



Research Article

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Thermal Behavior, X-Ray Diffraction and Morphological Studies on Renewable Resources Based Interpenetrating Polymer Networks

N. Mohanty¹, B. N. Guru¹, S. Mopapatra², N. C. Pal^{*2} and S. Lenka²

¹Department of Chemistry, Ajay Binay Institute of Technology, CDA, Cuttack, Odisha, India

²Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw University, Cuttack, Odisha, (India)

ABSTRACT

Agricultural wastes and natural oils have taken the priorities as raw materials for synthesis of polymers over the traditional petrochemical based raw materials. Interpenetrating Polymer Networks based on polyurethane of polyol modified linseed oil and 1,6-diisocyanatohexane with phosphorylated cardanol using benzoyl peroxide as initiator and ethylene glycol dimethacrylate as crosslinker were synthesized. The chemical structures of these polymers were confirmed by Fourier Transform Infrared Spectra. Various Thermal Analysis techniques were used to determine the percentage of decomposition of such polymer blends at the interval of 50^o celsius, ascertain the relative thermal stability of the polymers, evaluate temperatures of maximum rate of decomposition and study the exothermic and endothermic behavior of associated with decomposition process. Kinetic constants, order of reaction and energy of activation, were calculated at two different temperature ranges for the thermal degradation of polymers by the dynamic Freeman-Anderson method. It was observed that the relative thermal stability of such biopolymers not only depends on the NCO/OH molar ratio of the polyurethane component but also depends on the PU/PC weight ratio of the Interpenetrating Polymer Networks. The calculated kinetic parameters were also in good tune with observed thermal data. Surface morphology was studied by X-ray diffraction analysis and scanning electron microscopy. It was observed that the variation of NCO/OH molar ratio and PU/PC weight ratio has appreciable effect on the crystallinity and surface morphology of the polymers.

Keywords: Phosphorylated Cardanol, Linseed Oil, Polyurethanes, Interpenetrating Polymer Networks.

INTRODUCTION

In the current scenario, the whole world is searching for the renewable resources as substitutes for the conventional resources. In the field of polymer, researchers are making every effort to explore new monomers from renewable resources. Cardanol [1-3], a natural meta substituted phenol is one such monomer which is derived from cashew nut shell liquid (CNSL), an agricultural waste. CNSL products have not only industrial use but also have medicinal applications [4-8]. A large number of articles have been published on modification of cardanol using reactivity of hydroxyl phenyl group [9-11]. Interpenetrating Polymer Networks (IPNs) are the Interpenetrating Polymer Networks in network form in which at least one component is polymerized and/or cross linked in the immediate presence of the other [12, 13]. However, synthesis of Interpenetrating Polymer Networks (IPNs) using phosphorylated cardanol and linseed oil is yet to be studied. Hence, in the present study Interpenetrating Polymer Networks were synthesized using phosphorylated cardanol and polyurethanes derived from glycerol modified linseed oil with hexamethylene diisocyanate (HMDI) with different NCO/OH molar ratios and different PU/PC weight ratios in presence of benzoyl peroxide (BPO) as initiator and ethylene glycol dimethacrylate (EGDM) as the cross linking agent. The IPNs have been characterized by FTIR spectra and various thermal analysis techniques such as Thermogravimetric Analysis (TGA), Derivative Thermogravimetry (DTG) and Differential Thermal Analysis (DTA). The kinetic constants were calculated by using the Freeman-Anderson method. Morphology study of the IPNs was carried out by using SEM and XRD studies. The objective of our work is to explore and evaluate the

natural and agricultural resources of India by carrying out the result oriented study of techno economic feasibility of converting such resources into low cost IPNs with improved properties from the view point of commercial applications to meet the present demand for the reduction of consumption of petrochemical derivatives.

EXPERIMENTAL SECTION

Synthesis of Polyurethanes (PUs)

Linseed oil was heated to 250-260°C in an inert nitrogen atmosphere with 0.1568 g of PbO i.e. 0.05% litharge (oil basis) as catalyst and 80mL (1.5 times stoichiometric quantity) of glycerol with constant stirring to obtain polyol modified linseed oil (PL). 0.708g of polyol modified linseed oil was reacted with 0.504g of hexamethylene-1,6-diisocyanate (HMDI) at 45°C in methyl ethyl ketone (MEK) as solvent with constant stirring for 45 min until a viscous prepolymer (polyurethane) [14,15] separated out with NCO/OH molar ratio at 1.5. The same procedure was followed to prepare PU with NCO/OH molar ratio at 2.0.

Synthesis of Interpenetrating Polymer Networks (IPNs)

Anacardic acid (2-carboxylic -3- pentadecadienylphenol), the major component of Cashew Nut Shell Liquid was decarboxylated to cardanol by vacuum distillation [16-17]. A mixture of 150g (0.5 mol) cardanol and 49g of (0.5 mol) ortho-phosphoric acid was condensed at 175°C under vacuum to obtain phosphorylated cardanol (PC). The mixture of polyurethane (PU) and phosphorylated cardanol (PC) with different weight - to - weight ratios (35:65 ; 50:50) for 1.5 NCO/OH molar ratio and a weight - to - weight ratio (50:50) for 2.0 NCO/OH molar ratio were separately taken in MEK in a reaction vessel in presence of BPO and EGDM. The mixture was constantly stirred at room temperature by means of a magnetic stirrer for 15 min to get a homogeneous solution and thereafter the temperature was raised to 75°C to initiate the polymerization and stirring was continued for about 1h to get a viscous mass which was poured into a glass mould and kept in a preheated oven at 75°C for 24h. The thin film thus formed was cooled and removed from the mould and labeled. The feed composition data of the IPNs are furnished in Table 1.

Table 1 Feed Composition Data of IPNs

Sample Code	Composition	NCO/ OH molar ratio	PU / PC (wt. ratio)
IPN-1	PL ^a + HMDI ^b + PC ^c	2.0	50:50
IPN-2	PL + HMDI + PC	1.5	50:50
IPN-3	PL + HMDI + PC	1.5	35:65

^a Polyol modified linseed oil, ^b Hexamethylene diisocyanate, ^c Phosphorylated cardanol

RESULTS AND DISCUSSION

FTIR spectral analysis

The infrared spectra of the Interpenetrating Polymer Networks (IPNs) were obtained using Perkin Elmer FTIR spectrometer model paragon 1000.

The FTIR spectrum was used mainly to confirm the presence of component materials in the IPNs. The characteristic absorptions of IPN-1 corresponding to N-H stretching of >NH group at 3488.15 cm⁻¹, C-H stretchings (ss/as) of >CH₂ and -CH₃ groups at 2900.01 cm⁻¹ and 2926.11 cm⁻¹, N≡C stretching of -N=C=O for isocyanate terminating PU unit at about 2444.00 cm⁻¹, C=O stretching of >C=O in urethane linkage at 1738.95 cm⁻¹ were observed (Fig.1). Similar characteristic absorption peaks were observed for IPN-2 and IPN-3 as shown in Fig. 2 and Fig. 3 respectively.

Thermal analysis

Perkin Elmer Thermal Analyzer model PYRIS diamond USA was used for TGA, DTG and DTA measurements. 6.208 mg of IPN-1 with 5.5 mg alumina as reference was scanned between 45°C and 660°C at a heating rate of 10°C / minute in an inert nitrogen atmosphere (N₂ 100g/min) (Fig.4). In a similar way other IPNs were scanned for thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) measurements (Fig.5 and Fig. 6).

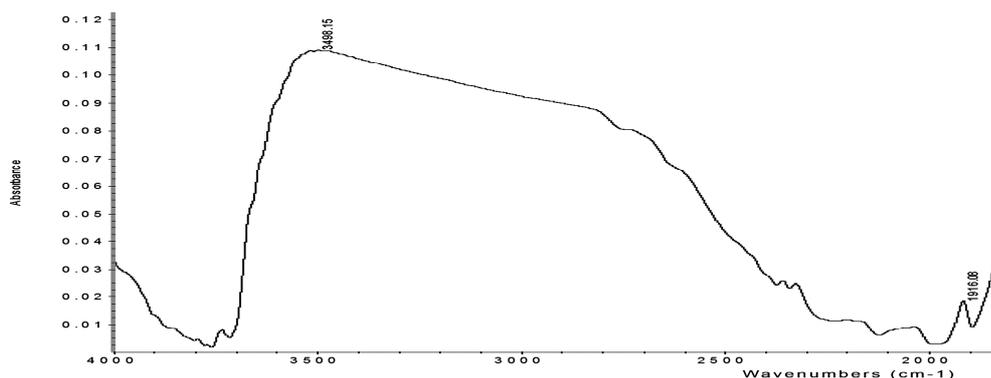


Figure 1 FTIR [IPN-1]

Figure 1: FTIR of IPN-1

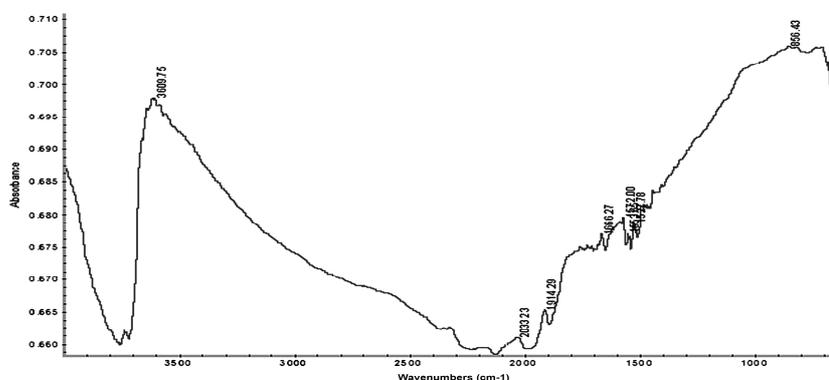


Figure - 2 FTIR [IPN-2]

Figure - 2 : FTIR of IPN-2

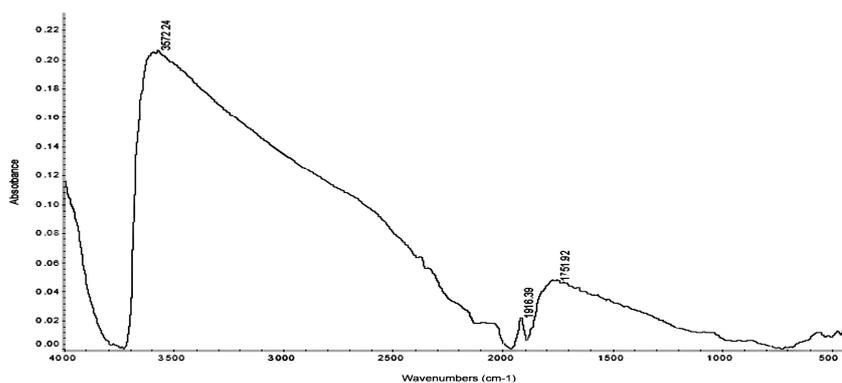


Figure - 3 FTIR [IPN-3]

Figure - 3 : FTIR of IPN-3

The Table 2 shows the data of the thermal decomposition of the IPNs at different temperatures at the interval of 50°C. The IPNs exhibit high thermal stability upto 150°C with only 0.48 %, 0.18%, and 0.46% of weight losses for IPN-1, IPN-2 and IPN-3 respectively due to loss of moisture retained in the sample. Only 5.31%, 5.73% and 7.05% of weight losses for IPN-1, IPN-2 and IPN-3 respectively in the range of 150°C to 250°C may be due to evaporation of solvent and elimination of small groups and other volatile material. Significant weight losses of 83.39%, 80.86% and 79.02 % for the IPN-1, IPN-2 and IPN-3 respectively recorded in the range of 250°C - 450°C can be attributed to the decomposition of benzene ring as already known that the breakage of main bonds in benzene ring occurs in

the range of 400°C- 450°C [10] along with main functional groups such as –OH, >NH, >C=O etc. and due to partial decomposition of cross linking with EGDM between PU and PC unit. Finally, about 8% of weight loss recorded in the range of 450°C to 600°C can be due to complete decomposition of crosslinkings with EGDM between PU and PC units.

Figure 4 : TG/DTG/DTA of IPN-1

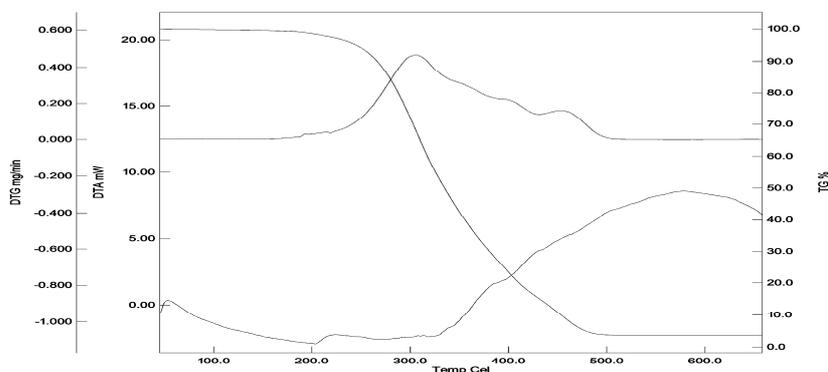


Figure 4 TG/DTG/DTA [IPN-1]

Figure 5: TG/DTG/DTA of IPN-2

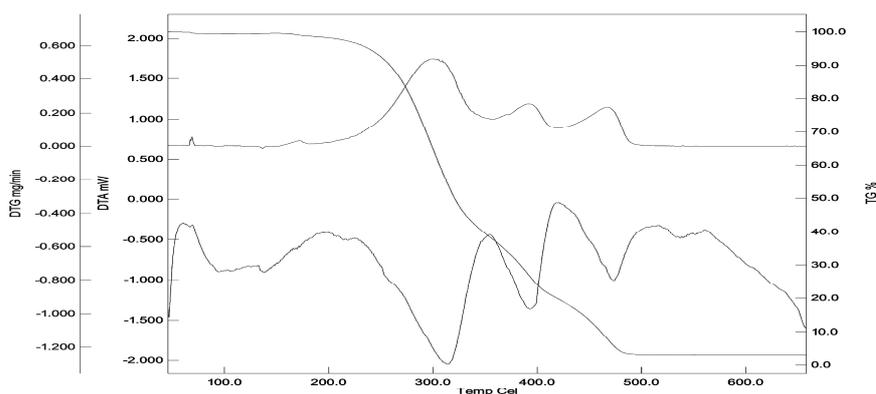


Figure 6 TG/DTG/DTA [IPN-3]

Figure 6 : TG/DTG/DTA of IPN-3

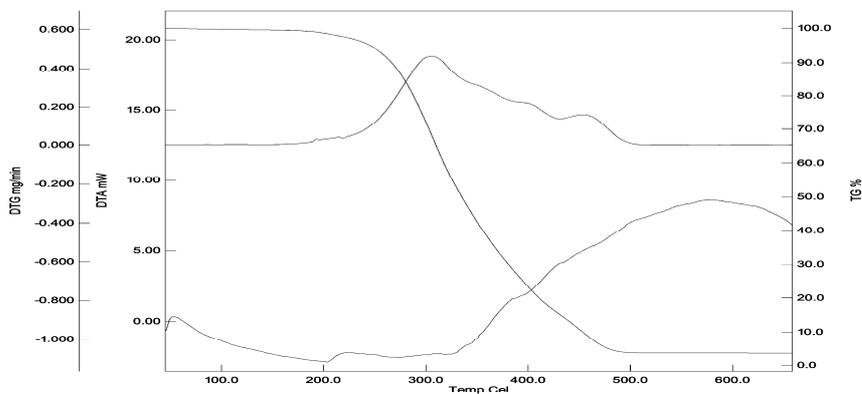


Figure 5 TG/DTG/DTA [IPN-2]

Table 2: Percentage of Thermal Decomposition of the IPNs at various Temperatures (°C)

Sample Code	100	150	200	250	300	350	400	450	500	550	600	650
IPN-1	0.27	0.48	1.4	5.79	27.98	57.4	76.66	89.18	96.27	96.37	96.37	96.4
IPN-2	0.09	0.18	1.04	5.91	29.11	55.95	72.52	86.77	97.02	97.10	97.10	97.1
IPN-3	0.55	0.46	1.78	7.51	35.17	60.46	76.00	86.53	96.94	97.07	97.1	97.1

Table3 DTA data of IPNs

Sample Code	Composition	NCO / OH molar ratio	PU/PC wt. ratio	Temperature °C	DTA Peak/oC		% of decomposition
					endo	exo	
IPN-1	PL+ HMDI+ PC	2.0	50:50	150-250	214.42		05.31
				250-450	307.00		83.39
				450-600		562.62	07.19
IPN-2	PL+ HMDI+ PC	1.5	50:50	150-250	161.85		05.73
				250-450	354.04		80.86
				450-600		504.79	10.33
IPN-3	PL+ HMDI+ PC	1.5	35:65	150-250	185.16		07.05
				250-450	546.85		79.02
				450-600	347.86		10.57

From the thermal decomposition data it is evident that all the IPNs exhibit high thermal stability upto 250°C. The IPN-2 is thermally more stable than the IPN-1 between 250°C to 450°C and thereafter there is no significant change in thermal stability of the two IPNs. The enhanced thermal stability of the IPN-2 compared to IPN-1 may be due to the increase in oil content of the PU component (the two IPNs having the same PU/PC weight ratio but varying NCO/OH molar ratio). Also IPN-2 is thermally more stable than IPN-3 in the same temperature range as expected due to the increase in PU content in the IPN-2 and the PU being linear is subjected to more crosslinkings.

Between 250°C and 350°C the order of thermal stability is IPN-2 > IPN-1 > IPN-3. It is further observed that thermal stability values of IPN-1 and IPN-2 between 350°C and 450°C are comparable where as in the same temperature range IPN-3 is more stable than IPN-1. Above 450°C there is no noticeable change in thermal stability of all the IPNs.

The study of TGA is supplemented by the study of its first derivative (DTG) curves. The DTG curves show the rate of thermal decomposition ($\mu\text{g} / \text{min}$) with respect to temperature. The DTG curve in Fig-4 shows that the IPN-1 has three peaks at 298°C, 387°C and 439°C with corresponding 454.5 $\mu\text{g}/\text{min}$, 227.545 $\mu\text{g}/\text{min}$ and 144.84 $\mu\text{g}/\text{min}$ rate of decomposition. The DTG curves in Fig-5 and 6 show similar peaks at 293°C with 467.15 $\mu\text{g}/\text{min}$, 396°C with 305.92 $\mu\text{g}/\text{min}$ and 459°C with 218.71 $\mu\text{g}/\text{min}$ rate of decomposition for IPN-2 and at 294°C with 510.59 $\mu\text{g}/\text{min}$, 385°C with 239.57 $\mu\text{g}/\text{min}$ and 462°C with 223.88 $\mu\text{g}/\text{min}$ rate of decomposition for the IPN-3. Overall, all the three IPNs showed similar behavior, however IPN-3 recorded highest rate of decomposition 510.59 $\mu\text{g}/\text{min}$ at 294°C.

DTA thermograms of the IPN-1 show an endothermic peak at 214.42°C and exothermic peak at 49.35°C, but in range of 450°C to 600°C only one exothermic peak at 562.62°C is observed. Similar exothermic and endothermic peaks are also recorded for the IPN-2 and IPN-3 which are listed in the Table 3. The DTA curves indicate that the thermal decomposition process for all the three IPNs is a three step reaction.

Kinetic Parameter Calculation

The mechanism of thermal degradation of polymers can be interpreted from calculation of kinetic parameters by the application of the Freeman-Anderson method. The equation used for the Freeman-Anderson method is

$$\Delta \log \left(-\frac{dw}{dt} \right) = n \Delta \log w - (Ea / 2.303R) \Delta (1/T)$$

where $-dw/dt$ is the rate of decomposition (calculated from DTG measurements), w is the residual mass (calculated from TG measurements) at constant difference in $1/T$ (0.1×10^{-3}), 'n' is the order of reaction and Ea is the energy of activation. Freeman-Anderson plots, Fig-7 and Fig-8, for kinetic parameters in the temperature ranges of 200°C to 315°C and 315°C to 450°C respectively were obtained by plotting $\Delta \log (-dw/dt)$ against $\Delta \log w$ corresponding to a constant difference in $1/T$. The kinetic parameters such as activation energy (Ea) and order of reaction (n) for the thermal decomposition are given in Table 4. The degradation process in all the IPNs is associated with large values

of 'Ea' and 'n' indicating the higher order of crosslinkings. The IPN-2 shows the highest order of reaction 7.99 in the temperature range 200°C to 315°C and hence is thermally most stable. The calculated kinetics parameters are in good agreement with the observed thermal data.

Figure 7: Freeman-Anderson Plots for 200-315°C

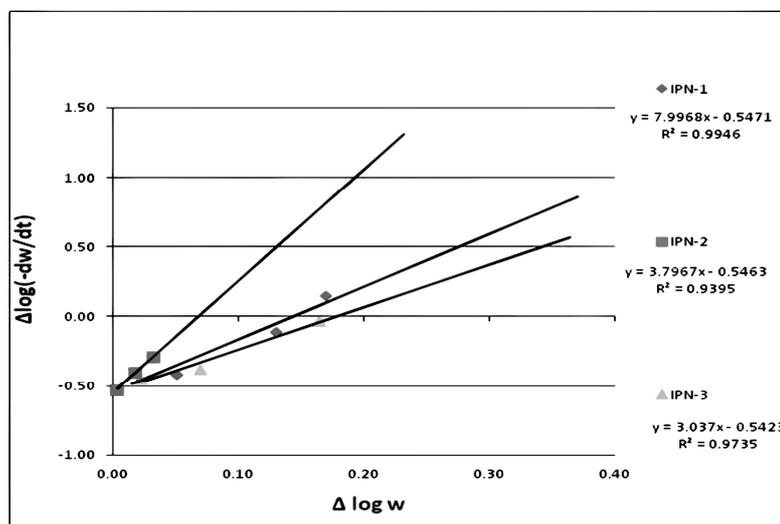


Figure 7 Freeman-Anderson plots for 200 - 315°C

Figure 8: Freeman-Anderson plots for 315 - 450 °C

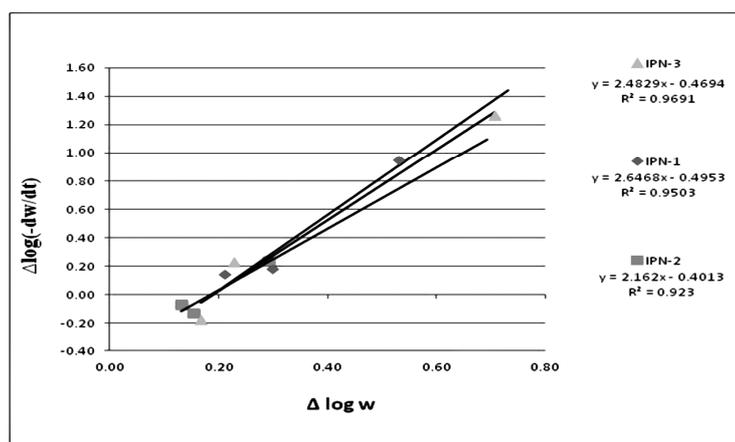


Figure 8 Freeman-Anderson plots for 315 - 450°C

Table 4 Kinetic Constants of Thermal Decomposition and Crystallinity of IPNs

Sample Code	Temperature °C	Ea (kJ mol ⁻¹)	n	X _{cr} (%)
IPN-1	150-250	104.60	3.79	27.48
	250-450	94.84	2.64	
IPN-2	150-250	104.75	7.99	30.95
	250-450	76.84	2.16	
IPN-3	150-250	103.83	3.03	26.94
	250-450	89.88	2.48	

X-ray diffraction (XRD) analysis

The degree of crystallinity of IPNs has been calculated by using XRD method. The scanning regions of the diffraction angles were 10⁰ to 30⁰ which covered most of the significant diffraction peaks of the polymer crystallites. The equation for degree of crystallinity is as follows $X_{cr} = A_c / (A_c + A_a)$, X_{cr} refers to degree of crystallinity, A_c refers to crystallized area and A_a refers to amorphous area on the x-ray diffractogram. The relatively sharp peaks were due to the scattering from crystalline region and the broad underlying hump is due to scattering from non crystalline regions. A horizontal base line was drawn between the extremities of the scattering

curves to remove the background scattering. The degrees of crystallinity of the IPNs calculated from the Fig-9 to Fig-11 were about 30% given in Table 4. The degree of crystallinity increases with increase of PU content due to the linear nature of PU and also with decrease in NCO/OH molar ratio due to higher extent of cross linking.

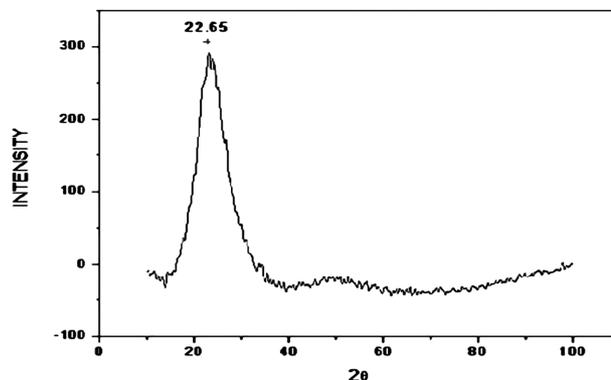


Figure 9 XRD [IPN -1]

Figure 9: XRD of IPN -1

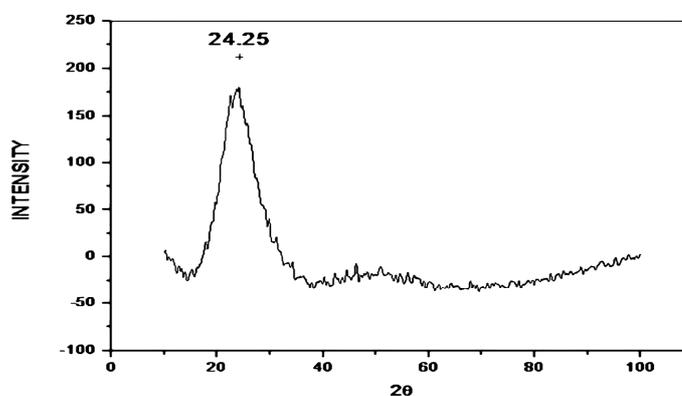


Figure 10 XRD [IPN-2]

Figure 10: XRD of IPN-2

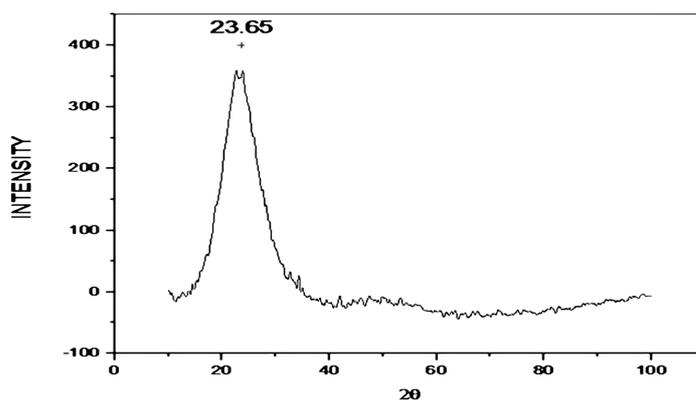


Figure 11 XRD [IPN-3]

Figure 11: XRD of IPN-3

SEM Study

Morphology of the IPNs was studied through SEM study. The SEM microphotographs of the IPNs (Fig-12 to Fig-14) indicate that the IPN-3 is less homogeneous compared to the IPN-1 and the IPN-2. So, it is observed that the surface morphology of the polymers can be improved by variation of the PU/PC weight ratio and NCO/OH molar ratio of the PU component of the interpenetrating polymer networks.

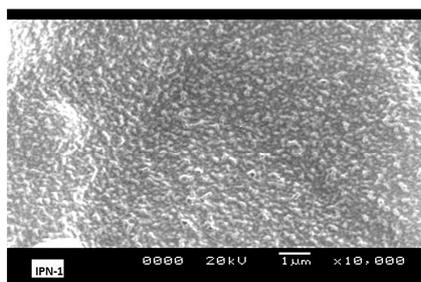


Figure 12A SEM [IPN-1]

Figure 12A: SEM of IPN-1

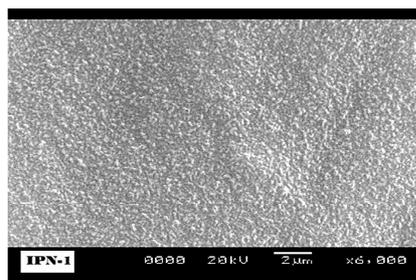


Figure 12B SEM [IPN-1]

Figure 12B: SEM of IPN-1

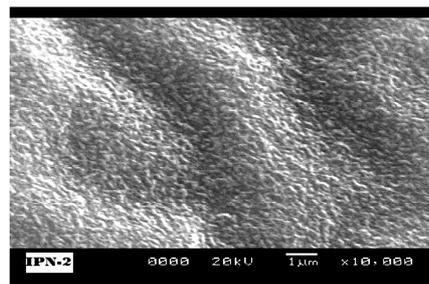


Figure 13A SEM [IPN-2]

Figure 13A: SEM of IPN-2

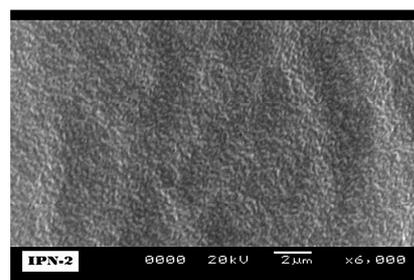


Figure 13B SEM [IPN-2]

Figure 13B: SEM of IPN-2

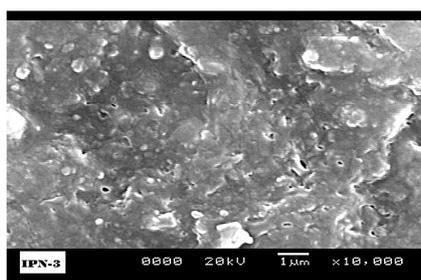


Figure 14A SEM [IPN-3]

Figure 14A: SEM of IPN-3

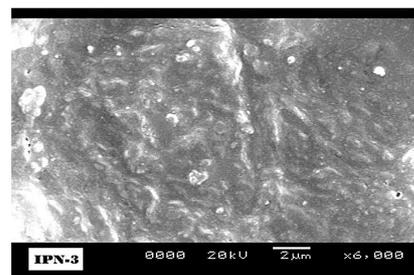


Figure 14B SEM [IPN-3]

Figure 14B: SEM of IPN-3

CONCLUSION

The biopolymers produced from cashew nut shell liquid and triglyceride oil have added advantage over the polymers from petroleum based monomers. These polymers are expected to be eco-friendly, cheaper and easily accessible than the petroleum based polymers. Interpenetrating Polymer Networks prepared from polyol modified linseed oil and phosphorylated cardanol are largely cross linked and have higher thermal stability with high mechanical strength and improved morphological property. The ultimate properties of IPNs depend upon various factors such as type of diisocyanate, NCO/OH molar ratio, nature of monomer and PU/PC weight ratio.

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