

Study of thermal properties of poly (α -methyl styrene) and polyurethane and their fullerene-based interpenetrating polymer network

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Thermal properties of pure poly (α -methyl styrene) (PAMS) and polyurethane (PU) and their fullerene based interpenetrating polymer network (IPN) was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Glass transition temperature (T_g) of pure PAMS and PU was recorded at 173°C and 120°C respectively and their thermal decomposition was found at 350°C and 348°C respectively and while glass transition temperature of their fullerene based IPN was recorded at 160°C and thermal decomposition was found at 392°C. A gradual increase in (T_g) value by the incorporation of vinyl polymer reveals the role fullerene as a nanomaterial in strengthening interpenetration as well as enhancement in thermal properties of reacting monomeric species. An enhanced thermal stability pattern of IPN than PAMS and PU was recorded, which indicates the incorporation of urethane and α -methyl styrene units into the polymeric network of fullerene surface. The conductivity pattern explains semiconductor character of the fabricated IPN. Scanning electron microscopic (SEM) exhibits dual phase morphology of IPN. Besides of these testing, IPN was also analyzed for permittivity and permeability which reveals enhanced dielectric as well as good electromagnetic properties. This interpenetration surely brings a great change in the various physiochemical and electrical properties and new class of IPN will be established. Such polymeric systems may be applicable in the field of semiconductor to a broader range. These IPN of moderate conductivity might be useful in the electronics science research area.

Keywords: Fullerene, polyurethane, interpenetrating polymer network, scanning electron microscopic technique.

INTRODUCTION

The concept of interpenetration was first introduced by Sperling *et al.* [1]. As we know, IPN is a mixture in a mesh form in which polymerization of one monomer occurs in the presence of other [2]. IPN is the combination of properties of the cross-linked to polymers. It is important know about sequential upgradation of IPN, which is of great concern, Buist and coworkers fabricated PU polymeric network, Gangopadhyay [3] prepared polypyrrole based IPN. IPN based biomaterial was observed by Banerjee *et al.* [4], Isiklan and coworkers [5] discussed application of IPN. Rokhade *et al.* [6] emphasized on drug release mechanism. Synthesis of dielectric elastomer was put forwarded by Patel *et al.* [7], Kulkarni *et al.* fabricated IPN hydrogel [8], Vlad *et al.* prepared immiscible IPN [9], Lu and Zang and coworkers [10] put forward their study on polymeric material based on castor oil and PU, Al *et al.* [11] synthesized chitosan-based semi-IPN, An *et al.* [12] gave a thermodynamic model of physical gels. A review was put forward by Patel and his coworkers [13], Singh *et al.* [14, 15] reported polyglycidyl methacrylate and acrylamide based IPN synthesis.

Athawale and Kolekar [16-18] synthesized glycerol and its IPN with poly (butyl methacrylate). Wang *et al.* [19] discussed the damping behavior of PU/poly (methyl methacrylate) (PMMA) simultaneous interpenetrating networks (SINs).

IPN-based hydrogels were fabricated from ethylene glycol dimethacrylate by Seon and coworkers [22] using free radical polymerization technique. Yufeng [20] and team members reported fullerene shape change. Karabanova [21] and coworkers studied miscibility study of (HEMA). Seon [22] and co-workers synthesized and characterized a semi-IPN. Vishal [23] and his co-workers recognized the importance of pH-sensitive delivery system of gelatin-polymethacrylic acid IPN. Russel and his group member [24] viewed tuning conversion.

Polymer-derived IPN involving fullerene has been known over decades for electronic applications. However, their thermal and electrical properties are not well explored. Monika [25] *et al.* synthesized fullerene films of ferrocenyl. They produced redox active films in a solution of Pd (II) derivatives of C₆₀. The film indicated the fullerene bonding to Pd atom, forming an IPN. In 2012 Bo [26] and co-workers reported high internal quantum. In 2015 Ting *et al.*

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[27] synthesized a polymer of fullerene and glycidyl azide. Thereafter in 2016 Jelena highlighted applications of IPN for vibration damping. Progress in fullerene-based OPV was reported by Ranjith [28] and co-workers. They had synthesized fullerene based semi-IPN using acrylonitrile and aniline, benzoyl peroxide and divinylbenzene. IPN was characterized by DSC, TGA, conductivity, FESEM, transmission loss (TL) and permittivity/permeability techniques. As a result of backbreaking work of this group, a stronger, tougher and conducting semi IPN is produced [29, 30]. Another important nanomaterials towards the polymer research has been discovered. This is the fullerene molecule exhibiting hollow sphere. This is good to see that fullerenes are stable but are not totally unreactive. Thus, the combination of fullerene with the vinyl reactive monomers brings about a new hope for better interpenetration of these units. This interpenetration surely brings a great change in the various physiochemical and electrical properties and new class of IPN will be established.

EXPERIMENTAL

Urethane, α -methyl styrene, fullerene (C60), divinyl benzene (DVB) and benzoyl peroxide (BPO) were procured (purity >99.5%) from various resources available in India. The polymer samples were prepared from raw materials through polymerization over 2.5 hours at 70°C. Fabricated polymer was dried and taken out for the testing. IPNs were fabricated at different concentration of F-PAMS, PU, DVB and BPO in solvent (toluene) for some required time (3 hours) at 60°C under an inert atmosphere.

Characterization of IPN

The synthesized IPN characterized using thermal analysis techniques. IPN was examined for swelling data in dimethyl formamide, using Flory-Rehner equation. Sample of mass 3-5 mg was analyzed by DSC on a V2.2 Dupont calorimeter, in N₂ region (heating rate 10°C/min). TGA was carried out on TGA V% V5 1A 2100, under nitrogen atmosphere at a heating rate of 10°C/min. IPN was tested for permittivity ($\epsilon^* = \epsilon' - j\epsilon''$) and permeability ($\mu^* = \mu'_r - \mu''_r$) values in X band (8.2-12.4 GHz) frequency region. IPN was characterized by SEM with a resolution of 100 nm.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR for fullerene peaks are 1430, 527 (for C-C vibration) and 1600 cm⁻¹ (C=C). For PAMS, it reveals peaks at 3000 (stretching), 1490 (C-C- and

C-H stretching vibrations), 699 (benzene ring C=C bending) and 1444 cm⁻¹ for bending vibrations and for PU linkage it assigns a signal at 3300 (NH units), 1710 (C=O stretching), 2913 (CH symmetric stretching), 2249 (-NCO group) 1489 and 1441 cm⁻¹ (CH₂ and CH bending). While the FTIR spectrum for IPN reveals the presence of fullerene at 549 for caged vibrations), 1600 cm⁻¹ (for C=C mode). PAMS shows the peaks at 3055 (stretching), 1495 (C-C- vibrations), 2981 (C-H) and 698 cm⁻¹ (benzene ring C=C out of plane bending). PU peaks are at 3200 (NH units), 1742 (C=O stretching of urethane linkage), 2798 (CH stretching of CH₂) and 2000 cm⁻¹ (-NCO) group. Change in the band positions of fullerene, PAMS and PU clearly explains that good interpenetration has taken place of IPN [31, 32] (Fig.1).

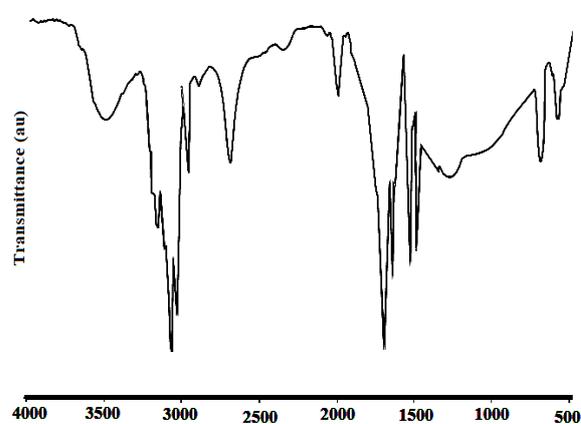


Fig. 1. FTIR spectrum of IPN

Thermal properties

Fig. 2a shows the TGA value at 392°C. Decomposition was found to be possessing higher value than PAMS and PU, which indicates incorporation of urethane into IPN. The enhancements in the thermal properties of the fabricated IPN is a result of proper interpenetration of the polymeric steps. This interpenetration strongly inhibits the chain mobility and improves the swelling behavior of the IPN and improves the T_g value and TGA value as well. DSC graph shows values (Fig. 2b) at 160°C, higher than T_g of PU (120°C) and lower than T_g of PAMS (173°C). The synthesized IPN reveals an increase in T_g value by 10-20°C, which may be the result of restricted chain mobility. PU are entangled to crosslink PAMS (interpenetration). PAMS provides stiffness and PU provides flexibility. Thus, it is clear that the IPN is a combination of both the strength and flexibility. It is important to note that IPN is also associated with the application of fullerene. Fullerene may be the answer for the toughness and conductivity of IPN. Fullerene works more or less towards the filler of

these fabricated IPNs and provides an overall stable and tough structure along with flexibility. It is also helpful in the interpenetration of the IPN.

Morphology

Structure of IPN of PAMS and PU is observed by SEM depicting dual phase morphology (Fig. 4). IPN is diversified and clear. The surface of fullerene, PAMS and PU is not smooth and possesses rough heterogeneous structure. It is expected that film morphology contains dual phase. One phase is the presence of fullerene- based PAMS and another phase is most probably the polymeric film of PU over this fullerene-based PAMS polymer in the form of interpenetration. Thus, a clear dual phase morphology and interpenetration is a signature of diversification and obviously enhanced physical, as well as thermal properties. Moreover, IPN species get a proper formation of the diversified product in better intermingled form. Thus, it is sure that the IPN structure is heterogeneous and different phases are clearly observed. This rough surface reveals the better interpenetration of the reacting species and cross-linker. Moreover, it may be deduced that dual phase morphology provides a chance for the bonding and interpenetration. Fullerene provides the proper conductivity to the IPN. Fullerene is also helpful in the interpenetration of the IPN.

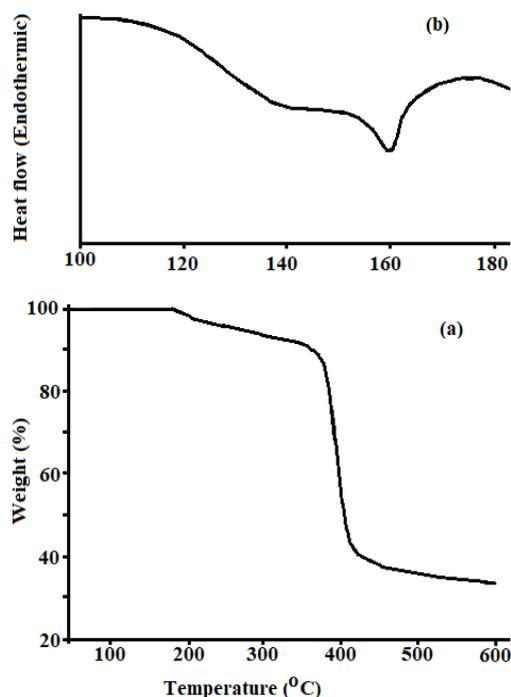


Fig. 2. TG (a) and DSC (b) curves of IPN

Electrical conductivity

Conductivity of IPN is $1.38 \times 10^{-6} \Omega^{-1}m^{-1}$ at frequency 20-50 Hz, revealing semiconductor

nature. These value of conductivity falls in the range of conductor range and insulator range. Which is an indication of broad-spectrum application of such polymeric network. Such polymeric systems may be applicable in the field of semiconductor to a broader range. The IPN of moderate conductivity might be useful in the electronics science research area.

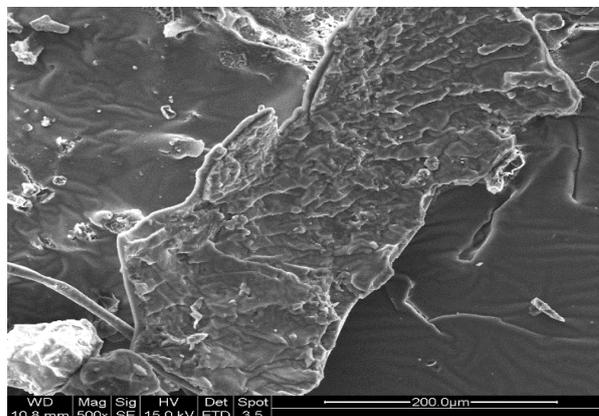


Fig. 3. SEM of IPN

Permittivity and permeability of IPN

Permittivity and permeability of any material is the property that throws light on the electromagnetic properties, dielectric properties along with the conductive behavior. The values of ϵ_r' , ϵ_r'' and $\tan\theta$ for IPN are 2.47, 0.15 and 0.08, respectively. Values range from 0.92 to 1.20, 0.01 to 0.103 and from 0.01 to 0.08 for μ_r' , μ_r'' and $\tan\theta$ respectively. Higher values of permittivity reveal good dielectric properties and enhanced permeability depicts enhanced electromagnetic properties. Such polymeric network may be used in various environments and domain such as defense field, medical, different laboratories, etc. These may be very useful as a semiconductor and they are applicable for dielectric purposes. It is to be concluded that these IPNs are very useful in dielectric materials. Thus, a combination of overall properties of the IPN is established.

Effect of components

Incorporation of fullerene, PU and PAMS shows increased swelling behavior. This enhanced swelling is applicable in various domains. They may be used for water retaining purposes too. As PAMS contains benzene ring in the planar form, so this may provide a strong backbone structure which obviously enhances the T_g values and thermal decomposition temperature. Thus, PAMS is responsible for providing an ordered and tough form to the IPN. Higher concentration of PAMS usually enhances relative polymer crystallinity and toughness while

PU is responsible for providing flexibility to the IPN. Increase in concentration of PU is a function of flexibility and greater degree of crosslinking between PU and fullerene-based PAMS phase. Increase in the concentration of DVB is directly responsible for the crosslinking and hence low chain mobility, which causes an increase in T_g . It is true that DVB is very helpful in the interpenetration of IPN. Thus, a change in the concentration of DVB efficiently affects IPN formation.

PU is commercially a very important organic polymer used in various applications such as rigid PU foam, coatings, adhesives, building and construction, composite wood, medical and flooring, etc. Besides these applications PU is mainly popular for its flexibility. Second monomer used in the research is α -methyl styrene. PAMS which is a polymer of α -methyl styrene provides the mechanical strength to the IPN. This may result into enhanced mechanical, as well as physiochemical properties of the IPN. Thus, this molecule is very helpful in the formation of the IPN.

As discussed above, these important properties of the polymers such as flexibility of PU and the stiffness and compactness of PAMS may be combined to a new and unique combination. Such an IPN is being synthesized which reflects these combined properties in the increase of T_g and TGA values. Such polymeric structures are very useful in the environment which hold alternating thermal behavior. Thus, such polymeric network may be applicable in vast domains such as defense, medicine, electronics, etc. Fullerene also played a great role in the improvement of strength of IPN. Thus, the enhancement of the thermal properties may be the result of proper interpenetration of these distinct species: fullerene, PU and PAMS combination. Basically, fullerene not only enhances the interpenetration but it also helps the IPN for inbuilt conductive and electromagnetic properties. It may also be deduced that preparation of such IPN systems may be

CONCLUSIONS

The synthesized polymeric network exhibits better thermal properties than PAMS and PU. The DSC analysis depicts higher value of T_g for the IPN as compared to PU, the thermal decomposition pattern of IPN was found to be possessing higher value than ranges PAMS and PU, which shows insertion of urethane units into the polymeric network. Thus, such polymeric network may be applicable in vast domains such as defense, medical, electronics, etc. Fullerene also played a great role in the improvement of strength of IPN. IPN surface

contains fullerene, PAMS and PU, which is not smooth. This reveals the presence of rough and heterogeneous domains under the immediate layer and dual phase morphology. Thus, it may be predicted that due to this heterogeneity which is a result of proper interpenetration has a direct impact on the chain mobility of the polymeric chains inside the polymeric network. This effect of the interpenetration causes the increase and enhancement of the thermal properties. Conductivity testing reveals the semiconducting character of IPN. Thus, at last this to say that we have fabricated IPN which possesses the desired and all required properties for various purposes. The research has provided a combination of the flexibility, toughness, electrical conductivity along with the electromagnetic properties.

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