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Synthesis and characterization of interpenetrating polymer network of Fullerene based poly (α-methyl styrene) and polyurethane

Mohd. Meraj Jafri[a,*], Meet Kamal[a], D.K. Singh[b], T.C. Shami[c], H.B. Baskey[c]

[a] Department of Chemistry, Christ Church Degree College, Kanpur, India
[b] Department of Chemistry, Retd. Prof. H.B.T.I., Kanpur, India
[c] Strategic Material Group, D.M.S.R.D.E, D.R.D.O, Kanpur, India

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ABSTRACT

A Novel flexible fullerene based interpenetrating polymer network (IPN) of poly (α-methyl styrene) and polyurethane is synthesized. The polymer network is characterized using infrared, ^{13}C NMR spectroscopy, differential scanning calorimetric analysis, thermo gravimetric analysis, conductivity analysis, transmission electron microscopic techniques, complex permeability and permittivity characteristics. Infrared spectral analysis of polymeric sample show characteristic peaks for fullerene at 1445, 549 and 1600 cm^{-1}, for poly (α-methyl styrene)(PAMS) at 3055, 1495, 2981 and 698 cm^{-1} and for polyurethane it reveals peaks at 3200, 1742, and 2798 cm^{-1}. The peaks recorded for ^{13}C NMR spectra shows the signal for fullerene at 136 ppm, for poly (α-methyl styrene) at 128, 62, 40 and 25 ppm and for polyurethane at 180.0, 63.2, 37.3 and 25.1 ppm respectively. The glass transition temperature value obtained from differential scanning calorimetric analysis is found to be 160 °C. The initial thermal decomposition of polymer network was studied by thermo gravimetric analysis which is found to 392 °C. The conductivity record reveals the semiconductor character of polymer network. The XRD pattern of IPN indicates semi crystalline nature. Transmission electron microscopic examination reveals clear dual phase morphology in the synthesized polymer network. Besides of these characterizations IPN is also analyzed for permeability and pemittivity, which reveals more or less semiconductor nature of synthesized IPN.

1. Introduction

To overcome the poor performance of conventional polymer, a new class of polymers "Interpenetrating polymer network (IPN)" came into existence. An IPN is a blend of two or more polymers in a network with one of the systems is being synthesized during immediate presence of another [1]. These networks are entangled such that cannot be pulled apart. IPN is different from polymer blends in a way that it is insoluble in solvents [2]. IPNs combine the characteristics of the cross-linked polymers. Researchers concluded their consideration of stepwise enhancement of IPN and their properties. Analysis of different sequential IPNs was performed by Sperling et al. [3], Zahao X et al. [4] reported synthesis of elastomer and gel from IPN, Buist and Gudgeon [5] synthesize IPN of polyurethane containing isocyanate group, thereafter Gangopadhyay[6] synthesized polypyrrole following the electrochemical polymerization, development of an IPN based on micro spherical formulation using emulsion crosslinking method was examined by Banerjee et al. [7], Isiklan [8] have extensively used carbohydrates and biodegradable polymers for controlled release formulation of drug having short plasma life. Rokhade et al. [9] worked on novel controlled release drug release system, Patel et al. [10] reported the synthesis of dielectric elastomer, Kulkarni et al. synthesized IPN hydrogel membranes consisting of sodium alginate and polyvinyl alcohol [11], Vlad et al., synthesized IPN with an immiscible components [12], some study on the use of castor oil as a component in PU with IPN's have been published by Zang et al. [13], Al-Kahtani Ahmed et al. [14] reported the synthesis of Chitosan based pH sensitive semi IPN microsphere for controlled release of diclofenac sodium, An et al. [15] reported a themodyanamic model of physical gels. Patel et al. [16] suggested review on hydrogel nanoparticles in drug delivery, A Singh et al. [17] reported synthesis and characterization of interpenetrating polymer network of polyglycidyl methacrylate and acrylamide. Through these polymer networks chemically compatible desired phase morphology can be achieved [18]. IPN have found important applications in various fields such as organic solar

* Corresponding author.
E-mail addresses: jafrimerajic05@gmail.com (Mohd.M. Jafri), meetk_dwi@yahoo.co.in (M. Kamal), dhruvks123@rediffmail.com (D.K. Singh), shamitc1@rediffmail.com (T.C. Shami), himanshudmsrde@gmail.com (H.B. Baskey).

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cells [19], Drug delivery [20], tissue engineering [21], polymer actuators [22] and energy harvesters [23]. Recently in order to overcome the problem of sensitive electronic machines, researchers are focusing on dielectric characteristics, microwave absorption and EMI shielding properties [24,25]. Nowadays polymer based composites are in demand as a microwave absorber and instead of conventional metal based one [26,27].

IPN offers the possibility of combining in network from which otherwise it is not possible to synthesize polymer with opposite properties [24] etc. Literature discussed above reveals that enormous work has been carried on IPN but fullerene based IPN using novel vinyl monomers is still scarce. Thus the present study reveals data on fullerene based poly (α-methyl styrene) and polyurethane with interpenetrating polymer systems. Present work aims for developing a network system based on these novel vinyl monomers explaining various physiochemical, thermal and electronic phenomena of IPN (Scheme 1).

2. Experimental procedure

Monomers [Urethane (Kemphasol, Art. No. K14848, $C_3H_7NO_2$) washed α-methyl styrene], Solvents, fullerene and divinyl Benzene (DVB) are taken for the experiment. Benzoyl peroxide (BPO) is recrystallized from chloroform.

2.1. Synthesis of polymer of fullerene based poly (α-methyl styrene) (F-PAMS)

The polymer samples are prepared by refluxing a suspension of α-methyl styrene (Sigma Aldrich) and fullerene in toluene. The system is kept on water bath for 2.5 h at 70 °C. Synthesized polymer are precipitated in methanol and dried.

2.2. Synthesis of IPN

IPNs are synthesized by systematic variations of concentration of fullerene based poly (α methyl styrene), urethane (Kemphasol, Art. No. K14848, $C_3H_7NO_2$), divinyl benzene and Benzoyl peroxide in toluene for 3 h at 60 °C under an inert atmosphere. The IPN obtained are vacuum dried to constant weight.

3. Characterization of ipn

The synthesized IPN is characterized using the spectroscopic techniques, thermal analysis techniques and transmission electron microscopic techniques, conductivity analysis and permeability and permittivity analysis.

3.1. Spectroscopic technique analysis

1. **Infrared (IR) spectroscopic studies:** The IR peaks of IPN are analysed on vertex 70 (Bruker) instrument.
2. **^{13}C NMR Spectroscopy:** ^{13}C NMR spectral analysis of fullerene based IPN of poly (α-methyl styrene) and polyurethane sample is carried out in an ECX 500-JEOL NMR spectrometer.

3.2. Thermal analysis

Differential scanning calorimetry (DSC) is performed on a V2.2 Dupont calorimeter, under nitrogen atmosphere at a heating rate of 10 °C/min. The sample weight is 3–5 mg.

3.3. Thermo gravimetric analysis (TGA)

TGA is carried on TGA V% V5 1A 2100, under nitrogen atmosphere at a heating rate of 10 °C/min.

3.4. Permeability and permittivity analysis

An Agilent Vector Network Analyzer (VNA) E 8364 B is employed to measure the reflection/transmission coefficients of the composite specimen in the X band (8.2–12.4 GHz) frequency region. Based on the measured scattering coefficients the complex permittivity and permeability is calculated using Nicholson-Ross-Weir (NRW) algorithm.

3.5. Transmission electron microscopy morphology (TEM)

The IPN is studied by TEM with a resolution of 100 nm. Samples are prepared by dissolving the powder in ethanol from which an aliquot is taken and deposited on a copper-graphite mesh grid. The sintered products are surface polished and electro polished at 230 K electrolyte of 25% HNO_3 and 75% CH_3OH. The magnification and electron diffraction patterns are calibrated in the TEM. The samples are then scanned in a 200 kV JEOL JEM 2000 EX transmission electron microscope.

3.6. Calculation of percentage extractable materials

The solute or uncross linked component of IPN is removed by soxhlet extractor using dimethyl sulphoxide (DMSO) as a solvent for better results. The percentage extractable material was calculated using the following equation.

$$\%\ \text{Extractable material} = \left(\frac{W_b - W_a}{W_a}\right) \times 100 \quad (1)$$

where W_b = Weight of IPN before extraction and W_a = Weight of IPN after extraction.

3.7. Swelling measurements

Cross-linked density of polymer network is calculated by measurements of solvent absorbency. The swelling data is calculated by soaking sample in different polar and nonpolar solvents such as dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dioxane, benzene or toluene until an equilibrium weight is achieved (~24 h). Weight measurements are made by blotting the samples and immediately weighing them. The percentage swelling is calculated according to the following relationship [28].

$$\%\ \text{Swelling} = \left(\frac{W_s - W_d}{W_d}\right) \times 100 \quad (2)$$

Where, W_s = weight of swollen IPN and W_d = Weight of dry IPN.

3.8. Crosslink density

IPN sample is taken and its cross-link density is determined by swelling data of IPN in DMF by using Flory-Rehner equation [29].

$$\frac{1}{M_c} = \frac{\left(\ln(1 - V_p) + V_p + X_{12}{V_p}^2\right)}{pV_1\left({V_p}^{1/3} - V_p/2\right)}$$

where, M_c = average molecular weight of IPN, p = density of IPN, V_1 = molar volume of solvent, and V_p = volume fraction of polymer in swollen gel, X_{12} = polymer solvent interaction parameter [30].

$$X_{12} = B + \frac{V_1\left(\delta_p - \delta_s\right)^2}{RT}$$