

Mechanical, thermal and morphological behavior of PVC-Poly(ethyl acrylate) full IPNs

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ABSTRACT: Full interpenetrating polymer networks (IPNs) of polyvinyl chloride (PVC) and polyethyl acrylate (PEA) were synthesized using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDMA) as the cross linkers of PVC and PEA respectively. The monomer ethyl acrylate was polymerized in presence of PVC with plasticisers and heat stabilisers and the two polymers were cross linked subsequently to generate full IPNs. The IPNs so produced were characterized with respect to their physico-mechanical, thermal and morphological properties and an attempt has been made to investigate the influence of cross linked PEA moieties in the cross linked major matrix of PVC. The properties revealed the significant effect of rubbery PEA on PVC in the cross linked network. The tensile strength showed a marginal decrease but there was a rise in elongation at break and toughness values at the initial stages due to the incorporation of cross linked PEA. The thermal behavior as envisaged from the thermomechanical analysis and thermogravimetric analysis results substantially prove the modification in the generated IPN systems over that of pure unmodified PVC. The changes in glass transition and degradation temperature indicate stability of the IPN samples. The morphological characteristics maintain good conformity with the mechanicals.

Keywords: Mechanical properties, morphology, polyethyl acrylate, polyvinyl chloride, thermal properties.

I. INTRODUCTION

Cross linking the polymeric chains provide an important way of diversifying the physical and chemical properties of polymers. 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[1]. They are characterized by their bi-continuous structure because in this case two polymers are brought into intimate contact without any chemical linkage between them. IPNs are mostly constituted of two polymer matrices, one being the major matrix which covers a larger proportion of the entire polymer mass and the other forming the minor matrix. When the major component is cross linked, semi 1 IPN results whereas when the minor component is cross linked, semi 2 IPN is generated. However, if both the matrices are cross linked, full IPNs are formed [2]. The degree of network interlocking between the components has a measurable effect on various mechanical properties such as modulus, hardness, and ultimate tensile strength (UTS), which in turn depends on whether either component of the network is crosslinked (semi IPN) or whether both of them are crosslinked. Increased network interlocking is expected to improve compatibility [3].

The present study highlights on modifying the properties of PVC by incorporating polyethyl acrylate as the polymeric modifier in the form of full IPN. The inherent problems of poor impact strength and difficult processing of rigid PVC are usually overcome by incorporation of suitable plasticizers and certain rubbery acrylate modifiers [4]. In such cases, there is every possibility of compromising on the mechanical properties of rigid PVC. In our case, we have tried to modify PVC with PEA so that the mechanicals of the full IPNs formed can be kept at par with original PVC or even better [5]. The full IPNs generated by cross linking both the matrices of PVC and PEA were characterized with respect to their mechanical and thermal properties and a correlation was established with the obtained morphology.

II. EXPERIMENTAL PROCEDURE

2.1 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 PEA.

2.2 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 recrystallised Bz₂O₂. 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.

2.3 Conditions of moulding

The powdery mix obtained as above was compression moulded 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/cm² at a temperature of 80°C to initiate and propagate acrylic polymerisation. 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. The mould was then allowed to cool down to the room temperature and the moulded sheet ejected.

2.4 Characterization

2.4.1 Mechanical properties

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

2.4.2 Thermal properties

The thermomechanical analysis of the various samples of PVC (containing plasticisers and stabilisers 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 180°C following a temperature program in which a heating rate of 10°C/min was maintained right from the ambient temperature.

Thermogravimetric analysis of the samples were obtained on a Perkin-Elmer Delta Series TGA thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20°C per min.

2.4.3 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 sputterer. The fractured surface of a tensile fracture specimen was inspected for morphology. The scale of magnification was 500X.

III. RESULTS AND DISCUSSION

3.1 Mechanical properties

The ultimate tensile strength of the full IPNs show an increasing trend after an initial decrease with increase in percentage of the polyacrylate within the range of concentration studied (Fig.1). The initial sharp fall in tensile strength as observed may be attributed to the breakdown in molecular alignment of crosslinked PVC chain structure by the incorporation of crosslinked, somewhat rubbery PEA molecules within it. At the later stages after about 10% PEA incorporation, the formation of *in situ* rubber phase followed by its simultaneous cross linking and more and more extent of interwinding with the crosslinked PVC matrix as dictated by the mode of synthesis results in increased UTS along with increasing percentage of PEA in composition.

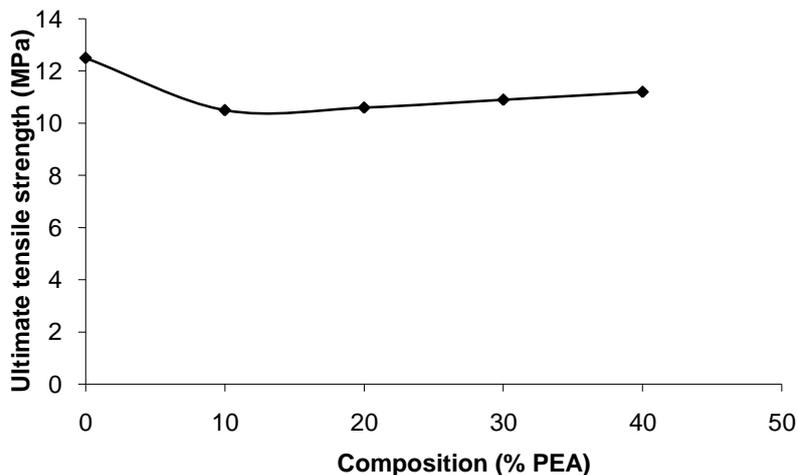


Fig. 1: Variation of ultimate tensile strength

The elongation at break of the various samples exhibit initial rise followed by a steady decrease. The sharp rise upto 10% PEA concentration may be ascribed to the effect of plasticisation imparted by the incorporation of crosslinked PEA moieties within the crosslinked matrix of PVC. The incorporation of more and more crosslinked PEA molecules in the continuous crosslinked matrix of PVC disrupts the structural regularities of PVC which breaks down the molecular packing and provides an alternative path length for dissipation of energy before its ultimate rupture resulting in increase in % EB and toughness [6].

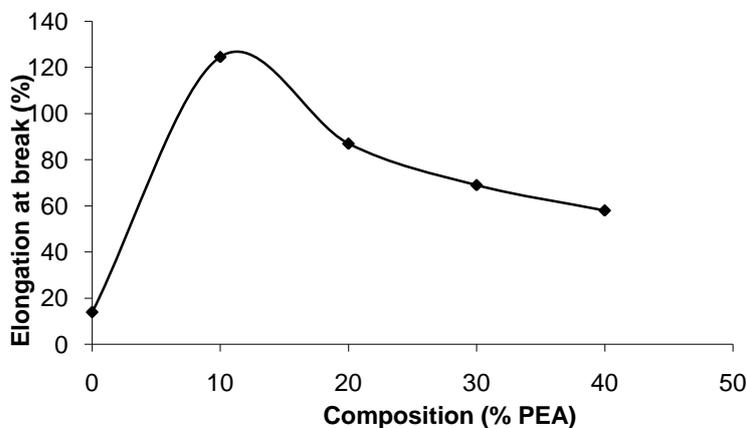


Fig. 2: Variation of percent elongation at break

3.2 Thermal properties

The thermomechanical plots display an initial expansion around 50°C followed by the penetration of the probe into the samples at a rate inversely related to the modulus. This is quite well expected from the fact that the dual cross linking of both the major and minor phases (PVC and PEA phases) offers some rigidity and stiffness within the system thus offering greater resistance to the penetration of the probe within the full IPN samples. The systems however indicate stabilisation over unmodified base reference compound PVC where the latter displays destabilisation and sharp fall while the former undergoes expansion and remains unaffected at the upper range of temperature.

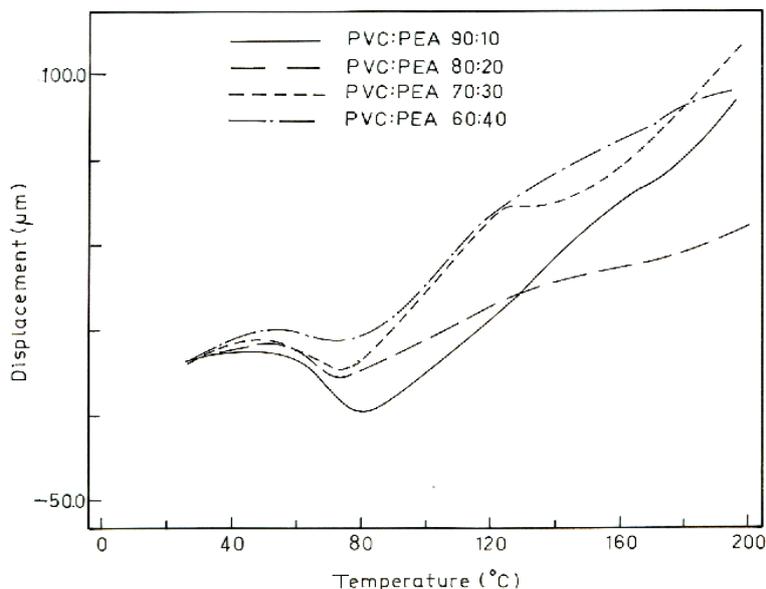


Fig. 3: Thermomechanical curves of PVC-PEA full IPNs

In TGA analysis, a delayed onset of degradation compared to the base reference compound PVC supports the fact of thermal stabilisation of the IPNs over the unmodified PVC. This may be assigned to the

scavenging of chloride radicals by PEA moieties (crosslinked in this case) thus preventing the formation of HCl which is responsible for conventional PVC degradation [7].

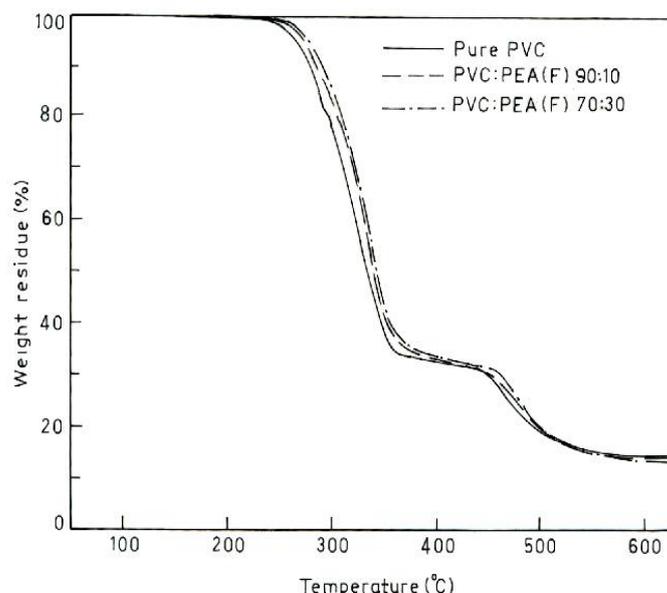
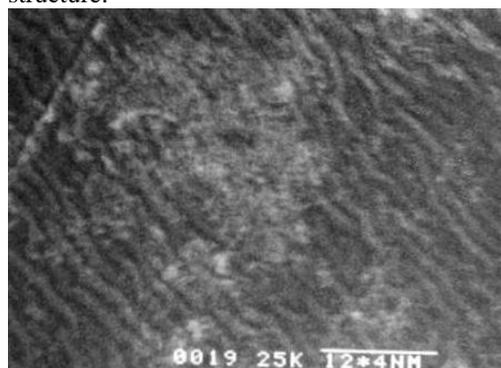


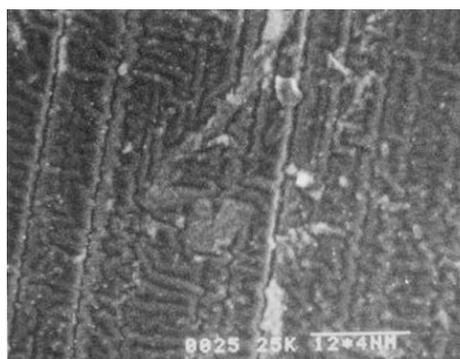
Fig. 4: TGA thermograms of PVC-PEA full IPNs

IV. MORPHOLOGY

The scanning electron micrographs indicate some phase compatibility at the initial stages when PEA content is low followed by gradual formation and separation of the microfibrils and their consequent interwinding resulting in kinked structures [8]. The fibrillar mode of morphology gradually undergoes regularisation producing completely regular distinct phase separated fibrils exhibiting cocontinuity in phase structure.



PVC: PEA (F) 90:10



PVC:PEA (F) 60:40

Fig. 5: Scanning electron micrographs of PVC: PEA full IPNs

V. CONCLUSION

In this study, it is observed that the mechanical properties display a dynamic behaviour with the quantity of PEA 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 depending on the dose of PEA incorporation. The mechanicals are supported by morphology as explicit in the scanning electron micrographs.

REFERENCES

- [1] R. Chakrabarti and D. Chakraborty, Studies on Engineering properties of PVC-PMMA semi interpenetrating polymer networks, *Journal of Applied Polymer Science*, 97, 2005, 1725-1735.
- [2] U. K.Saroop, K. K.Sharma and K. K. Jain, *Journal of Applied Polymer Science*, 38, 1989, 1401.
- [3] K. Pielichowski and B. Janouski, *Journal of Thermal and Analytical Calorimetry*, 80, 2005, 147.

[4] R. Chakrabarti and D. Chakraborty, Engineering properties of PVC-PBMA semi1 and semi2 interpenetrating polymer networks, *Journal of Applied Polymer Science*, 107, 2008, , 966-975.

[5] J. W. Barlow and D. R. Paul, *Polymer Engineering and Science*, 21, 1981, 985.

[6] R. Chakrabarti and D. Chakraborty, Modification of Poly(vinyl chloride) by IPN formation with Poly(ethyl acrylate), *Journal of Applied Polymer Science*, 113, 2009, 3450-3459.

[7] I C Mcneill (1977), *In Developments in Polymer Degradation-1*, N Grassie, Ed.; Applied Science: Essex, UK, Chapter 6.

[8] Y. Yang, H. Fujiwara, T. Chiba and T. Inoue, *Polymer*, 39, 1998, 2745.