Mechanical and Thermomechanical Characterization of PVC/Polyalkylacrylate Blends

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ABSTRACT: The effect of blending poly(ethyl acrylate) and poly(butyl acrylate) in various proportions with suitably stabilized and plasticized polyvinyl chloride (PVC) was studied with reference to their physical, mechanical, thermal, and morphological properties. The tensile modulus and ultimate tensile strength indicated a rise initially, followed by their steady decrease with increasing concentration of the polyalkyl acrylates. A corresponding behavior of elongation at break and toughness are exhibited. The various polyblends exhibit thermal stability over unmodified PVC, as reflected from their thermomechanical studies, in which the penetration is also inversely related to the respective moduli. The biphasic cocontinuous systems as explicit from the morphological studies support phase mixing at the initial stages, with subsequent phasing-out tendency, with increasing percentage of polyalkyl acrylate incorporation. The thermomechanical parameters are in conformity to their mechanical parameters, which have been further supported by their morphological studies. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3698–3703, 2006

Key words: blends; thermal properties; mechanical properties; morphology; poly(vinyl chloride)

INTRODUCTION

The inherent problems of poor impact strength and the difficulty in processing of poly(vinyl chloride) (PVC) have been reported to be overcome by the process of blending with certain other polymeric materials, which are referred to as impact modifiers and processing aids.[1,2] The incorporation of acrylic polymers in PVC is analogous to the rubber toughening of glassy polymers.[3,4] The present study entails the blending of two types of polyalkyl acrylates, namely poly(ethyl acrylate) (PEA) and poly(butyl acrylate) (PBA), in a matrix of PVC and their characterization with reference to their mechanical, thermal, and morphological properties.

The polyacrylates are well known to be rubbery in character, having glass transition temperatures T_g below room temperature (T_g of PEA is –27°C and PBA is –45°C). These rubbery polyacrylates, when incorporated within PVC, exert their modifying influences in improving the toughness of the blended systems.[5] The influence of the more rubbery PBA moieties, however, appears to be more pronounced in improving the toughness and elongation at break (EB), with variation in PBA content. The increment in ductility is also associated with a simultaneous decrease in the load bearing characteristics, as manifested by modulus and ultimate tensile strength (UTS).[6–8]

EXPERIMENTAL PROCEDURES

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. Poly(ethyl acrylate) (PEA) and poly(butyl acrylate) (PBA) from M/s Burgoyne (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 it alkali-free as 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 initiator for acrylic polymerization.

Synthesis of blends

A weighed amount of purified polyalkyl acrylate was taken in a test tube and thoroughly mixed with 2% by weight (based on PEA or PBA) of recrystallized Bz_2O_2. PVC resin was weighed, such that a predetermined ratio with respect to the monomer as weighed earlier

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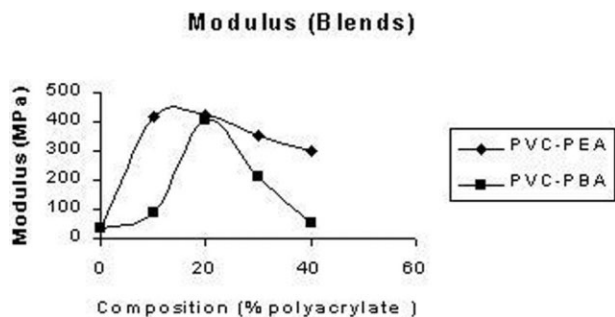
Modulus (Blends)

Figure 1 Variation of modulus with blend composition.

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 the 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 sheets, 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^2 at 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 further 20 min to ensure complete polymerization of residual monomer 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 like ultimate tensile strength (UTS), percent elongation at break (% EB), modulus, and toughness. ASTM D 638 method was followed. A crosshead speed of 3 mm/min 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 ±±5%.

Specific gravity

The two physical parameters of the blends (namely specific gravity of the various blends) were determined by following the Archemedes principle.

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 PEA and PBA 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 8 g 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°C/min was maintained right from the ambient temperature.

The DSC analysis of the samples were carried out in a Perkin–Elmer DSC-7 apparatus at a heating rate of 10°C/min.

Morphology

The surface morphology was, however, done in a trinocular polarizing light microscope from Kruss (optromic), Germany, with a magnification of 200×. The samples were about 0.5 mm in thickness.

RESULTS AND DISCUSSION

Mechanical properties

The modulus and UTS of PVC-PEA and PVC-PBA systems, as depicted in Figures 1 and 2, display an initial upward swing followed by a steady decrease at the later stages of polyalkyl acrylate incorporation within the PVC matrix. On incorporating the polyacrylates into the linear PVC matrix, the molecular interaction between the two participating polymeric components possibly comes into play. The properties
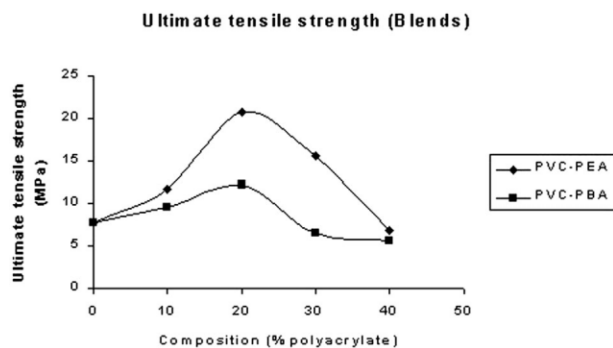
Ultimate tensile strength (Blends)

Figure 2 Variation of UTS with blend composition.

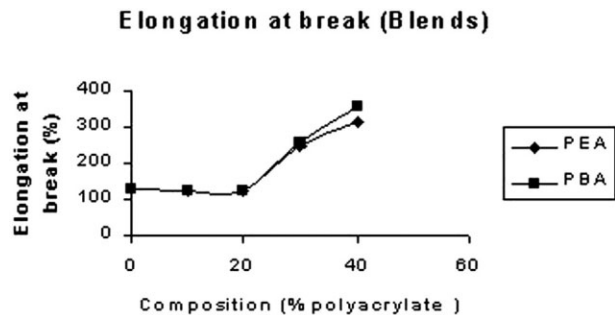**Elongation at break (Blends)**

Figure 3 Variation of EB with blend composition.

exhibited by the different blend systems may be considered as an effect of two opposing forces operating simultaneously[5,8–10]; the secondary valence force due to formation of H bonds through the strongly electronegative chlorine in PVC and the α hydrogen of the ester group present in PEA and PBA appears to be predominating over the weakening dipolar forces between the adjacent PVC chains.

The increases in modulus and UTS of the blends up to an optimum level of 20% PEA and PBA incorporation may possibly be attributed to another possible intermolecular hydrogen bonding between the α hydrogen of vinyl chloride chain unit with the ester carboxylate group. These two factors can be accounted for the observed miscibility in this region of acrylate incorporation.

At the later stages of polyacrylate incorporation, the plasticizing influence of the somewhat rubbery polyalkyl acrylate moieties appears to play the major role. An increase in the percentage of polyalkyl acrylate beyond an approximate threshold concentration of around 20% imparts flexibilization within the linear chains of PVC and nullifies the effect of the interaction as mentioned earlier. The observed facts in the present case simulate the "antiplasticization" phenomenon exhibited by PVC polymers at temperatures below T_g.

The effect of the even more rubbery and bulky PBA plays a more dominating role. It is worth mentioning in this context that the deterioration in strength properties after an optimum level of 20% of PBA incorpo-
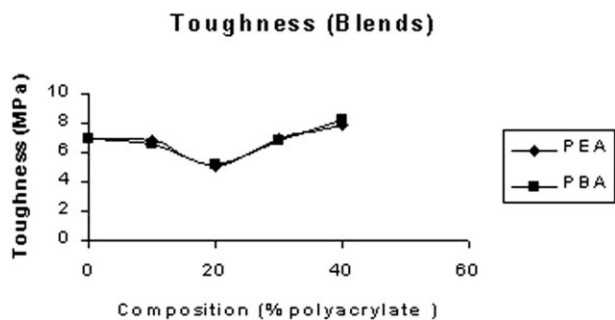
Toughness (Blends)

Figure 4 Variation of toughness with blend composition.

Specific gravity vs composition

(a)

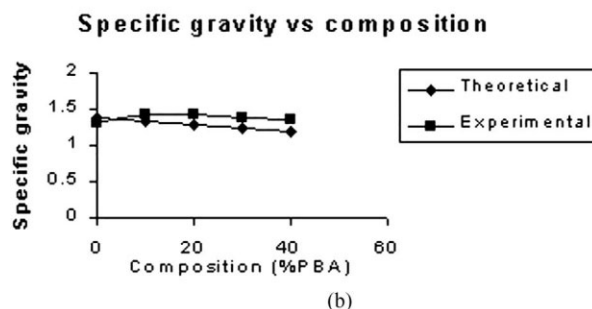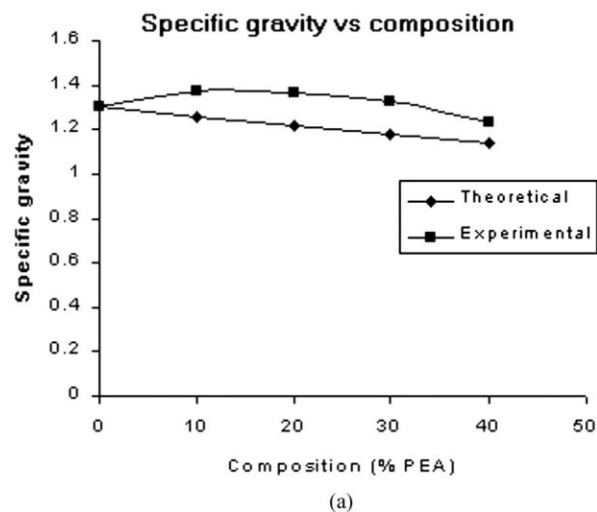**Specific gravity vs composition**

(b)

Figure 5 (a) Variation of specific gravity with PVC-PEA blend composition. (b) Variation of specific gravity with PVC-PBA blend composition.

ration is even more sharp and drastic, thus, revealing the influence of the even more rubbery PBA in modifying the tensile behavior with respect to the pure reference compound PVC.

The changes in EB and toughness are in accordance with the changes in modulus and UTS, as shown in Figures 3 and 4, with the exception of some contradiction at initial stages where we can find very little changes up to a concentration of about 20% of PEA and PBA incorporation. It may possibly be argued that, within this range of concentration, there has been an increase in the packing density as has already been mentioned, and proper free volume for chain slippage has not been generated. However, beyond the threshold concentration of the polyacrylates (around 20%), there has been a steady increase in EB%. The blends of PVC-PBA, however, exhibit marginally higher elongation than do the PVC-PEA blends at higher doses of the polyacrylates, which appear to be quite obvious because of the more rubberiness of PBA.

The toughness of the PVC-PEA and PVC-PBA blend systems also demonstrates a similar pattern like that of changes in EB%. Thus predominance of the interactive secondary valence forces over the expected softening because of the plasticizing effect of the polyac-
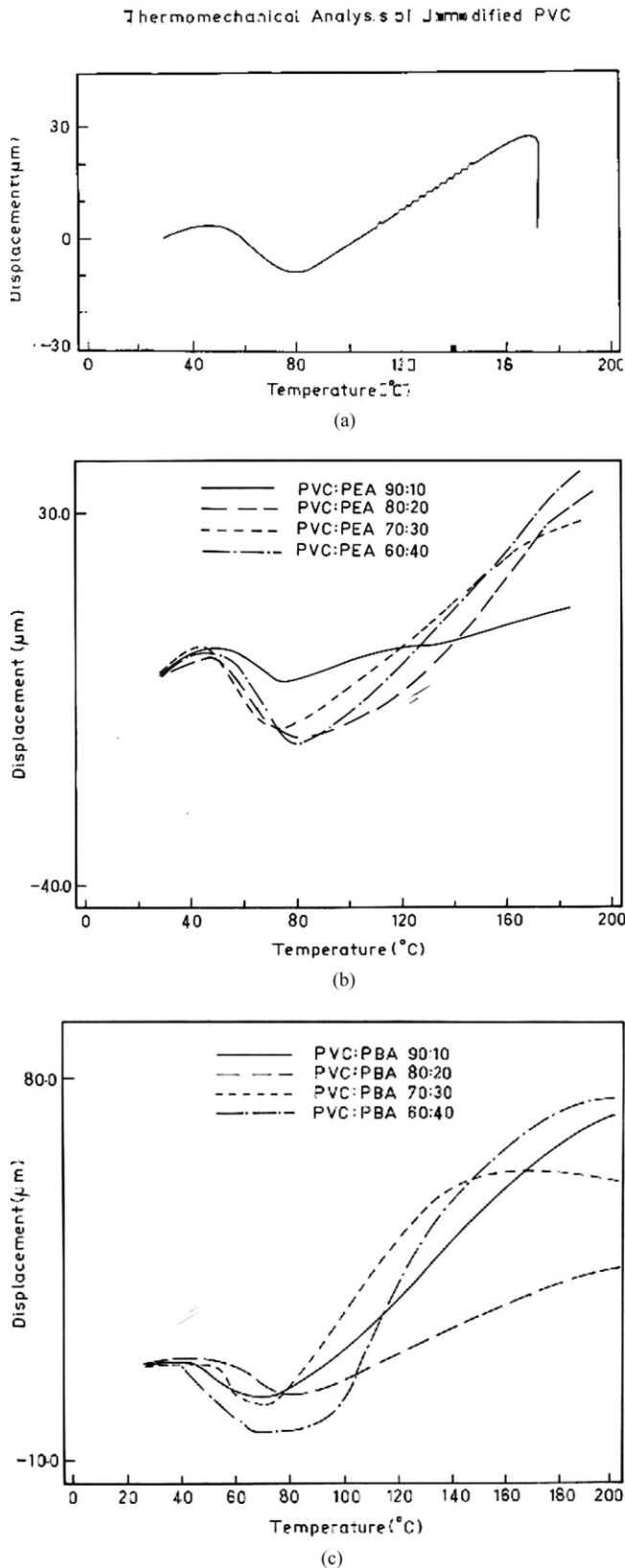
Figure 6 (a) TMA plots for the pure reference compound PVC. (b) TMA plots for PVC-PEA blends. (c) TMA plots for PVC-PBA blends.

rylate chains is demonstrated at the earlier stages of acrylic incorporation, followed by the classical mechanism of rubber toughening once an optimum concentration of PEA and PBA is reached.[11,12]

It is quite interesting to note that the specific gravities of the various blends of different composition under study always lie above the theoretically predicted values for the blends under consideration (Fig. 5). This is also indicative of some sort of secondary interactive forces through hydrogen bonding between the two polymers. The extent of bonding goes through a maximum and then decreases with increasing PEA and PBA content, possibly because of the decreasing availability of the proportionate amount of PVC at the later stages, when the experimental values almost merge with the theoretical ones within the ranges of concentration studied. Thus, though the PVC chains are expected to be thrown apart by the plasticizing influence of the polyalkyl acrylate moieties, the chains appear to concentrate because of this secondary valence force and, hence, a rise in specific gravity is observed.[13]

It is also interesting to note that when compared to the PVC-PEA blend system, the experimentally determined figures for PVC-PBA system lie marginally above the theoretical curve, which may possibly be ascribed to the fact that the extent of H bonding in such case is however limited by the sterical hindrance of the relatively bulkier butyl group.

Thermomechanical study

The thermomechanical data of both the types of blends under consideration reveal that the probe is slightly pushed up by the expansion of the samples up to a temperature around 50°C, displaying marginal expansion (Fig. 6). The onset of softening is followed by the penetration of the probe into the samples at a rate inversely related to their moduli. This is further followed by the expansion of the samples up to the temperature under consideration, displaying characteristic stability over unmodified PVC.[14,15]
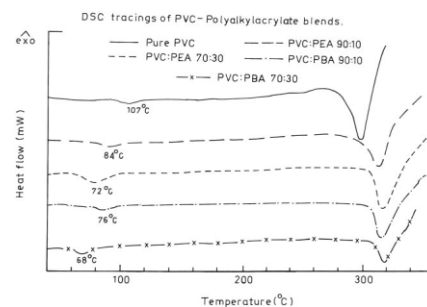

Figure 7 DSC tracings of reference compound PVC, PVC-PEA, and PVC-PBA blends.
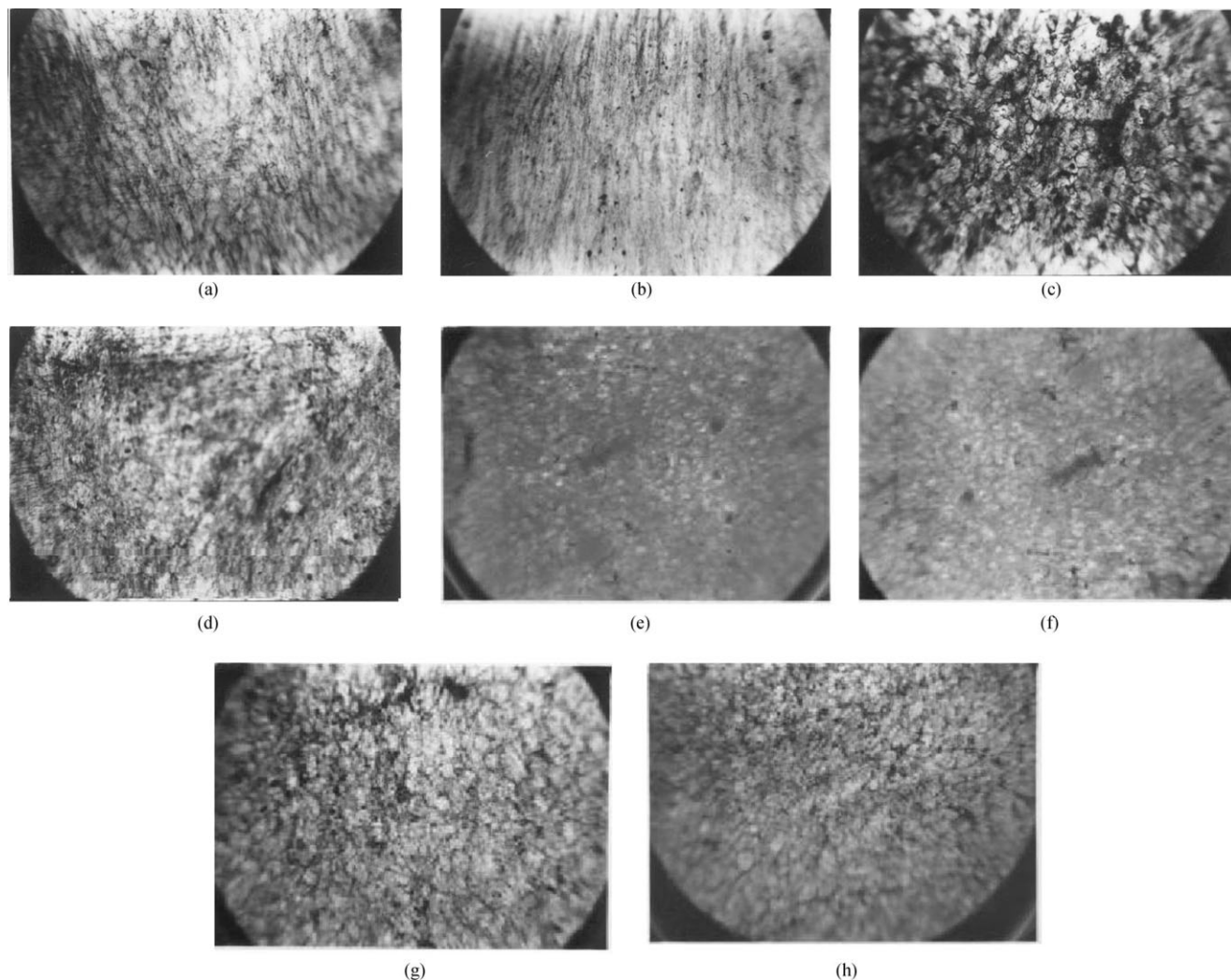
Figure 8 Optical micrographs of the blend systems. Optical micrographs of (a) PVC:PEA (90:10), (b) PVC:PEA (80:20), (c) PVC:PEA (70:30), (d) PVC:PEA (60:40), (e) PVC:PBA (90:10), (f) PVC:PBA (80:20), (g) PVC:PBA (70:30), and (h) PVC:PBA (60:40).

It is quite apparent that the softening range of the blends gradually widens with increasing proportion of *in situ*-formed PEA. The initial softening that appears to commence at around 50°C (for almost all the blends) is found to be shifted for the individual blend under study. The extent of shifting (the point beyond which the expansion starts) increases with increase in PEA content. In this context, it is also clear that the degree of softening (as given by the depth of penetration calculated from the initial starting point) is also a function of PEA content in the blend. It is also interesting to note that the nature of expansion, the rate of expansion per degree in particular, changes in a regular manner with increasing proportion of PEA within the range of temperature considered. From the slopes of different curves, it can be seen that beyond the peak softening temperature, the 60:40 blend appears to have the highest coefficient of expansion, while the 90:10 blend has the least.

The softening point of different blend systems gradually increases in a regular manner as the nPBA content increases. The rate of expansion beyond the softening point is found to be a function of composition and hence the nPBA content. The resistance offered by the blends at lower level of incorporated PBA is found to be gradually lost as the PVC content in the blend decreases (in other words, as the nPBA content increases), a phenomenon which is manifested by the gradual steepening of the curves with higher doses of nPBA.

DSC study

The DSC curves of the thoroughly dried representative samples of PVC-PEA and PVC-PBA blend systems (ratios considered in both the cases being 90:10 and 70:30, respectively) are depicted in Figure 7. The glass transition of PVC appears to remain almost un-

affected at the initial stages of the polyacrylate incorporation. Thus it is observed that although the T_g of PEA and PBA differ widely, they could hardly influence that of the pure PVC. However, at the later stages, the glass transition of PVC decreases. As expected, the plasticizing influence of PBA on PVC appears to be more pronounced particularly at the higher level of its incorporation when compared to that of PEA.[16]

The degradation characteristics of the systems, as revealed from the DSC studies at higher temperatures, exhibit increasing stability of the blended systems over that of the pure reference compound PVC. This again conforms to our earlier observation on the thermomechanical results, wherein unmodified PVC compound is found to show poor stability. In contrast, the blended samples remained unaffected at the higher experimental temperature (as PVC) under study.

Morphology

The optical micrographs of the system under consideration display homogeneity up to an optimum level of the polyacrylate incorporation, followed by the typical structure of a heterogeneous polymer blend (Fig. 8), with characteristic sharp boundaries between the two phases. The compatibility and homogeneity as observed at the lower level of PEA and PBA incorporation are however absent at the higher levels, owing to the phasing out tendencies and agglomeration of the dispersed rubbery phases, which is again reflected by the fall in the mechanicals after an optimum range of the polyacrylate incorporation.[17,18]

In case of PVC-PEA system, the dispersed PEA particles at their early stages of incorporation in the PVC matrix appear to be present in both diffused and phase separated particles, the extent of which gradually increases at the cost of diffused particles. Furthermore, the elongated particles at lower level of PEA content gradually give their way to the large phase-separated conglomerated particles. In case of PVC-PBA system, droplet morphologies of the dispersed PBA phase in the presence of linear PVC matrix are exhibited. At the early stages, the droplets appear to be distributed in somewhat dissolved state in the matrix, with only a few ones showing a tendency to come out of the phase. The particles are more or less uniform in their sizes and shapes. However, with increasing concentration of PBA, the distribution appears to be more multimodal, with proportionate increases in bigger droplets and an enhanced tendency toward phase separation becoming more prominent. Within

the range of PBA concentrations studied, the droplets appear to deviate from their globular characteristics and exhibit an affinity toward elongational flow. Although, at higher level of PBA incorporation, PBA phase separation becomes evident, there is always a mentionable content of dissolved rubbery phase present in the PVC matrix.[19]

CONCLUSIONS

The systems under study reveals the effect of blend formation of PVC with PEA and PBA over that of the unmodified reference compound. The introduction of the acrylate moieties into the PVC matrix raises the mechanical properties up to the threshold concentration of 20% polyalkyl acrylate incorporation and also generates thermal stability. The combination of two polymers also creates a directing influence one over the other, which is explicit from the micrographs. It is thus evident that the formation of blend has a measurable effect on the various mechanical properties and thermomechanical stability, which in turn modifies the pure reference compound PVC.

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