reliance Industries Ltd. (Mumbai, India) was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulphate (TBLS) from M/s Kalpana Industries (Daman, India) were used as suitable plasticizers and stabilizers, respectively. Methyl methacrylate (MMA; M/s Burgoyne) 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 tested by litmus paper) and drying over fused calcium chloride ( $\text{CaCl}_2$ ). It was finally vacuum distilled. Benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ) from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as initiator for acrylic polymerization.

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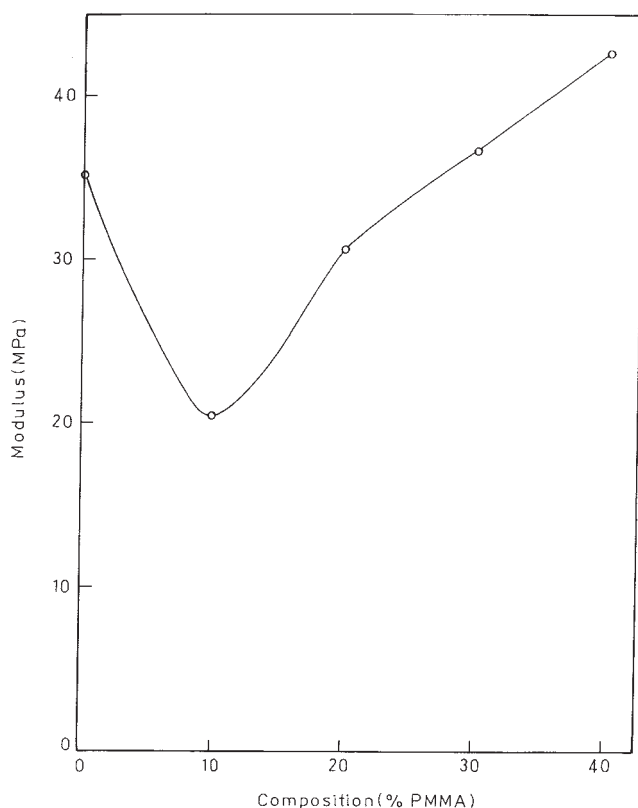


Figure 1 Variation of modulus with blend composition.

### Synthesis of blends

A weighed amount of purified MMA was taken in a test tube and thoroughly mixed with 2 wt % (based on MMA) 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 airtight 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 as prepared above along with plasticizer and stabilizer. Dry mixing was further continued until a thoroughly mixed blend of PVC and monomer was obtained. The mix was then compression molded into a sheet by subjecting a three-piece mold under pressure and heat in two stages.

Initially, the mold was compressed under a pressure of 15 tons/cm<sup>2</sup> at a temperature of 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 a further 20 min to ensure complete polymerization of residual MMA if any. The mold was

then allowed to cool down to room temperature and the molded sheet was ejected.

### Measurements

#### Tensile properties

An Instron Universal Testing Machine (model 4204) was used for measuring the tensile properties such as UTS, percent elongation at break (%EB), modulus, and toughness. ASTM D638 method was followed. A crosshead speed of 3-mm/min was maintained. All testing was 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  $\pm 5\%$ .

#### Physical properties

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

#### Thermal properties

Thermogravimetric analysis (TGA) of the various blend samples was obtained on a Perkin-Elmer Delta

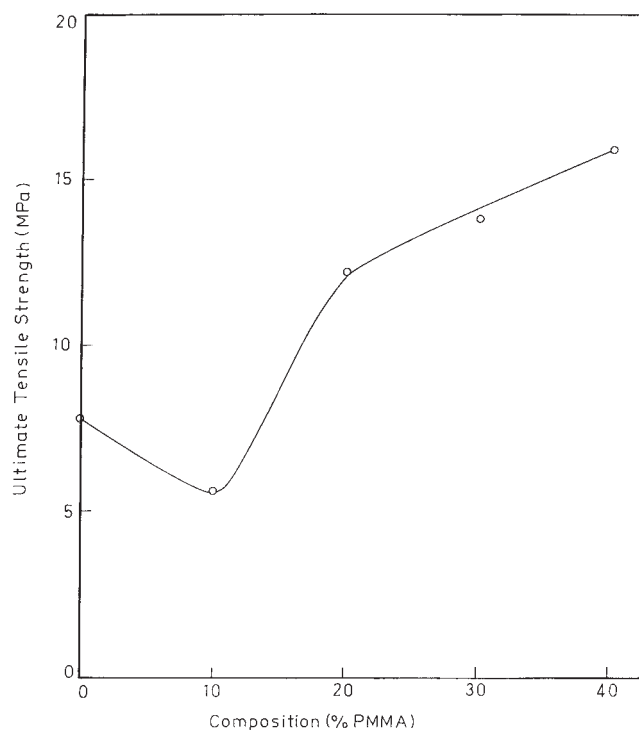


Figure 2 Variation of ultimate tensile strength with blend composition

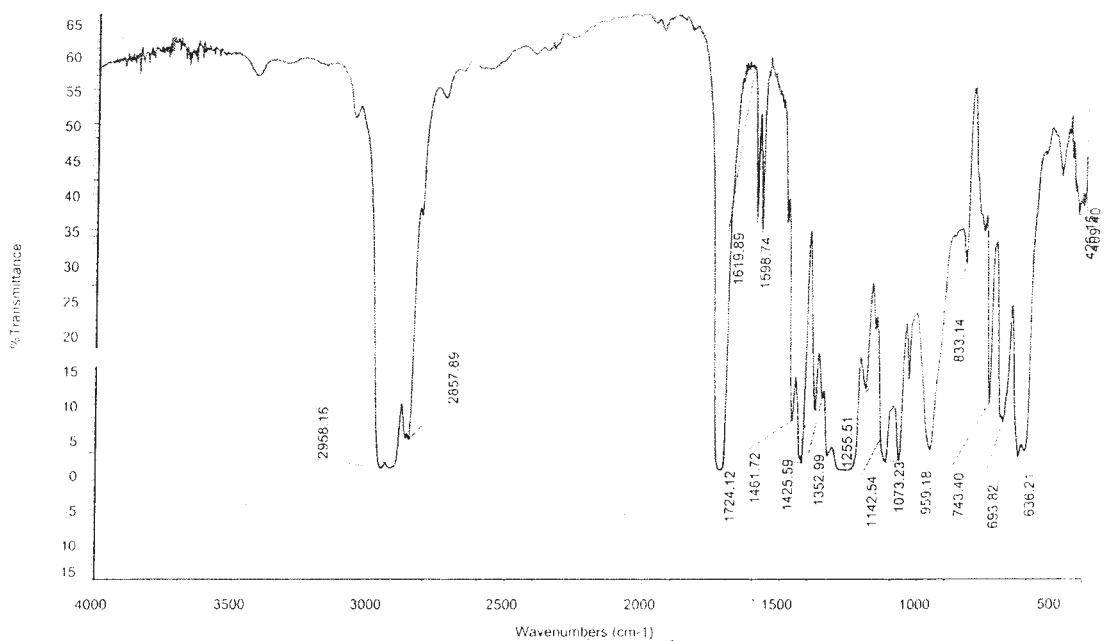
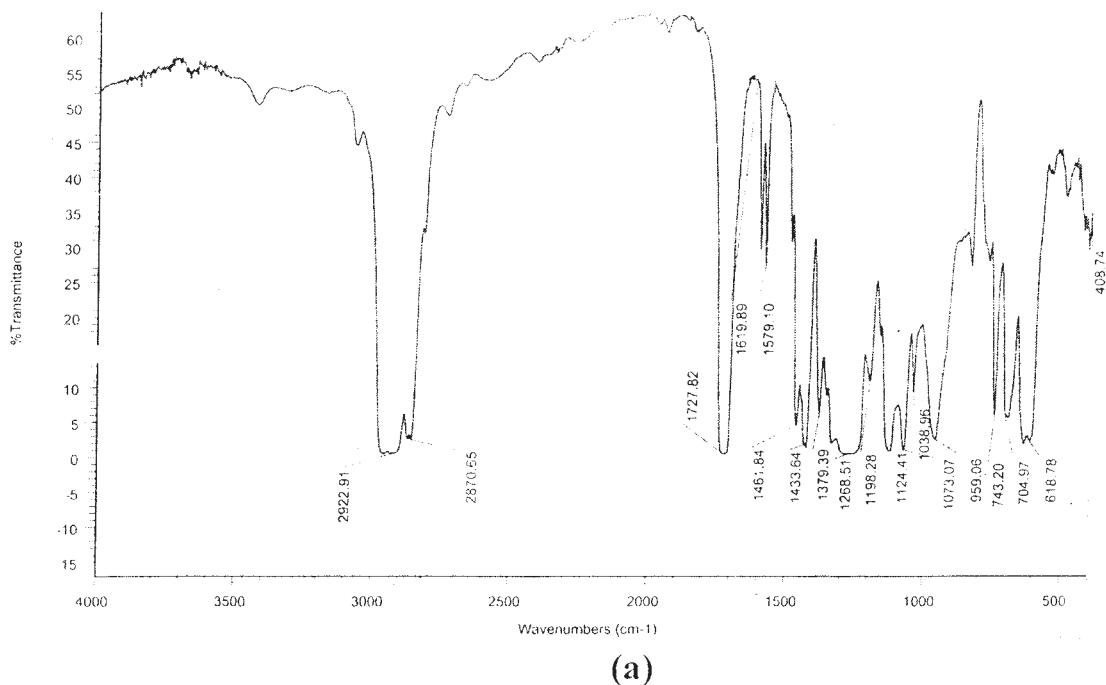


Fig 3(b)

Figure 3 FTIR plots for the base PVC compound and a blend system. (a) Base PVC compound; (b) PVC : PMMA, 80 : 20.

Series TGA-7 thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20°C per min. The samples ranging between 6 and 10 mg in weight were used for the TGA analysis.

The thermomechanical analysis of the various samples of PVC (containing plasticizers and stabilizers in proportion to which they are present in all the blends) and its blends with *in situ* formed PMMA were carried

out in a TMA apparatus from Shimadzu (model TMA 50) in the presence of oxygen. The thermooxidative characteristics were studied under a constant load of 8 throughout the experiment by 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°C/min was maintained right from the ambient temperature.

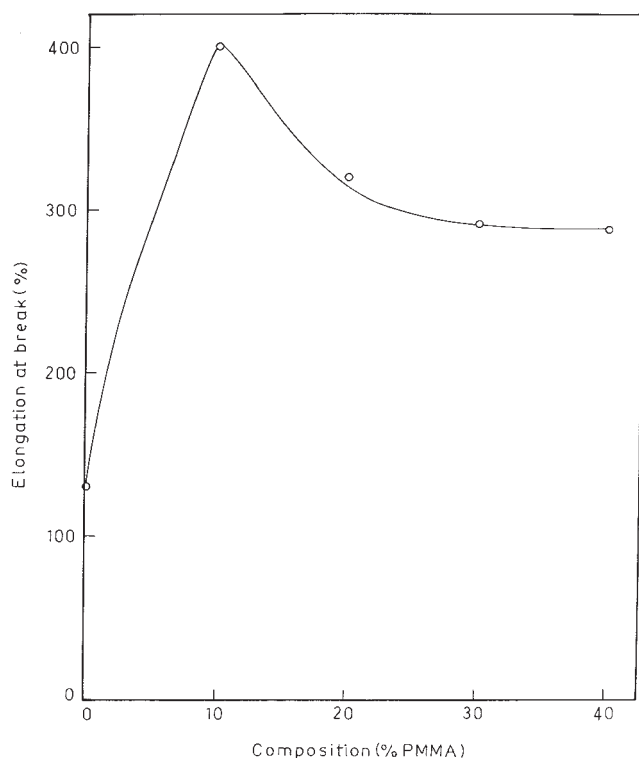


Figure 4 Variation of percent elongation at break with blend composition.

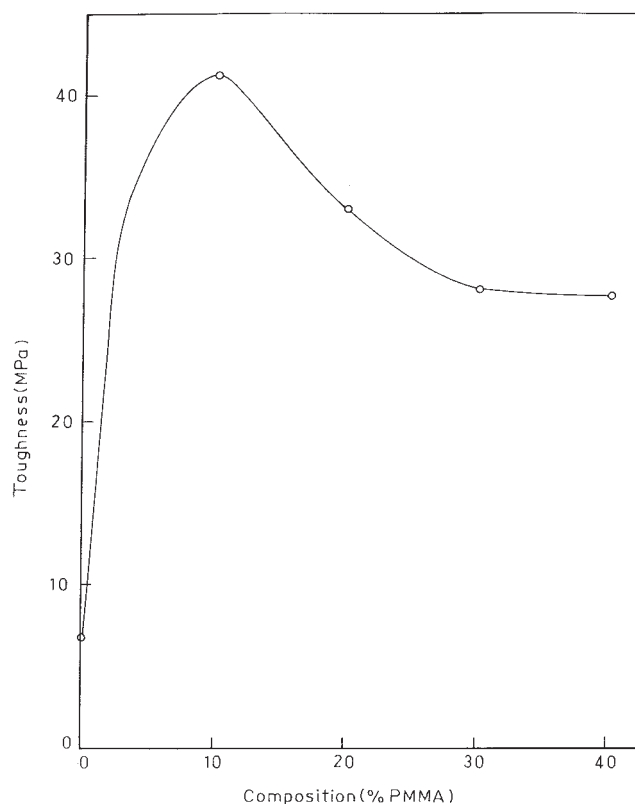


Figure 5 Variation of toughness with blend composition.

### Morphology

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

The surface morphology was, however, done in a trinocular polarizing light microscope from Kruss (optromic) (Germany) with a magnification of X 40. The samples were about 0.5 mm in thickness.

## RESULTS AND DISCUSSION

### Mechanical properties

Both the moduli and the UTS exhibit a decreasing trend with increasing proportions of PMMA to the extent of 10% of PMMA incorporation beyond which there is a steady increase in both of these parameters within the ranges of concentration studied, as shown in Figures 1 and 2. The somewhat plasticized PVC, as was used in various blends, undergoes further plasticization initially with the incorporation of stiff and rigid PMMA, which by virtue of its bulky molecular structure throws apart the stiff and rigid chains of PVC and thus synergizes the function of the already present conventional plasticizer DOP, which in turn reduces the dipole-induced dipole interactions exerted

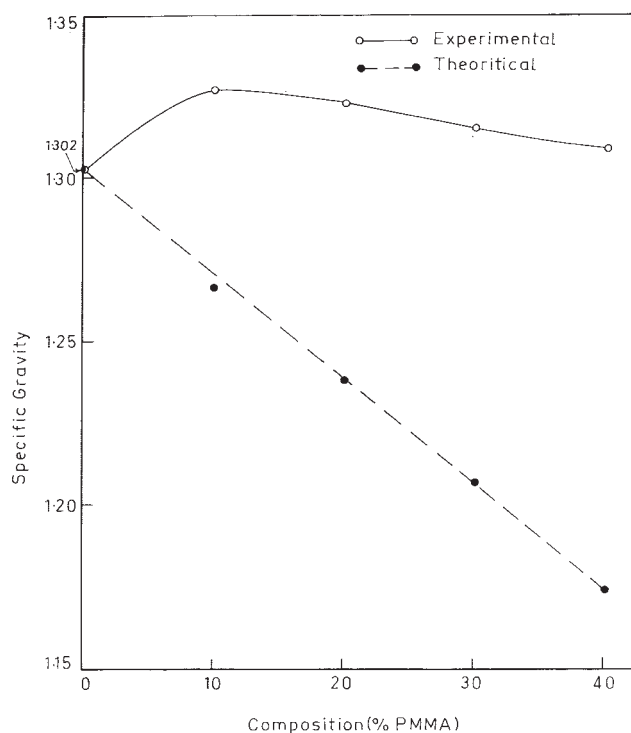


Figure 6 Variation of specific gravity with blend composition. (—) Experimental; (---) theoretical.

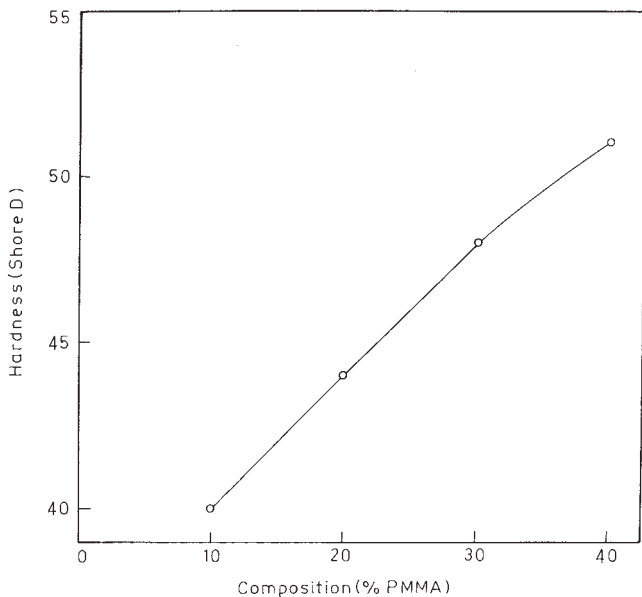


Figure 7 Variation of hardness with blend composition.

by polar C—Cl bonds on the neighboring chains to an extent far more than DOP alone. Beyond 10% of PMMA incorporation, we observe reversal of behavior in its modifying influences on PVC. The two mechanical parameters now undergo an upward swing and demonstrate a steady increase, the rate of which gradually ceases at the higher level of PMMA incorporation. It is quite interesting to note that within the range of 20–30% of PMMA incorporation, the plasticizing influences of the modifier were more than compensated for and a blend of higher modulus and UTS results (with respect to plasticized PVC without any modifying resin).

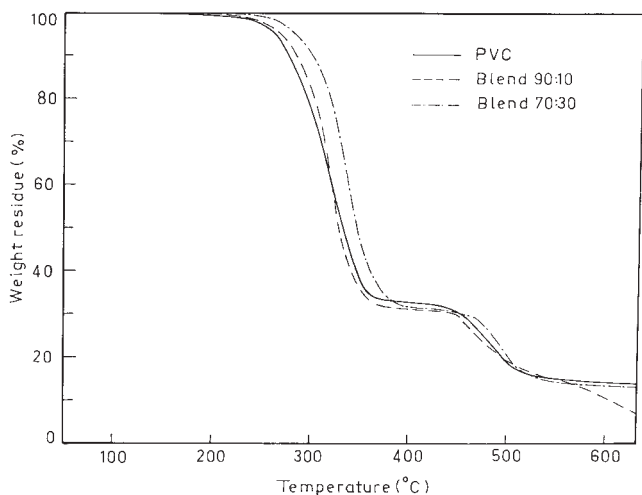


Figure 8 TGA plots for the base PVC compound and the blend systems. (—) Base PVC compound; (---) PVC : PMMA, 90 : 10; (- - -) PVC : PMMA, 70:30.

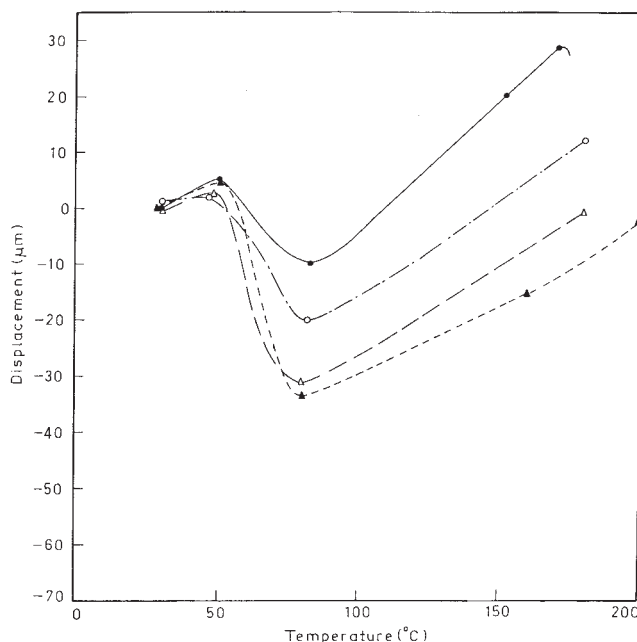


Figure 9 TMA plots for the base PVC compound and blend systems. (—) Base PVC compound; (---) PVC : PMMA, 90:10; (- - -) PVC : PMMA, 80:20; (—) PVC : PMMA, 70:30.

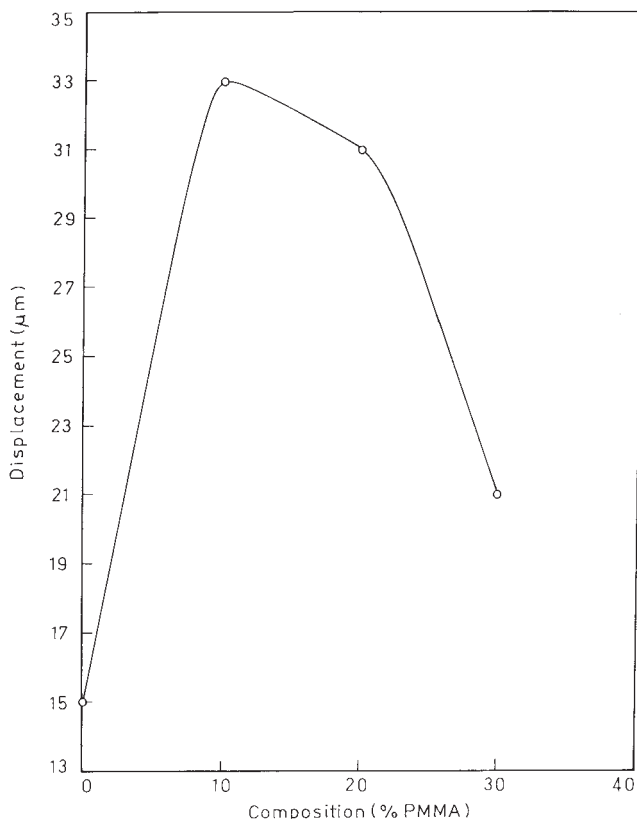
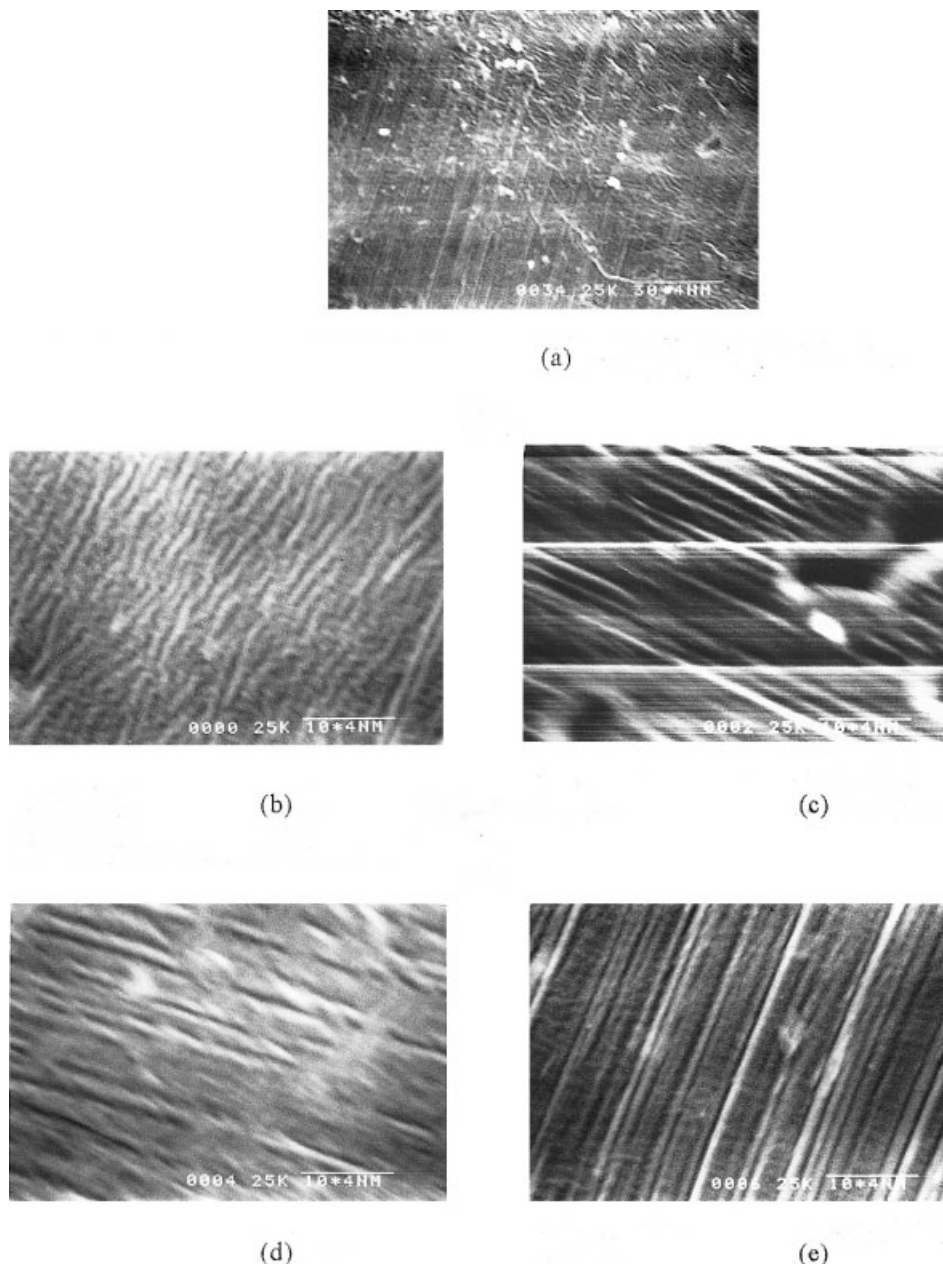


Figure 10 Variation in penetration as obtained from TMA experiment with blend composition.



**Figure 11** Scanning electron micrographs for base PVC compound and blend systems. Magnification, X 300. (a) Base PVC compound; (b) PVC : PMMA, 90:10; (c) PVC : PMMA, 80:20; (d) PVC : PMMA, 70:30; (e) PVC : PMMA, 60:40.

The improved property of such blends may be attributed to specific interactions such as H-bonding and dipole–dipole interactions between molecules of the constituent polymers.<sup>9</sup> It was suggested that the  $\alpha$ -hydrogen of vinyl chloride can interact with the ester carboxylate group (H-bond acceptor of the acrylic polymer) to form a hydrogen bond and is also a key factor in achieving miscibility.<sup>9–12</sup> The close value of the solubility parameters of PVC and PMMA might also be expected to account for the compatibility and hence, enhances the properties. The intrinsic rigidity and stiffness of PMMA can also be accounted for such improved properties.

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 PMMA, as shown in Figure 3(a, b). The typical absorbance due to C—Cl in the base compound at  $704\text{ cm}^{-1}$  undergoes a decrease in frequency ( $693\text{ cm}^{-1}$ ) in the blend in the presence of methacrylate esters, which may possibly be attributed to a feeble interaction between the C—Cl dipole and the  $\beta$ -hydrogen of the methacrylate esters.

The %EE and the toughness of the various blends of PVC and PMMA, as shown in Figures 4 and 5, conformed to our expectations. In both cases, there is a sudden jump in their corresponding values initially

up to a level of 10% of PMMA incorporation in conformity to a decrease in modulus and UTS as observed earlier, beyond which there is a steady decrease in their values, and finally, levels off within the ranges of concentration studied. However, both these, mechanics always lie much above the corresponding values of unmodified (no PMMA) plasticized resin.

The inclusion of the rigid, hard, dispersed phase of PMMA 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 PMMA than PVC. This order is determined by entanglement density<sup>13,14</sup> and by the shear yield stress of the glassy polymer. PMMA has a high entanglement density but a higher yield stress.<sup>15</sup> In contrast to the mechanism of rubber toughening (rubber itself being stretchable and absorbing the energy for crack propagation), the *in situ* generated rigid domains of PMMA 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, particularly, where there are many cracks, interfere with one another, reducing the stress at the tips of the cracks, sometimes leading to a stoppage of the growth of the cracks. Thus, more energy is required for propagating the crack, and hence, high toughness develops. Moreover, as the path length traversed by a crack increases as it is to propagate at the interface of the apparently biphasic blend, the elongation also increases.<sup>16,17</sup>

It is quite interesting to note that with increasing *in situ* generated PMMA content beyond 10%, both the toughness and the elongation at break decreases. From the polarizing light micrographs (Fig. 12), it can be observed that the number of dispersed PMMA particles increases and there is also a coalescing tendency of the particles with progressive increases in PMMA content. Thus, the path length for cracks to propagate decreases, and hence, the reduction in toughness and % EB decreases. The rigid PMMA particles can also be expected to exert their influence as its content increases in the matrix. The decrease in the number of cracks attributed to the increasing sizes of domains coupled with the intrinsic rigidity of the dispersed PMMA phase may be assumed to offset the large increase in toughness of PVC observed at the initial stages of PMMA incorporation. However, tough PVC blends with strength almost equivalent to unmodified plasticised PVC results.

### Physical properties

#### Specific gravity

Figure 6 demonstrates both the actual specific gravities and the theoretical ones obtained by applying the

simple rule of additivity for various blends of PVC and PMMA. Both the curves exhibit a decreasing trend of specific gravities with increasing proportion of *in situ* formation of PMMA of relatively lower specific gravities. The remarkable feature of this graph lies in the very sluggish decreasing pattern of actual curve compared to the ideal theoretical one, and second, the actual specific gravities of the various blends are always higher than the theoretically predicted values. Moreover, the differences in specific gravity values increase more and more as the proportion of PMMA increases.

This positive deviation of the specific gravities can be attributed to the specific interactions such as H-bonding and dipole–dipole interactions between molecules of the constituent polymers.<sup>5</sup> Blaga and Feldman,<sup>5</sup> Barlow and Paul,<sup>9,10</sup> and others<sup>11,12</sup> have suggested that  $\alpha$ -hydrogen of vinyl chloride can interact with the ester carboxyl group to form an H-bond, leading to more compactness and the rise in specific gravity. The extent of H-bonding is expected to increase with increasing proportion of PMMA.

#### Hardness

Hardness, being a surface phenomenon shown in Figure 7, of the various blends exhibits a somewhat different mode of changes with variation in PMMA content. The hardness increases almost linearly and progressively with increasing proportion of PMMA. The stiff and rigid domains of the dispersed and somewhat miscible (because of the close values of the soluble parameters) PMMA phase, coupled with the possibility of H-bond formation as described earlier leads to a steady increase in hardness within the ranges of PMMA concentration studied.

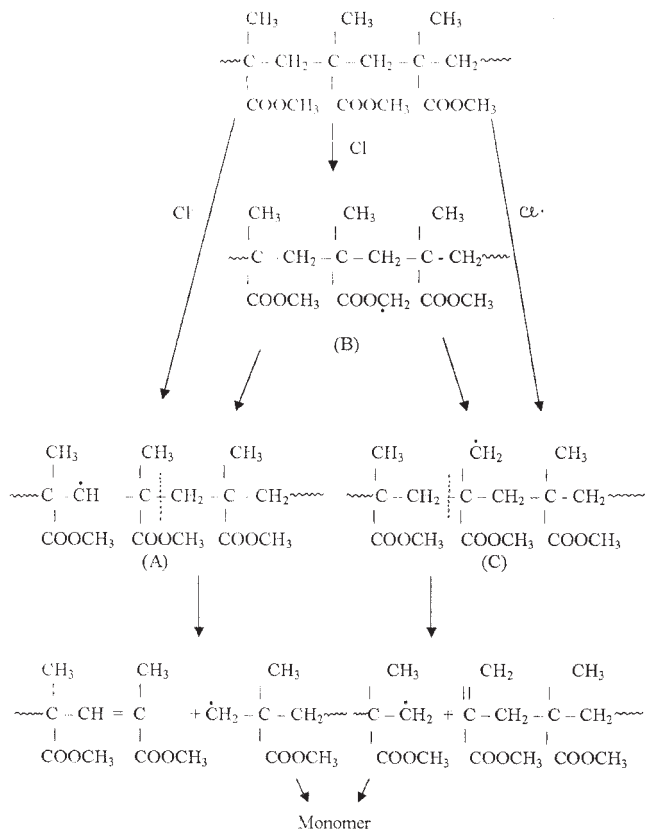
### Thermal properties

#### Thermogravimetric analysis

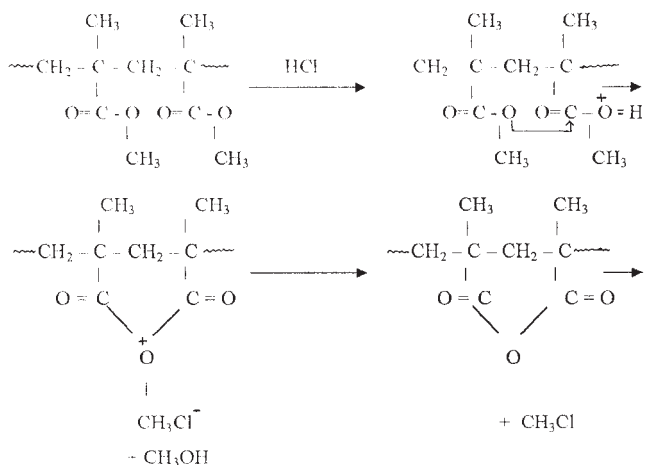
The thermogram, Figure 8 of PVC (reference compound), and its various blends with PMMA clearly indicate an overall increase in thermal stability of the blends over PVC. The delayed onset temperature of degradation for the blends in both the stages of degradations, namely, the quantitative dehydrochlorination followed by scission of the resulting polyenes, is a salient feature of the thermal characteristics of such blends, which further increase with increasing proportion of PMMA. The high percentage residue left at elevated temperature and the slow rates of degradation of the blends compared to PVC are also distinctive features of the figure.

A suitable explanation for such stabilization of PVC may be found as follows. Dehydrochlorination as considered to be the first stage in thermal degradation of

PVC is not random, but proceeds along the chains following the initial loss of hydrogen chloride. This process is assumed to be a free-radical process involving the initial formation of chlorine radicals (intermediate in the dehydrochlorination of PVC).<sup>18</sup> This chlorine radical fails to form HCl as it interacts with the PMMA, as follows:



Secondly, even if the HCl is produced, it fails to catalyze the process of subsequent degradation as it reacts with the ester group of PMMA as follows:



The extent of each of these two processes does not need to be great to produce the effects observed.<sup>19</sup> The chloride radical Cl causes the PMMA chain to break and subsequently unzip quite readily at low temper-

atures. Reaction with HCl, on the other hand, presumably a slower process, gives rise to anhydride rings, which acts as locking groups reducing the zip length of depolymerization and thus stabilizing the chain. Moreover, the unzipped monomer (MMA) is considered to be a very good radical scavenger and thus scavenges the chloride radicals immediately as they are formed.

In this way, there is a mutual stabilizing effect whereby PVC is stabilized by PMMA in blend by not allowing the Cl radical to form hydrogen chloride and subsequently not permitting the HCl, even if formed by forming an anhydride type of structure as shown above.

### Thermomechanical analysis

The thermomechanical data of various blends of PVC are shown in Figure 9. It is quite interesting to note 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 extent of penetration versus composition, as shown in Figure 10, reveals that, at the initial stages of PMMA incorporation, the lowering of rigidity due to breakdown in chain structure has led to softness, whereas at later stages, the slow and gradual association of stiff and rigid PMMA particles probably accounts for the decreased penetration within the range of PMMA incorporation studied.

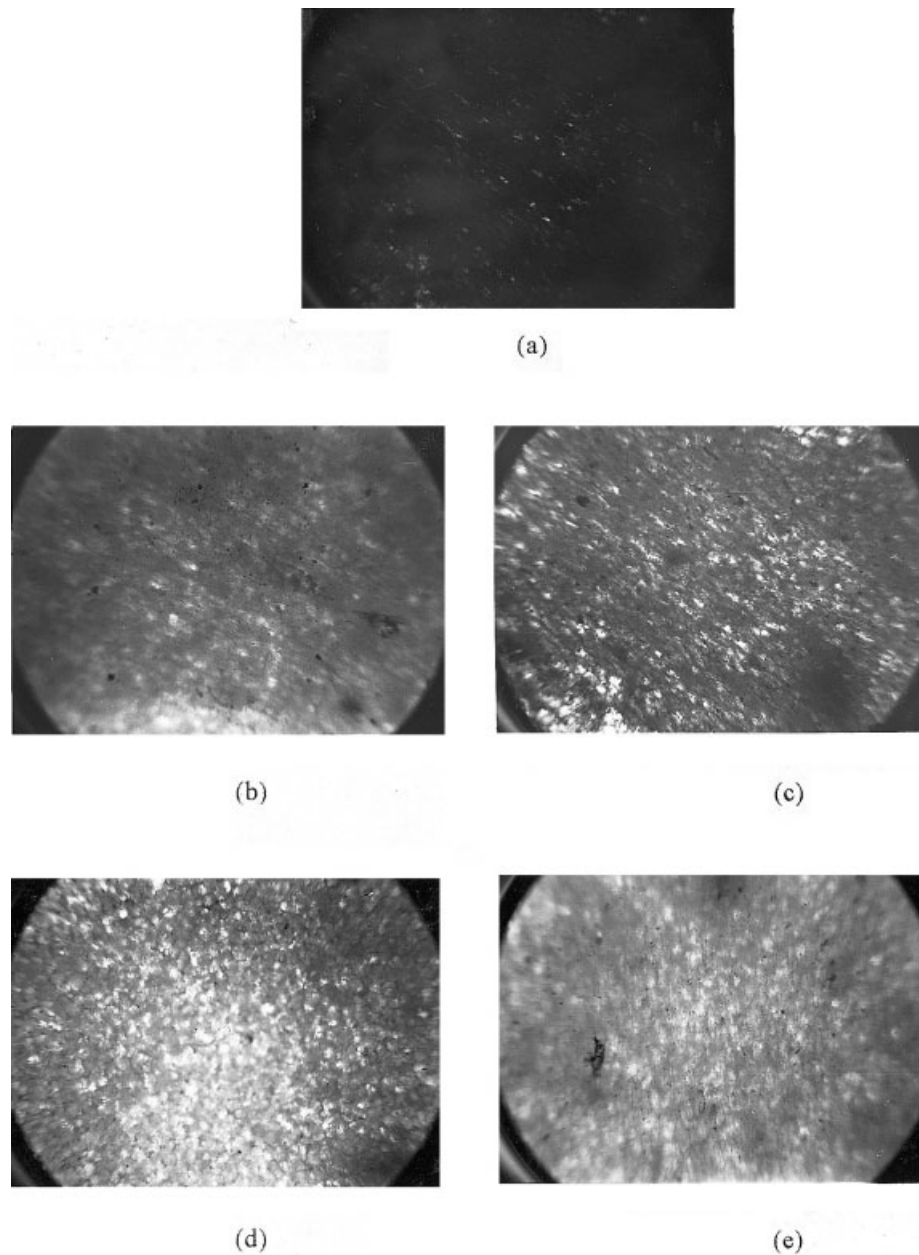
The onset temperature of softening of plasticized PVC and its blends with PMMA undergoes a decrease with an increasing proportion of PMMA possibly because of the more and more irregularity in structure imparted by PMMA. In any case, the effect is not so pronounced possibly because of stiff particles of PMMA. Once the blend has softened completely, the molten sample undergoes expansion until the upper test temperature is reached. While at this stage, PVC shows breakdown and a sharp fall; the other blend samples remain stable and exhibit stabilization over PVC.

### Morphology

#### Scanning electron microscopy

The SEM micrographs shown in Figure 11 clearly indicate changed surface morphologies of the various blends when compared to that of pure PVC. PVC appears to exhibit microcharacteristics somewhat resembling a rigid and glassy surface. The blends exhibit two phase morphologies, although the boundary region of the phases are not very sharp and there appears to be some phase mixing, as can be predicted





**Figure 12** Polarizing light micrographs for base PVC compound and blend systems. (a) Base PVC compound; (b) PVC : PMMA, 90:10; (c) PVC : PMMA, 80:20; (d) PVC : PMMA, 70:30; (e) PVC : PMMA, 60:40.

from the proximity of their respective solubility parameters. The homogeneity in phase mixing, as can be encountered at the lower level of PMMA incorporation, is, however, absent in higher doses within the range of concentration studied. (This may possibly be attributed to the increased toughness and elongation as it breaks down the regularity in stiff chain structure of PVC.) At a higher level of PMMA incorporation, somewhat regularity in structure (due to association of a large number of PMMA particles) appears to develop, which leads to an increase in modulus and UTS and a concomitant decrease in elongation and toughness.

#### Polarizing light microscope

The polarizing light micrographs (Fig. 12) display the typical structure of a heterogeneous polymer blend. There exists a continuous phase (dark one) of PVC and the dispersed phase of PMMA (white). The formation of PVC resin matrix is preceded by the formation of PMMA 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 PMMA particles inhibit such interaction and plasticize the resin matrix beyond the extent to which

it was plasticized by the DOP already present in the formulation. However, the extent of plasticization that was achieved at the initial stages of PMMA incorporation appears to be missing at later stages possibly because (1) the cocontinuous formation of matrices and (2) the greater number of PMMA particles generated at higher concentration undergo aggregation and intend to exert their own rigid and brittle behavior. However, there seems to be a combined effect of the brittle behavior of PMMA phase coupled with possible interaction between the ester group of PMMA and the C—Cl of PVC, as shown earlier, counteracting the increment in toughness imparted by the presence of a large number of PMMA particles and their aggregates.

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