

Mechanical, Thermomechanical, and Morphology of PVC/PBMA Blends and Full IPNs

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Received 10 March 2005; accepted 9 June 2005

DOI 10.1002/app.22378

Published online 6 December 2005 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Blends and full IPNs' of poly(vinyl chloride) and polybutylmethacrylate (PBMA) have been synthesized and characterized with respect to their mechanical, thermomechanical, and morphological properties. Both the systems displayed a rise in the modulus and ultimate tensile strength and a consequent decreasing tendency of elongation at break and toughness are exhibited. The influence of crosslinking of the two polymers as has been done in case of full IPNs over the ordinary blends is quite well understood from these properties. The thermomechanical analysis revealed a substantial rise in stability with increasing methacrylate concentration in the system and this is quite apparent

from the softening characteristics of the different samples under study. 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 PBMA incorporation. The thermomechanical parameters are in conformity to their mechanicals which have been further supported by their morphological studies. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2033–2038, 2006

Key words: blend; interpenetrating network; poly(vinyl chloride); thermal properties; morphology

INTRODUCTION

The development of polymer blends and grafts have added new dimensions to the use of more common polymers for speciality applications. Interpenetrating polymer networks belong to the special category of polymer blends in which two crosslinked polymers are physically intertwined and one of which is crosslinked in the immediate presence of the other.¹ The present study aims at the synthesis and characterization of poly(vinyl chloride) (PVC)/polybutylmethacrylate (PBMA) blends and full IPN's (in which both the polymers are crosslinked), and a comparative study of the two with respect to the reference compound PVC. The restricted domain size of the dispersed phase in a full IPN enhances molecular mixing and thus promotes phase miscibility. It has been previously shown that in PVC/PBMA blends, the carbonyl group of the methacrylate ester moieties of PBMA acts as an electron donor and the α hydrogen of PVC as an electron acceptor that facilitates dipole-dipole interactions between the two, and thus resulting in close packing of the molecules.² However, the degree of network interlocking also has a measurable effect on the various mechanical properties such as modulus, hardness, and ultimate tensile strength.^{3–6}

Most IPNs although exhibit a greater or lesser degree of phase separation, an increased percentage of interlocking is, however, expected to improve the compatibility, which helps in preventing phase separation.^{7–13} The thermal analysis of the system under consideration is expected to show some stability over the base reference compound PVC and also reveal some significant features in interpreting the morphology.

EXPERIMENTAL

Materials

PVC (Reon) grade K67 was procured from M/s Reliance Industries Ltd., India, and was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulfate (TBLS) from M/s Kalpana Industries Ltd. (Daman, India) were used as suitable plasticizers and stabilizers, respectively. Diallyl phthalate (DAP) from M/s Burgoyne was used as a crosslinker for PVC.

Butyl methacrylate (BMA) from Berger Paints of India Ltd. 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 dried over fused CaCl_2 . It was finally vacuum distilled. Benzoyl peroxide from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Al-

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drich Chemical Company Inc., USA, was used as the crosslinker for PBMA.

Synthesis of blends and full IPNs

A weighed amount of purified BMA was taken in a test tube and thoroughly mixed with 2% by weight (based on BMA) 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 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.

The full IPN's were made by adding 2% by weight of acrylic crosslinker and five parts of DAP (with respect to the weight of PVC taken) in addition to the process followed for preparing blends, the other conditions however remained unaltered.

Conditions of molding

Initially, the mold was compressed under a pressure of 15 tons/cm² at a temperature of 80°C to initiate and propagate acrylic polymerization. This was allowed to continue for 30 min for acrylic polymerization to be initiated and propagated to a measurable extent. 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 polymerization in case of blends and crosslinking of both PVC and PBMA in case of full IPN's. The mold was then allowed to cool down at room temperature and the molded sheet ejected.

Measurements

Mechanical testing

An 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 using the method of ASTM D638. A cross head speed of 3 mm/min was maintained. All testings were carried out at room temperature. Toughness of the 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 measure-

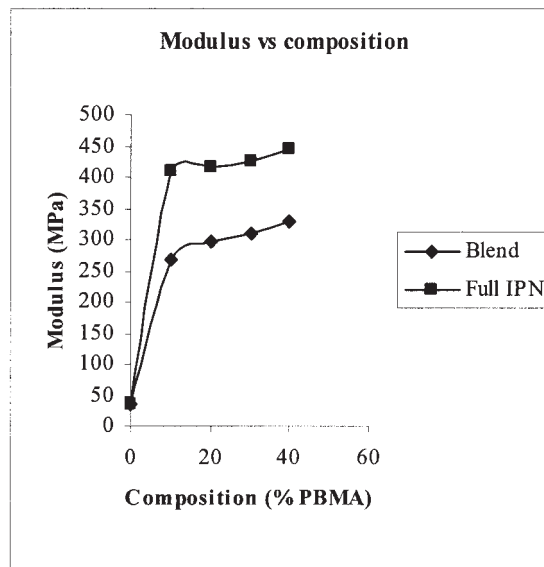


Figure 1 Variation of modulus of blends and full IPNs with composition.

ments, and typical scattering range of the results was $\pm 5\%$.

Specific gravity

The specific gravity of the various blends and IPN's was determined by following the Archimedes' principle.

Thermomechanical testing

The thermomechanical analysis of the various samples were carried out in a thermomechanical analyzer from Shimadzu (model TMA 50) in presence of oxygen. The thermooxidative characteristics were studied under a constant load of 8 g throughout the experiment using a compressive mode of probe upto 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.

Morphology

The scanning electron microscope (SEM) (model Hitachi S415A) was used for morphological studies after suitable gold coating on the samples.

RESULTS AND DISCUSSION

Mechanical properties

Both the modulus and the ultimate tensile strength of the blends and full IPN's show an increasing tendency with increase in percentage of methacrylate within the

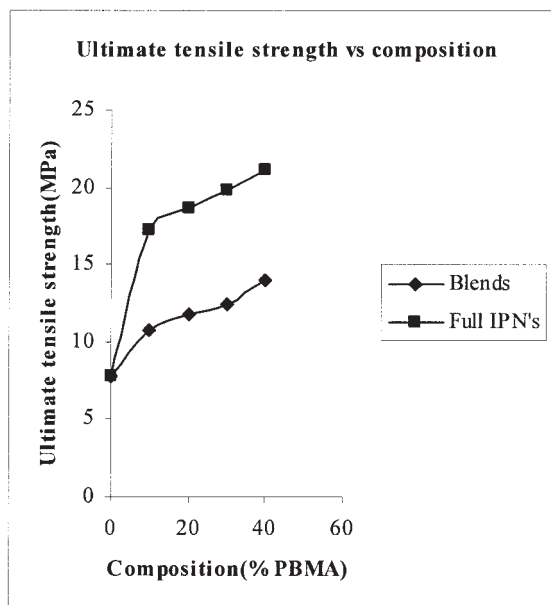


Figure 2 Variation of ultimate tensile strength of blends and full IPNs with composition.

range of concentration studied, as shown in Figures 1 and 2. The carbonyl group of the PBMA ester moieties formed in situ acts as an electron donor and the α hydrogen of PVC as an electron acceptor.¹ This induces dipole–dipole attraction between the two polymeric phases, which is supposed to enhance molecular interaction. The modulus and UTS of the blend and full IPN samples exhibit a steady rise initially up to a level of about 10% of PBMA incorporation compared with plasticized PVC alone without any modifying resin. This is somewhat contrary to the normal expectation, where the rigid molecular chain structure is expected to be somewhat degraded with the incorporation of PBMA and a normal reduction in strength properties was supposed to be imminent. In contrast, we find an enhancement in properties, and this may possibly be attributed first to the new dipole–dipole interaction generated between the carbonyl group of the methacrylate and the α hydrogen of PVC and second to the directing influence of the modifying PBMA resin. The α hydrogen of PVC is suggested to form a hydrogen bond with the ester carboxylate group (H bond acceptor of the acrylic polymer), and hence forms the key factor in achieving miscibility.^{14–17}

The modulus and the UTS values of the full IPN's are somewhat higher than that of the corresponding blends. This may be due to the consequent interwinding of the individual phases and the formation of crosslinks, which reduces the flexibility and introduces rigidity and stiffness to the existing linear chains of PVC and PBMA. The effect of dipole–dipole interaction and H bonding as encountered in blends has been further synergized by the influences of the

crosslinks present in the cocontinuous intertwined matrices. The values of these two mechanical aspects increase progressively with increase in % PBMA of concentration in composition. The somewhat slow and steady rise in these two mechanical aspects beyond an optimum concentration of around 10% at a remarkably reduced rate with respect to the one observed earlier might possibly be attributed to an equilibrium reached between the rate of breakdown of the regular chain structure of PVC and the formation of more and more H bonds between —C=O group of methacrylate α hydrogen of PVC, as discussed earlier.

The elongation at break and toughness of the various samples as explicit from Figures 3 and 4 show somewhat increasing trend initially followed by a steady fall as expected along with increasing percentages of PBMA. The incorporation of PBMA molecules into the continuous matrix of PVC disrupts the structural chain regularities of PVC, which breaks down the molecular packing as evidenced from the specific gravity curves (Fig. 5), and provides a greater path length (path around the periphery of the dispersed particles) for dissipation of energy before its ultimate rupture. In case of full IPN's, the incorporation of the crosslinked dispersed phase, however, also induces some fibrillar characteristics into the system as observed from the scanning electron micrographs (Fig. 7). This effect appears to develop cocontinuity in phase structure of the resulting IPN. PVC undergoes deformation by shear mechanism and therefore produces a ductile response to tensile loading.^{18,19} This is further expected to be enhanced by the slippage of one fibril over the other, which raises its elongation before

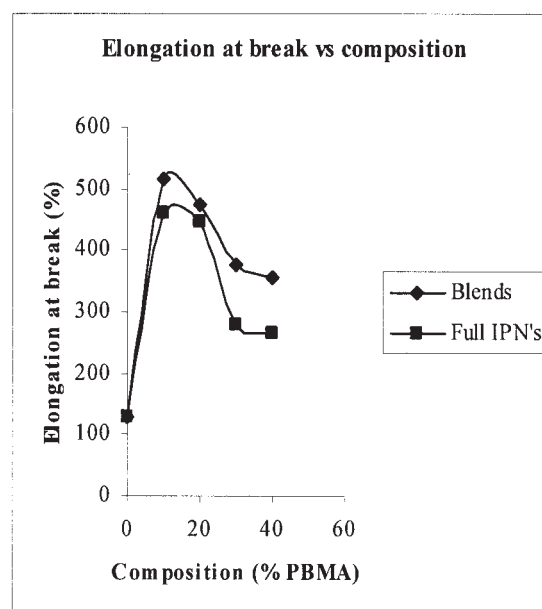


Figure 3 Variation of elongation at break of blends and full IPNs with composition.

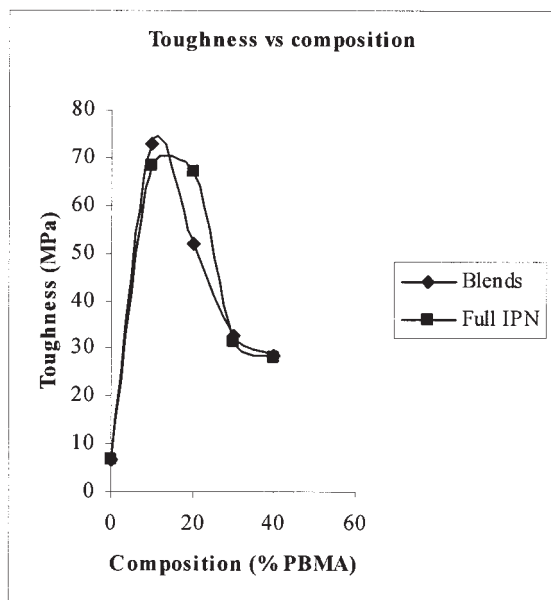


Figure 4 Variation of toughness of blends and full IPNs with composition.

rupture. The combined effect of these two conditions results in an increased elongation at break and toughness values upto a level of about 10% PBMA incorporation.

The decreasing trend of these two parameters at the latter stages are, however, in conformity to our expectations. The PBMA molecules within the matrix of PVC provide some stress concentration points. The frequency of these stress concentrators increases with rising PBMA content. Besides the PBMA particles acting as stress concentrators, the statistically formed occasional H bonds stand in the way of elongation.

Specific gravity

The decreasing trend of specific gravities of both the systems with increasing PBMA concentration are depicted in Figure 5. This can be quite well explained from the fact that the entry of PBMA molecules within the PVC unmodified matrix (without any modifying resin) throws apart the regularly arranged chains of PVC and breaks up the molecular alignment to a certain extent. This increases the intermolecular spaces and occupies more volume. This is further raised with the rise in methacrylate content. The specific gravities of the systems under consideration are thus reduced.

However, the full IPN's exhibits somewhat sharper decreasing trend than the blends, which may be possibly due to the higher compactness of the molecules originating from the dual crosslinking of PVC and PBMA chains.

Thermomechanical analysis

The thermomechanical data of the various blend and IPN samples have been shown in Figure 6. In case of

blends, the probe is very slightly pushed up by the expansion of the samples upto a temperature around 50°C displaying marginal expansion, excepting the sample of 90:10 composition that shows continuous expansion at a faster rate after displaying a small extent of softening at around 60°C. The onset of softening exhibited by the other blends is followed by the slow and gradual penetration of the probe into the samples reaching its maximum at the final softening point showing characteristic stability of the samples with increasing percentage of PBMA concentration. The higher softening temperature range with increase in proportion of PBMA in composition accounts for increased stability of the PVC matrix. The chloride radical Cl causes the PBMA chains to break and subsequently unzip quite readily at low temperatures.^{20,21} The unzipped monomer is also considered to be a very good radical scavenger, and thus scavenges the chloride radicals immediately as they are formed in the system. The PBMA molecules thus exert a stabilizing action over unmodified PVC, which is further raised with increasing content of PBMA.

The full IPN's on the other hand does not display an expansion around 50°C, but exhibits expansion of the samples initiating at a temperature of around 80°C. The rate of expansion decreases progressively with increasing percentage of PBMA concentration. The formation of crosslinks of the two polymeric phases possibly arrests the expansion of the samples at the earlier stages. The rise in the concentration of methacrylate ester raises the stability of PVC matrix and consequently lowering the rate of expansion correspondingly as is evidenced from the Figure 6. The full

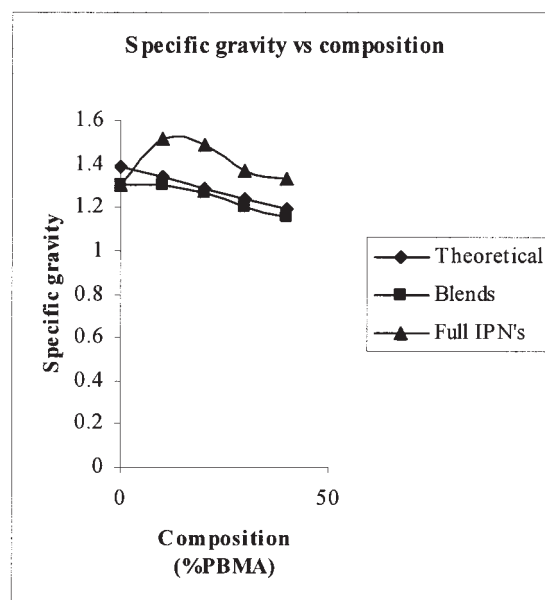


Figure 5 Variation of specific gravity of blends and full IPNs with composition.

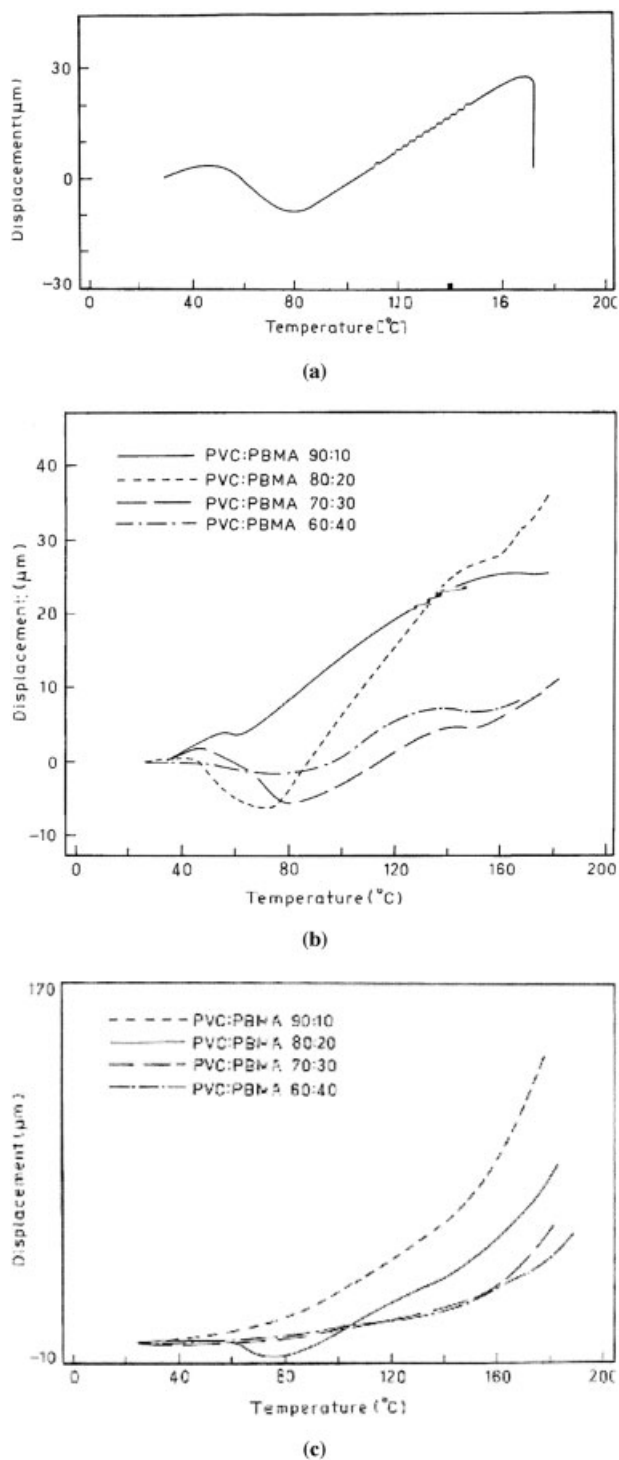


Figure 6 (a) Thermomechanical analysis of pure base compound PVC, (b) thermomechanical analysis of blends, (c) thermomechanical analysis of full IPNs.

IPN's thus appears to be relatively more stabilized with respect to the blends alone. Furthermore, the softening range of the full IPN samples appear to be much wider with little or no changes particularly in the temperature region, where the different blend samples almost softened completely.

Morphology

Scanning electron microscopy

The SEM micrographs shown in Figure 7 clearly indicate changed surface morphologies of the various blends and full IPN systems along with composition. The PBMA phase is dispersed almost uniformly within the PVC network as has been envisaged by the fibril shaped white phase. With the increase in crosslinked PBMA content in full IPNs, somewhat changed dispositions are observed. The whitish PBMA phase (fibrillar in shape) either becomes thick or tends to form kinks. However, during the initial stages of PBMA incorporation, a tendency toward intermingling (mixing) with the crosslinked PVC is displayed by the gradual diffusing nature of the fibrils toward their respective ends. The formation of fibrillar PBMA phase is almost always attended with macro phase separated irregularly shaped globules of PBMA that is present to a greater or lesser degree in all the IPN samples. Toward the higher end of PBMA incorporation, a mosaic or tile type distribution pattern is observed, which might be expected to enhance the mechanical properties by way of easy stress distribution through them. The behavioral aspect of distribution appears to be more pronounced in case of blend formation although at the initial stages, somewhat occluded domain structure is observed where some-

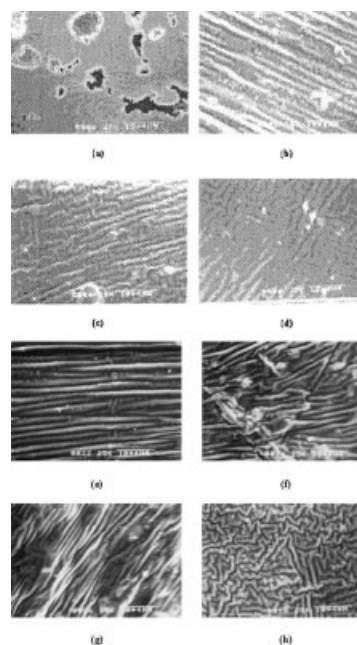


Figure 7 Scanning electron micrographs for blends and full IPN systems. (a) PVC : PBMA blend 90 : 10, (b) PVC : PBMA blend 80 : 20, (c) PVC : PBMA blend 70 : 30, (d) PVC : PBMA blend 60 : 40, (e) PVC : PBMA full IPN 90 : 10, (f) PVC : PBMA full IPN 80 : 20, (g) PVC : PBMA full IPN 70 : 30, (h) PVC : PBMA full IPN 60 : 40.

times substantial proportion of PVC gets entrapped within a boundary wall of PBMA. These enclosed domains vary in their sizes and shapes possibly because of localized agglomeration of the PBMA phase.

The formed elongated fibrils in full IPNs appear to extend although the PVC matrix in which the degree of orientation of the fibrils decreases with increase in proportion of PBMA. The fibrillar structure is more compact and dense in case of full IPNs, as expected.

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