Chemical Science Review and Letters ISSN 2278-6783

Research Article

Physico-Mechanical and Thermal properties of PVC-PEMA Full Interpenetrating Polymer Networks in relation to their Morphologies

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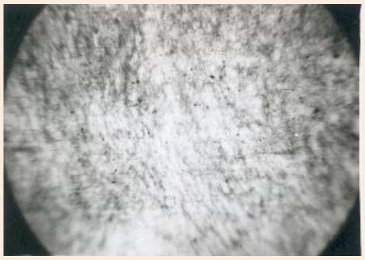
Abstract

Polyvinyl chloride (PVC) and polyethyl methacrylate (PEMA) are blended to form full interpenetrating polymer networks (IPNs) using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDMA) as the cross linkers of PVC and PEMA respectively. The full IPNs have been synthesized to investigate any modification of properties over PVC. PVC along with plasticizers and heat stabilizers was mixed with ethylene methacrylate monomer in definite proportion along with the respective cross linkers of the polymers. The mass was then subjected to polymerization followed by subsequent cross linking of the two polymers. The full IPNs so formed exhibited a drop in modulus and ultimate tensile strength up to 10% of PEMA incorporation after which it exhibited a steady rise with higher percentages of PEMA. The elongation at break and toughness however displays a steady rise followed by a reduction but the values throughout remains above unmodified PVC. The thermal behavior as revealed by the thermomechanical analysis curves and differential scanning calorimetric results show modification of properties in their glass transition and degradation temperatures. The morphologies as envisaged by the scanning electron microscopy and optical microscopy maintain relevant conformity with the mechanicals.



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Keywords: Polyvinyl chloride, Polyethyl methacrylate, mechanical properties, thermal properties.

Introduction

Interpenetrating polymer networks constitute the class of polymer networks where two cross linked polymer networks are physically interpenetrated and at least one of which is cross linked in the immediate presence of the other. Cross linking the polymeric chains provide an important way of diversifying the physical and chemical properties of polymers. The mechanical and thermal properties are generally enhanced at the cost of processibility of the polymers. The cross linking technology is investigated as a major tool in case of PVC to enhance its applicability [1]. The degree of interlocking between the components has a measureable effect on the various mechanical properties like the modulus, ultimate tensile strength and hardness. Increased network interlocking is expected to improve the compatibility [2]. Because of their interlocking configuration, the extent of phase separation is frozen in such that the properties are not influenced by subsequent ageing. The properties are influenced by the two phase morphology that develops during IPN formation.

PVC is commonly used as a general commodity plastic because of its excellent electrical and corrosion resistance, self extinguishing characteristics, low cost and recoverability [3]. But its low impact strength and poor thermal stability poses a limitation on its applications. The inherent problems of processing rigid PVC are also quite well known and are overcome by the use of certain plasticizers. In such a case there is every possibility of compromising on the mechanical properties of rigid PVC. In our study, we have tried to modify PVC by incorporating polyethyl methacrylate as the polymeric modifier wherein it is supposed to improve the processibility and the thermal characteristics by way of full IPN formation. Paul and Barlow have suggested that the α hydrogen of PVC can interact with the ester carboxylate group (H bond acceptor of the acrylic polymer) to form hydrogen bond and is also a key factor in achieving miscibility [4]. Also, there is a probability of interaction between the C-Cl dipole of PVC and the hydrogen of the methacrylate ester. These two phenomena can account for increased strength of the IPNs and thus interpenetrating networks of PVC and PEMA can be expected to display improved tensile as well as toughness behavior [5].

The present study focuses on the full IPN formation of PVC and PEMA where both matrices are cross linked in order to balance the processibility with the physico-mechanical properties. The IPNs formed were characterized with respect to their mechanical and thermal properties and a correlation was established with the obtained morphology.

Experimental

Materials

PVC (Reon) grade K 67 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. Benzoyl peroxide from Loba Chemie (India) was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company Inc. was used as the crosslinker for PEMA.

Synthesis of full IPNs

A weighed amount of purified monomer was taken in a test tube and thoroughly mixed with 2% by weight (based on monomer taken) of recrystallized Bz_2O_2. 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. 5 parts by weight of DAP w.r.t. PVC was then added in the mix. The monomer containing initiator was then added to the premix of PVC. EGDM to the extent of 2% by weight of the monomer taken was initially added to the monomer mix. Dry mixing was further continued unless a thoroughly mixed powder was obtained.

Conditions of Molding

The powdery mix obtained as above was compression molded into sheets by subjecting a three piece mould under pressure and heat in two stages. Initially, the mould (0.95 m x 0.65 m x 0.001 m) was compressed under a pressure of 15 tons/cm^2 at a temperature of 80ºC to initiate and propagate acrylic polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160ºC while the pressure was maintained at the same level. The mould was then allowed to cool down to the room temperature and the molded sheet ejected.

Characterization

Mechanical properties

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like modulus, ultimate tensile strength, elongation at break and toughness. In the process of measurement, ASTM D638 method was followed.

Thermal properties

The thermomechanical analysis of the various samples of PVC (containing plasticizers and stabilizers in proportion to which they are present in the samples) 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 0.008 kg throughout the experiment by using a compressive mode of probe upto a temperature limit of 180ºC following a temperature program in which a heating rate of 10ºC/min was maintained right from the ambient temperature.

The differential scanning calorimetry (Mettler 822e) of the samples was carried out up to a limit of 350ºC at a heating rate of 10ºC/min 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 0.005 to 0.008 gm.

Morphology

Scanning electron microscopic studies were carried out in a scanning electron microscope (Hitachi model S415A) after suitable gold coating on the samples. Completely dried samples were coated with a thin layer of gold using a high vacuum gold sputtered. The fractured surface of a tensile fracture specimen was inspected for morphology. The scale of magnification was 500X.

An optical microscope from Krüss (optromic) (Germany) was used to study the surface morphology of the undeformed samples having thickness < 0.5 mm to get a relative idea of the mode of distribution of domains, sizes of the domains, physical state of the domains and mode of their growth as dictated by the method of synthesis, compatibility, etc. The scale of magnification used was 200 X.

Results and Discussion

Mechanical Properties

The mechanical properties of PVC-poly(ethyl methacrylate) full IPNs as depicted in figures 1 and 2 reveals decreasing order of modulus and ultimate tensile strength values with increasing concentration of PEMA upto a concentration of 10% of PEMA incorporation beyond which there is a slow and steady rise in the mechanicals under study. The sharp initial reduction is due to the breakdown in the regular crosslinked chain structure of PVC which is far less than compensated by the crosslinked PEMA moieties [6]. But at the later stages two opposing forces namely the chain disruptive forces exerted by the incorporation of PEMA into the regular chain structure of PVC and the formation of close, compact matrix by the way of crosslinking within itself are operative and it appears that the combined effect of crosslinking of both the matrix and the dispersed phase predominate in influencing the mechanicals at the later stages.

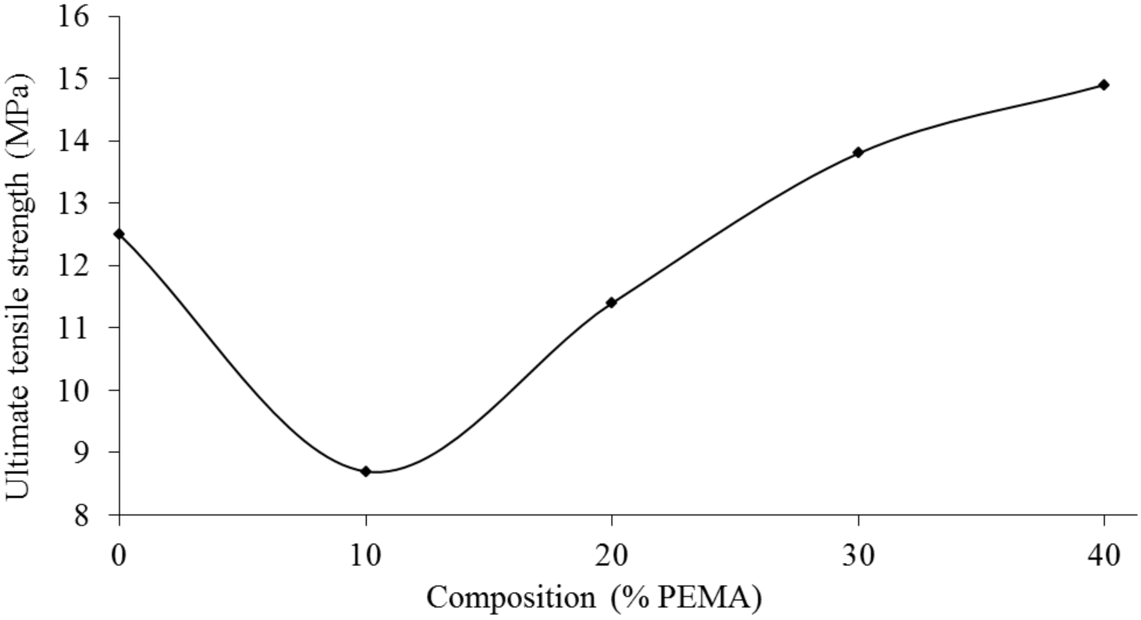


Figure 1 Variation of Young's modulus of PVC-PEMA full IPNs

The elongation at break and toughness of the system under consideration in figures 3 and 4 show somewhat increasing trend initially followed by a steady fall as expected along with increasing percentages of the polymethacrylate into the system. With the introduction of crosslinked PEMA moieties within the crosslinked network of PVC, the molecular alignment gets disrupted and crosslinked PEMA gets interpenetrated. Although these dispersed PEMA acts as stress concentrators, they also help in absorbing the crack propagation energy and thus raise the % EB and toughness up to a level of around 10% of PEMA incorporation. Beyond this, the IPN compositions having more and more PEMA loses ductility owing to the presence of higher compact and crosslinked PEMA content, thus allowing the PVC chains to come closer and widen the possibility of intermolecular crosslinking [7]. This also leads to more and more interpenetration as can be envisaged from their respective scanning electron micrographs.

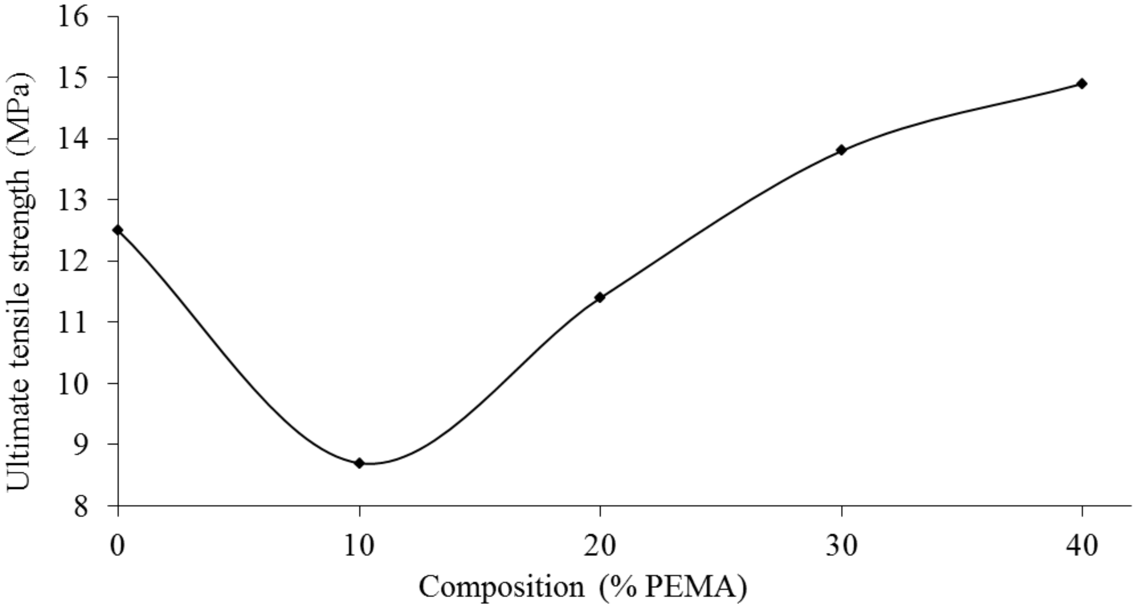


Figure 2 Variation of ultimate tensile strength of PVC-PEMA full IPNs

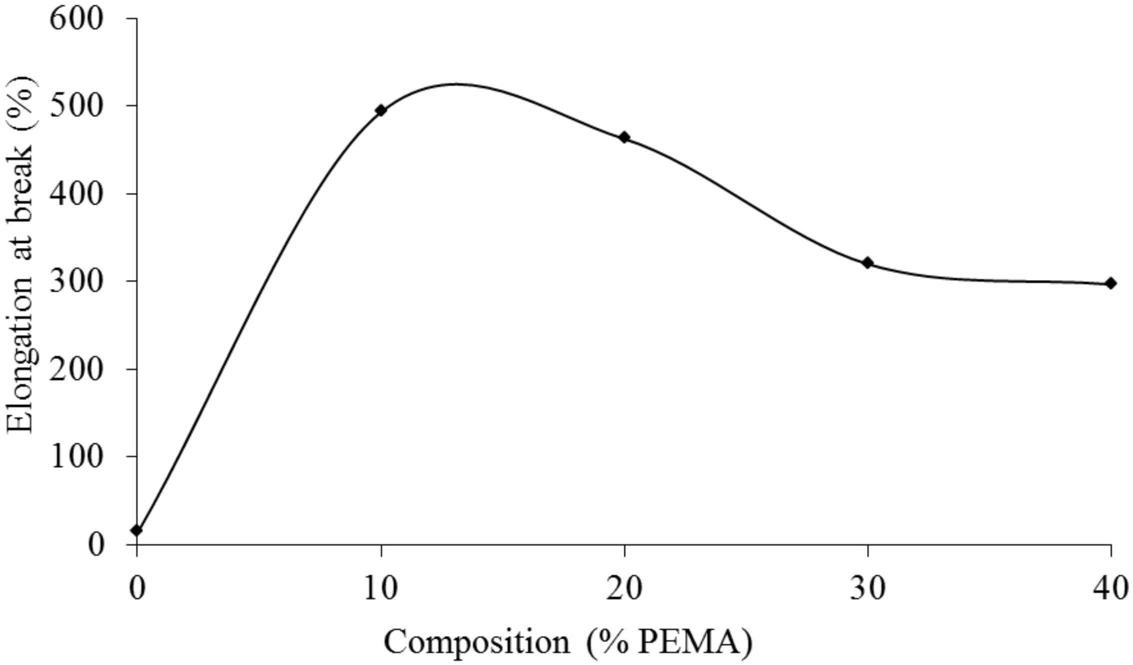


Figure 3 Variation of percent elongation at break of PVC-PEMA full IPNs

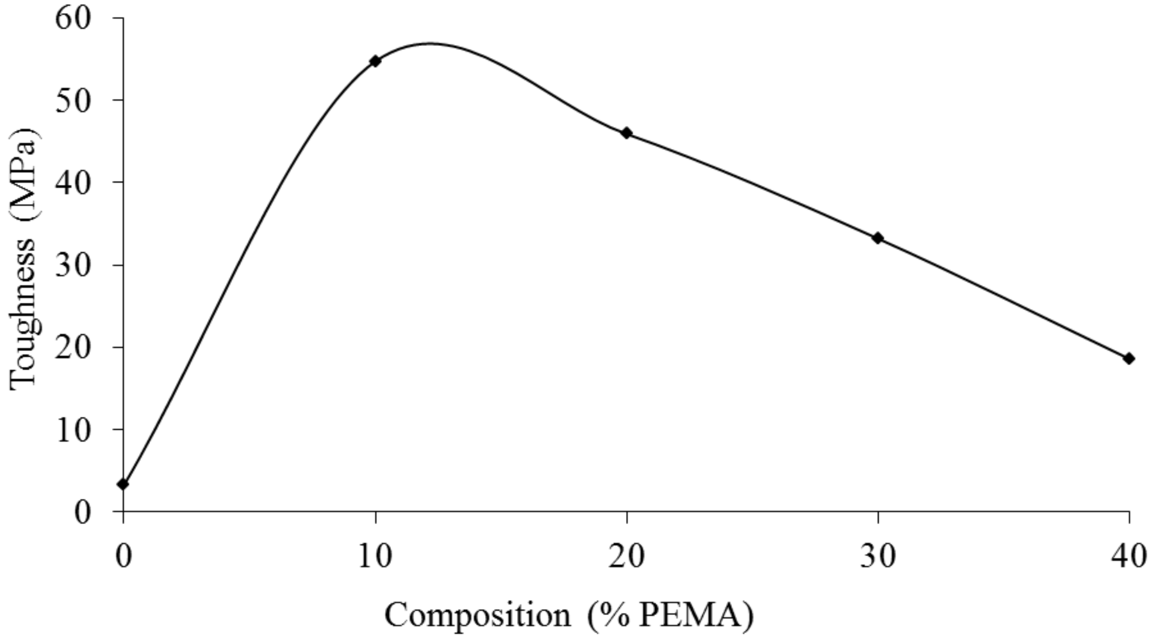


Figure 4 Variation of toughness of PVC-PEMA full IPNs

Thermal Properties

Thermomechanical analysis: The thermomechanical data of the various full IPNs as in figure 5 under consideration indicate that in all cases, the probe is slightly pushed up by the expansion of the samples up to a temperature around 50ºC displaying marginal expansion. The onset of softening is accompanied by the simultaneous penetration of the probe into the samples at a rate inversely related to their moduli [8]. However, both the phases being crosslinked in this case, the initial expansion around 50ºC and the penetration of the probe are however limited as the systems develop somewhat compactness in structure and offers resistance towards penetration respectively. The full IPNs exhibit relative stabilization over unmodified pure reference compound PVC.

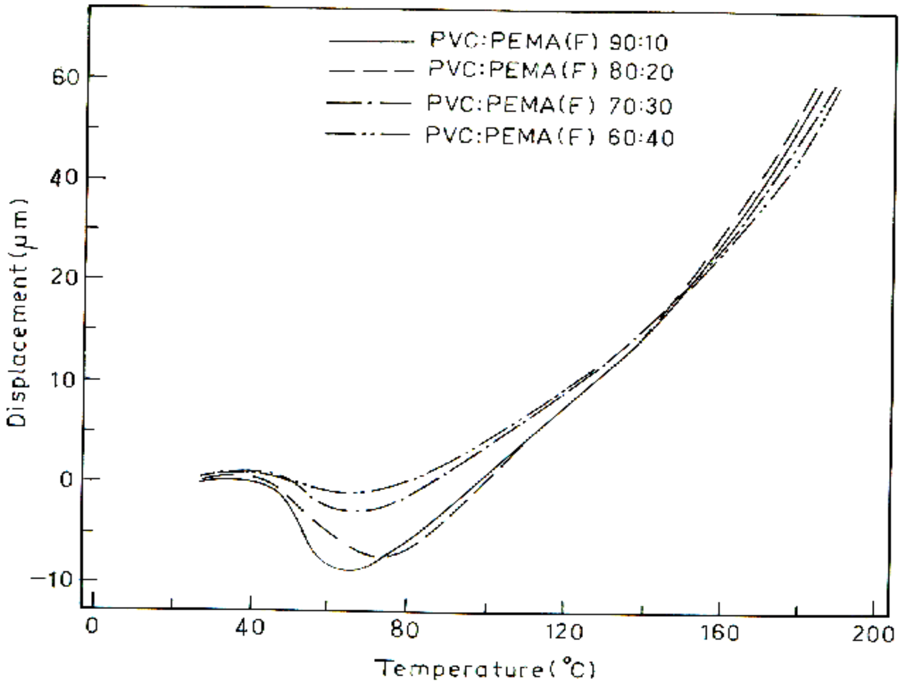


Figure 5 Thermomechanical curves of PVC-PEMA full IPNs

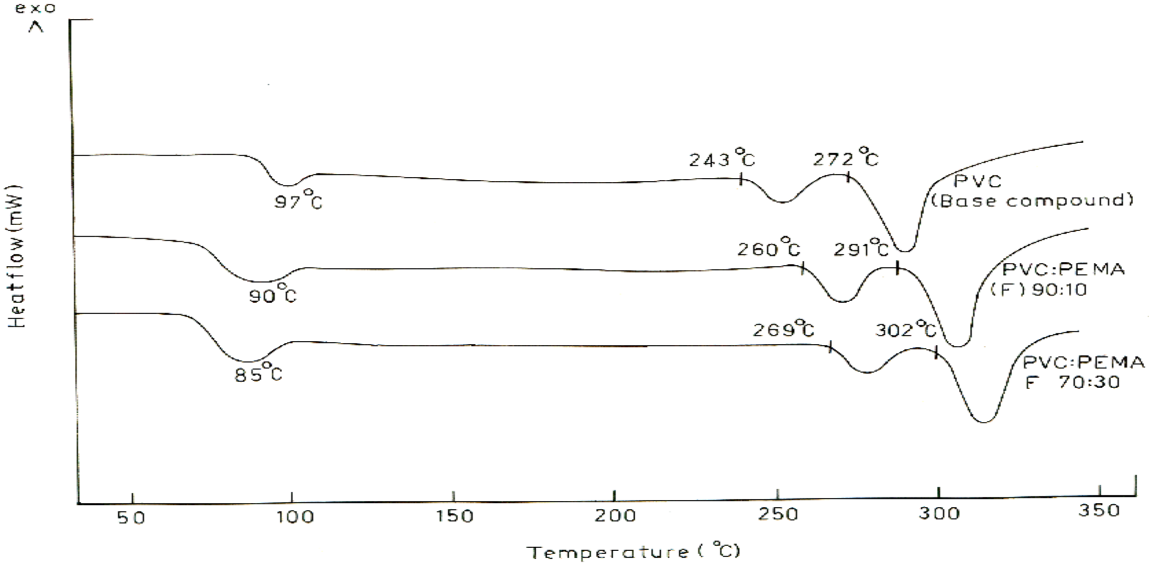


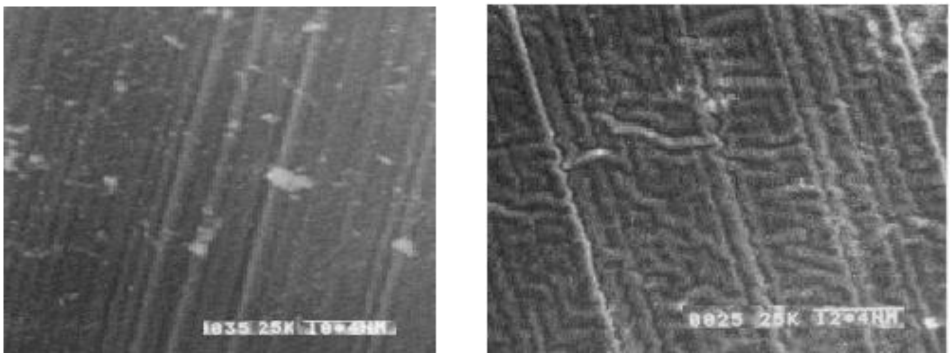
Figure 6 DSC curves of PVC-PEMA full IPNs

Differential scanning calorimetry

The DSC tracings as depicted in figure 6 denotes increasing trend of plasticization along with increasing concentration of the modifying crosslinked PEMA resin. The generation of cross links within the major and minor phases individually appears to influence the glass transition temperature and the consequent onset of degradation very little. However, the PEMA incorporated PVC (both phases crosslinked) exhibit delayed onset of degradation temperature compared to pure PVC [9]. The two stage of degradation are manifested and in both cases we can find an increase in temperature of incipience of degradation.

Morphology
Scanning electron microscopy

The scanning electron micrographs as in figure 7 of the system under consideration reveal phase heterogeneity in the form of fibrillar structures. The fibrils of the phases of full IPNs appear to be more distinct and prominent at the later stages. Some of the fibrils which are relatively short appear to be dissolved in the matrix along with some bigger and smaller droplets and thus conforming the observed ductility [10]. The regular lamellar arrangement of the fibrillar layers become thick and thin and finally lead to be kinked as it gets entangled with the major matrix with increasing PEMA content.

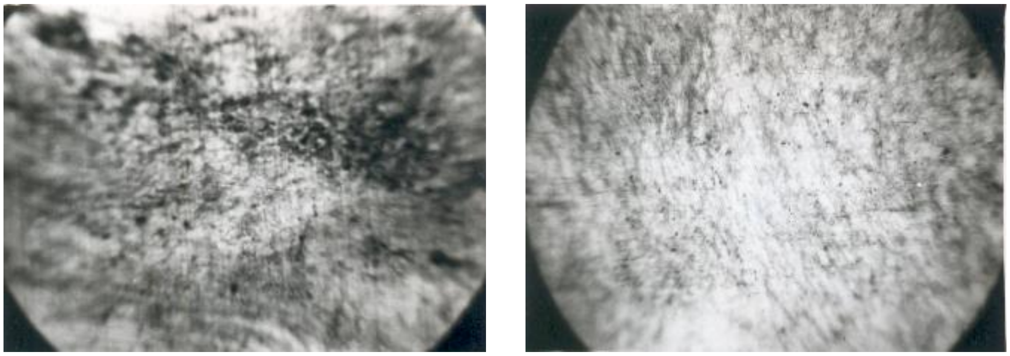


PVC:PEMA (F) 90:10 PVC:PEMA (F) 70:30

Figure 7 Scanning electron micrographs of PVC-PEMA full IPNs with magnification 500X

Optical microscopy

The optical micrographs of the PVC-PEMA full IPN system, as shown in figure 8, display a discontinuous irregular distribution of the PEMA phase in a crosslinked PVC matrix at the very early stages of PEMA incorporation. A random distribution of cells of varying sizes are found in which the dispersed phase forms the cell walls which sometimes coalesce with neighboring cell walls. With increase in PEMA content however uniformity in distribution appears to develop and the cells also become more and more regular. At higher levels of incorporation the cells appear to be depleted and some portions of PEMA appear to be dissolved in PVC.



PVC:PEMA (F) 90:10 PVC:PEMA (F) 70:30

Figure 8 Micrographic morphologies of PVC-PEMA

Conclusion

The present study deals with the modification of PVC with PEMA by the formation of full IPNs with both the matrices. It has been observed that the mechanical properties display a dynamic behaviour with the quantity of PEMA incorporated and there is an improvement in mechanical properties in terms of ultimate tensile strength, elongation at break and toughness than unmodified cross linked PVC. There has been a notable modification in thermal behaviour where thermal stability is exhibited in the full IPNs depending on the dose of PEMA incorporation. The studies have been confirmed by TMA and DSC analysis. The morphology supports the observed mechanicals which is explicit from the scanning electron and optical microscopy.

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Publication History

Received	15th Mar 2014
Revised	28th Apr 2014
Accepted	30th Apr 2014
Online	26th May 2014