

**GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES**  
**THE SYNTHESIS AND FTIR, KINETICS, TG/DTG/DTA, SEM AND EDS STUDY OF**  
**INTERPENETRATING POLYMER NETWORKS (IPNS) DERIVED FROM**  
**POLYURETHANES OF POLYOL MODIFIED COSTOR OIL AND HMDI AND**  
**CARDANOL BASED DYES**

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**ABSTRACT**

Agro based raw materials such as polyol modified castor oil polyurethanes and cardanol based dyes were used to synthesize interpenetrating polymer networks. Such polymers prepared using benzoyl peroxides as initiator and ethylene glycol dimethacrylate as cross-linker and not studied intensively were characterized by FTIR study and various thermal technique such as TGA, DTG and DTA. The kinetic parameters such as activation energy ( $E_a$ ) and order (n) of reaction were calculated by using the Freeman-Anderson method. The effects of change in PU/CD weight ratio and NCO/OH molar ratio of polyurethanes on thermal properties of such polymers were studied.

**Keywords:** *Cardanol, Cardanol based dyes, Polyol modified Castor oil, Polyurethanes, Interpenetrating polymer networks.*

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**I. INTRODUCTION**

Now a days, the synthesis of agricultural products based polymers as potential substitutes for petroleum based polymers is not only needful to cut-down the mounting concern of the environmentalists but also inevitable to meet the need of the hour for the limited consumption of petrochemicals [1,6]. The objective of the present work is to exploit 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 cost-effective Interpenetrating Polymer Networks (IPNs) with improved properties from the view points of commercial applications to meet the need of the hour for the reduction of consumption of petroleum. The work on IPNs from renewable resources was initiated by sperling [7,8,9].

Cardanol (cashew phenol), a potential biomonomer with an unsaturated side chain at meta position and obtained from decarboxylatoin of anacardic acid [10] a major component of the Cashew Nut Shell Liquid, was modified into a number of new dye monomers using different aromatic amino compounds by diazoreaction. Such cardanol based dyes and polyol modified castor oil polyurethanes in different weight ratios were allowed to react in presence of benzoyl peroxide (BPO) and ethylene glycol dimethacrylate (EGDM) to form a number of interpenetrating polymer networks a dynamic class of polymer blends in network forms in which at least one component is polymerized and cross-linked in presence of other.

The IPNs have been characterized by Fourier Transform Infrared (FTIR) spectra and thermal analysis techniques such as Thermogravimetric Analysis (TGA), Derivative Thermogravimetry (DTG) and Differential Thermal Analysis (DTA). The kinetic parameters such as order of reaction (n) and energy of activation ( $E_a$ ) were calculated by using the Freeman-Anderson method. Morphology was studied by the SEM technique.

## II. EXPERIMENTAL

### Preparation of Cardanol Based Dye (CD)

8.57 g (0.05 mol) of 2-amino-4-chlorobenzoic acid was dissolved in 13 mL (0.15 mol) of conc. hydrochloric acid and 5 mL of water. The solution was cooled to 0-5 °C. An ice cold aqueous solution of sodium nitrite of about 3.45 g (0.05 mol) in 18 mL of water was slowly added to it with constant stirring for 3-4 min until a positive test for nitrous acid was obtained. An ice cold alkaline solution of 15 g (0.05 mol) of cardanol, obtained by common procedure [7,9], in 40 mL of 5% (w/v) NaOH solution was prepared. The ice cold diazonium salt solution was immediately added slowly with constant stirring to the cold alkaline cardanol solution. A brilliant red coloured azo dye was obtained [11].

Table – 1 Feed composition data (IPNs)

Sample code	Composition		NCO/OH	PU/DM
IPN-1	PC+HMDI+CDof chlorobenzoic acid	2-Amino-4-	1.2	35:65
IPN-2	PC+HMDI+CDof chlorobenzoic acid	2-Amino-4-	1.2	50:50
IPN-3	PC+HMDI+CDof chlorobenzoic acid	2-Amino-4-	1.6	50:50

### Preparation of Polyol Modified Castor Oil (PC)

Castor Oil (CO) is chiefly a naturally occurring triglyceride of a hydroxyl acid that is ricinoleic acid. (12-hydroxy-9-octadecenoic acid) was obtained from the local market in the purified form. About 350 mL of castor oil taken in a three necked flask fitted with thermometer, reflux condenser and a mechanical stirrer was heated to 250°C in an inert nitrogen atmosphere. Then 0.1682 g of PbO (0.05%, oil basis) as catalyst with 80 mL of glycerol was added to the hot oil with constant stirring. The temperature was maintained at 210°C until one volume of reaction mixture gave a clear solution in one volume of methanol. The reaction mixture was cooled and excess of glycerol was removed by thoroughly washing with 20% of acetone solution to obtain polyol modified castor oil (PC) and there after dried under vacuum at 80°C for 6 h.

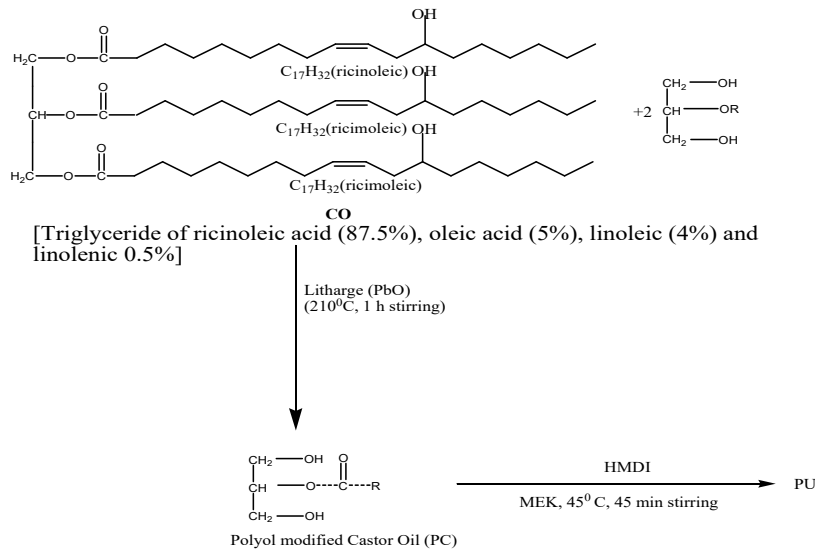
### Synthesis of Polyurethanes (PUs)

0.372 g of polyol of modified castor oil was allowed to react with 0.302 g of hexamethylene diisocyanate to maintain the NCO/OH molar ratio at 1.2. The above reaction was carried out in a small reaction vessel at 45°C in 5 mL of methyl ethyl ketone with constant stirring for 45 min until a pale yellow viscous polyurethane separated out. Polyurethane was also prepared with NCO/OH molar ratio at 1.6 using same di-isocyanate and polyol modified castor oil.

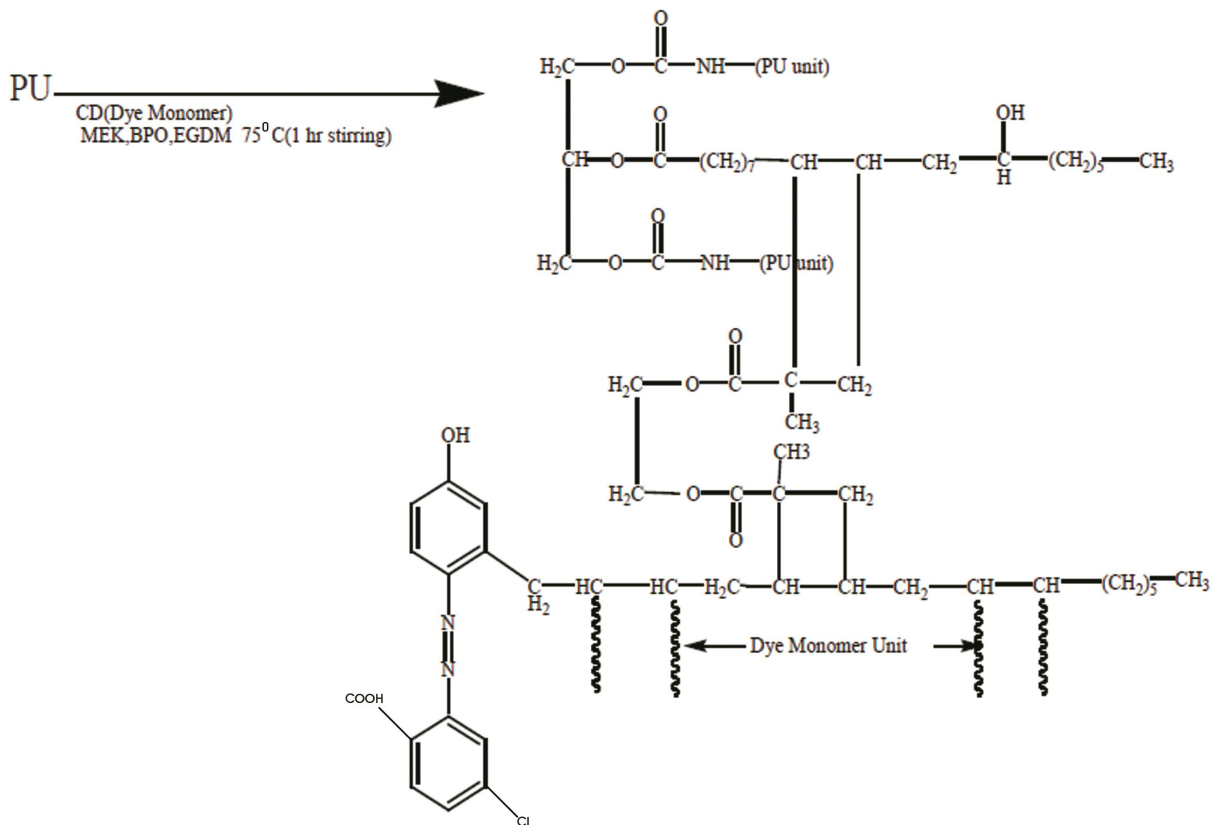
### Synthesis of Interpenetrating Polymer Networks (IPNs)

The polyurethanes (PUs) with NCO/OH molar ratio at 1.2 and 1.6 and cardanol based dye monomer (CD) in different weight to weight ratios (35:65, 50:50) were taken in methyl ethyl ketone 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 about 15 min to get a homogeneous solution and thereafter the temperature was raised to 75°C and stirring was continued for about 1 h to get a viscous mass which was poured into a glass mould and kept in an oven at 75°C for 24 h. The thin film thus formed was cooled and removed from the mould and labelled for characterization at the Central Research Facility, IIT, Kharagpur, India. The feed composition data of IPNs are furnished in Table 1.

The expected scheme of the reaction involved in the synthesis of interpenetrating polymer networks is given in schemes 1 and 2.



Scheme – 1 (Synthesis of PU)



Scheme – 2 (Synthesis of IPN)

III. RESULTS AND DISCUSSION

FTIR Spectra

Fourier-Transform Infrared (FTIR) spectra of the interpenetrating polymer networks were obtained using Perkin Elmer FTIR spectrometer model - Nicolet – 6700 thermofisher scientific. A small amount finely powdered sample was mixed with about 100 times its weight of powdered potassium bromide (KBr) and pressed into a small disc about 1 mm thick. Elmer FTIR spectra were analyzed by studying intensity of the absorbance peaks and comparing with the control spectra to identify the presence of functional groups and component materials in the IPNs. FTIR spectra of the IPNs 1, 2 and 3 are given in the figures 1, 2 and 3 respectively.

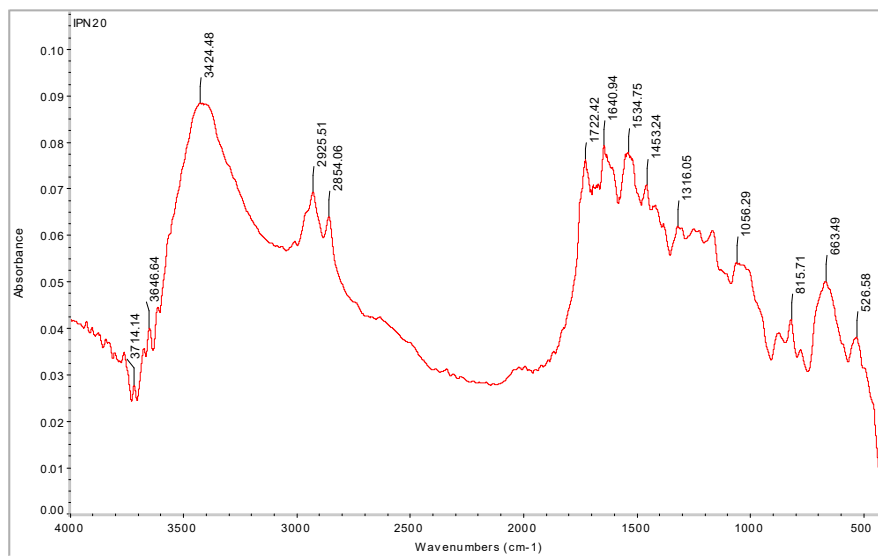


Fig.1: FTIR spectra [IPN - 1]

Polyol modified Castor Oil + HMDI + CD of 2-amino -4-chlorobenzoicacid

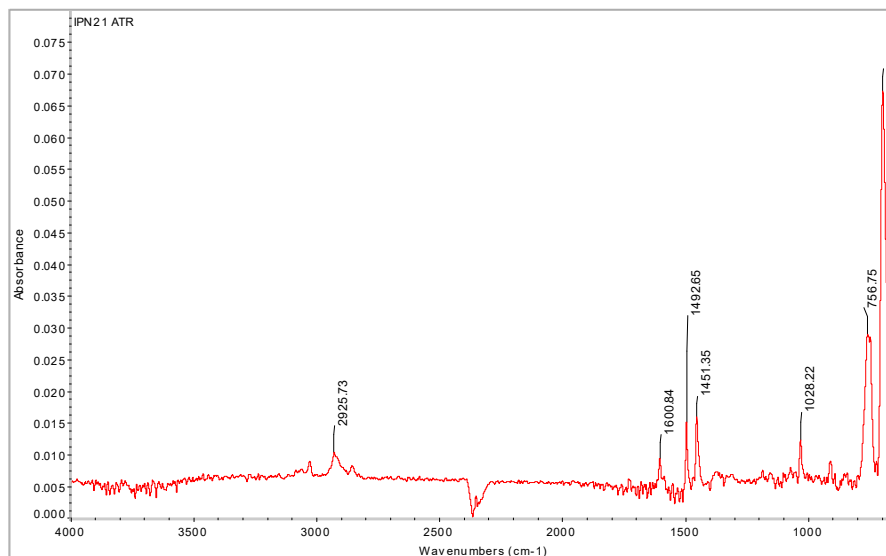


Fig.2: FTIR spectra [IPN - 2]

Polyol modified Castor Oil + HMDI + CD of 2-amino -4-chlorobenzoicacid

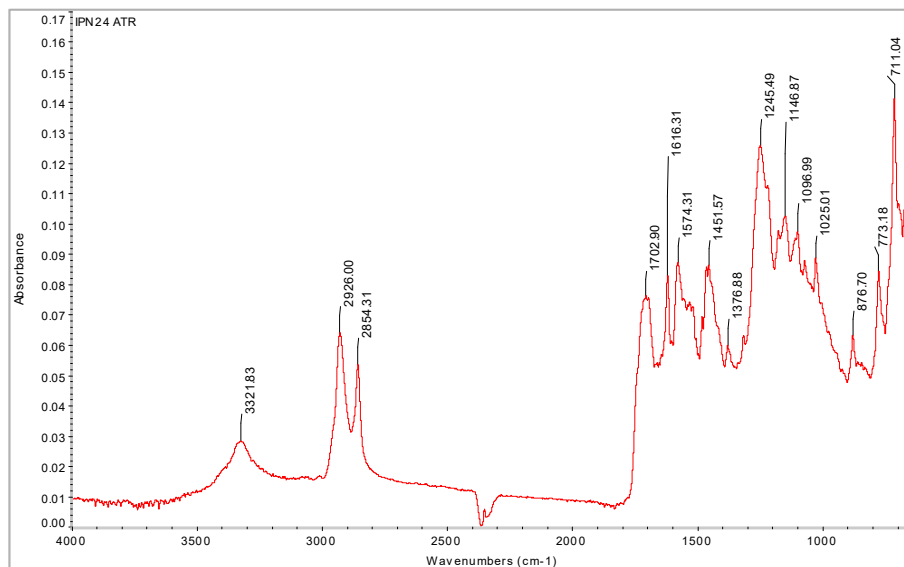


Fig.3: FTIR spectra [IPN - 3]

#### Polyol modified Castor Oil + HMDI + CD of 2-amino -4-chlorobenzoic acid

The FTIR spectrum was used mainly to confirm the presence of component materials in the IPNs. The characteristic absorption of IPN-1 corresponding to O-H stretching of COOH group at  $3646.64\text{ cm}^{-1}$ , N-H stretching of  $>\text{NH}$  group at  $3393.57\text{ cm}^{-1}$ , C-H asymmetric and symmetric stretching of  $>\text{CH}_2$  and  $\text{CH}_3$  groups at  $2967.59\text{ cm}^{-1}$  and  $2854.06\text{ cm}^{-1}$ , C=O stretching of urethane linkage at  $1749.33\text{ cm}^{-1}$ , C-O stretching of OH group at  $1056.29\text{ cm}^{-1}$ , C-Cl stretching vibration at  $776.58\text{ cm}^{-1}$  were observed.

The characteristic absorptions of IPN-2 corresponding to C-H asymmetric stretching of  $>\text{CH}_2$  &  $-\text{CH}_3$  groups at  $2925.73\text{ cm}^{-1}$  and C-Cl stretching of Cl group at  $756.75\text{ cm}^{-1}$  were observed.

The characteristic absorptions of IPN-3 corresponding to N-H stretching of  $>\text{NH}$  group at  $3424.48\text{ cm}^{-1}$ , C-H asymmetric and symmetric stretchings of  $\text{CH}_3$  &  $>\text{CH}_2$  groups at  $2926.00\text{ cm}^{-1}$  &  $2854.31\text{ cm}^{-1}$ , C=O stretching of urethane linkage at  $1702.90\text{ cm}^{-1}$ , C-Cl stretching of Cl group at  $773.18\text{ cm}^{-1}$  were observed.

#### IV. THERMAL ANALYSIS

Perkin Elmer thermal analyzer model PYRIS diamond USA was used for thermogravimetric analysis, derivative thermo gravimetry and differential thermal analysis for TGA, DTG and DTA measurements. 10.88 mg of IPN-1 with 10.5 mg of alumina as reference material was scanned between 50 and  $650^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$  in an inert nitrogen atmosphere [ $\text{N}_2(\text{XL})$ , 100 mL/ min], (Fig. 4). In the same way IPN-2 and IPN-3 were scanned for TGA, DTG and DTA measurements (Fig.5 and Fig.6).

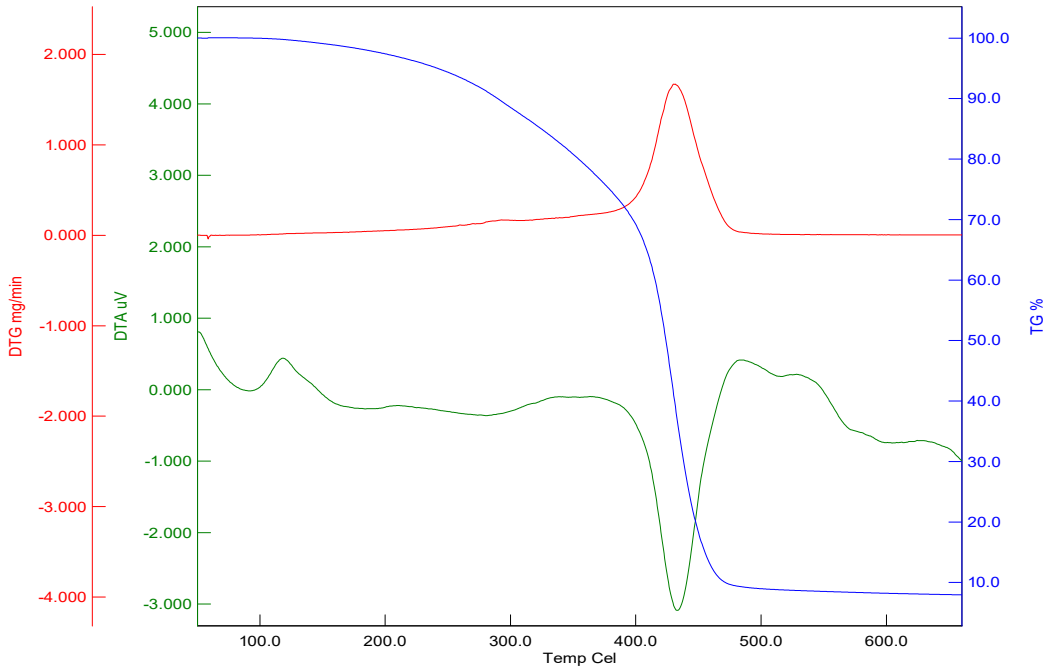


Fig. 4: TG/DTG/DTA of IPN-1

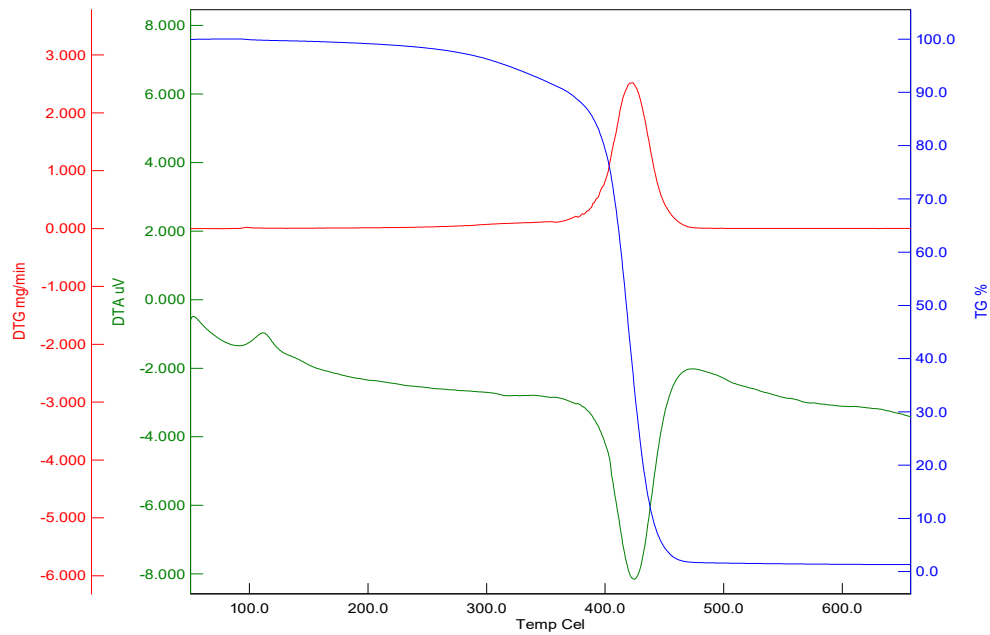


Fig. 5: TG/DTG/DTA of IPN-2

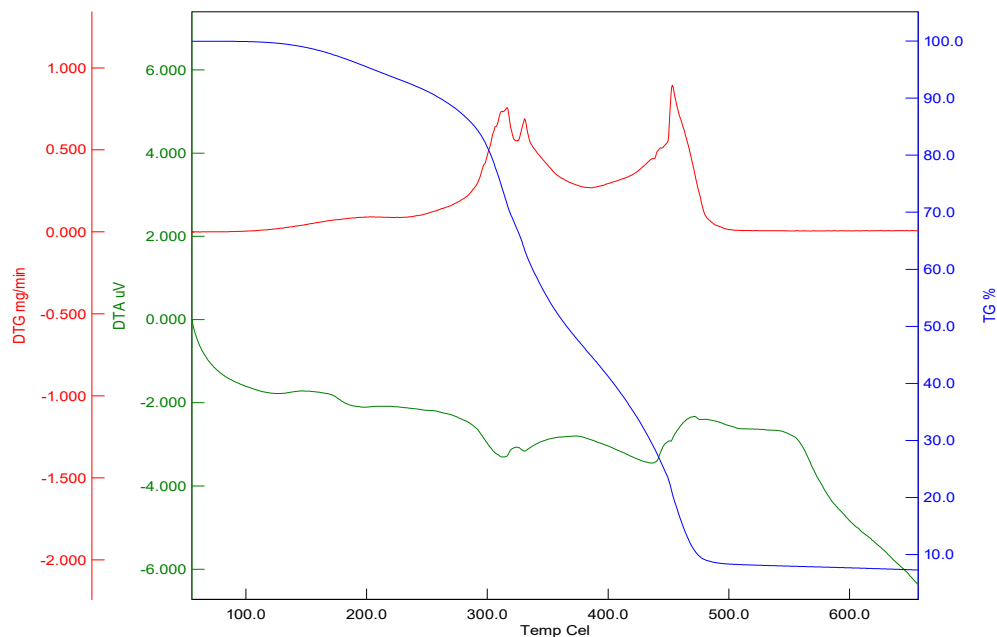


Fig. 6: TG/DTG/DTA of IPN-3

The samples have been analysed with respect to the following variations taking into consideration (a) NCO/OH molar ratio (b) PU/CD wt. ratio.

Table – 2: Percentage of mass loss of IPNs at various temperatures ( $^{\circ}$ C)

IPNs/Temp	100 $^{\circ}$ C	150 $^{\circ}$ C	200 $^{\circ}$ C	250 $^{\circ}$ C	300 $^{\circ}$ C	350 $^{\circ}$ C	400 $^{\circ}$ C	450 $^{\circ}$ C	500 $^{\circ}$ C	550 $^{\circ}$ C	600 $^{\circ}$ C
IPN-1	0.02	0.89	2.60	5.63	11.46	19.19	30.84	81.75	91.02	91.47	91.78
IPN-2	0.09	0.40	0.84	1.68	3.72	7.91	20.68	95.46	98.39	98.52	98.62
IPN-3	0.08	1.12	4.52	8.78	18.58	45.07	58.78	76.83	91.65	92.01	92.31

The **Table – 2** describes the percentages of mass losses of the IPNs at various temperatures at the interval of 50  $^{\circ}$ C calculated from TG curves. All the IPNs were found thermally stable up to 150 $^{\circ}$  C with only 0.89% (IPN-1), 0.40% (IPN-2) and 1.12% (IPN-3) mass losses due to loss of moisture retained in the sample. Mass losses increase slowly and occur in the three steps.

Step-1: In the temperature range of 150 $^{\circ}$ C - 250 $^{\circ}$ C the weight losses are 4.74%, 1.28% and 7.66% for IPN-1, IPN-2 and IPN-3 respectively which may be due to evaporation of solvent and other volatile matters, if any.

Step-2: Significant weight losses i.e., about 76.12%, 93.78% and 68.05% for IPN-1, IPN-2 and IPN-3 respectively occur in the temperature range of 250 $^{\circ}$ C - 450 $^{\circ}$ C which can be attributed to the decomposition of the benzene ring along with main functional groups such as –OH, >NH and >C=O, etc and also due to partial decomposition of cross linking with EGDM between PU and CD units.

Step-3: Finally in the temperature range of 450 $^{\circ}$ C - 600 $^{\circ}$ C the weight losses of 10.03%, 3.16% and 15.48% for IPN-1, IPN-2 and IPN-3 respectively may be due to complete decomposition of the crosslinking with EGDM between PU unit and CD monomer unit, i.e., separation of two monomer units.

From the decomposition data it is evident that all the IPNs in the present study are thermally stable. Comparing IPN-1 with IPN-2, it is observed that IPN-1 is thermally more stable than IPN-2 above 400  $^{\circ}$ C where major decomposition takes place. So thermal stability of the IPN increases with the same NCO/OH molar ratio but with the decreasing PU/CD weight ratio. This may be due to the increase in dye monomer content in the IPN with enhanced degree of crosslinking's.

Comparing IPN -2 with IPN-3, it is observed that IPN-2 is thermally more stable than IPN-3 up to 400<sup>0</sup> C. So up to 400<sup>0</sup> C, the thermal stability of the IPN increases with the same PU/CD weight ratio but with decreasing NCO/OH molar ratio. This may be due to the increase in oil component and the polyurethane.

It is useful to compare the TGA thermograms with their first derivatives. The peaks indicate the No. of decomposition steps. The DTG curves show the rate of thermal decomposition ( $\mu\text{g}/\text{min}$ ) with respect to temperature. The derivative thermogravimetric curves for IPN-1 (**Fig.4**) shows two peaks at 284, 428<sup>0</sup> C corresponding to maximum rate of decomposition 155  $\mu\text{g}/\text{min}$  and 163  $\mu\text{g}/\text{min}$  respectively. **Fig. 5** shows similar peaks at 419<sup>0</sup> C with 248  $\mu\text{g}/\text{min}$  maximum rate of decomposition for IPN-2. **Fig. 6** shows three peaks at 314<sup>0</sup> C with 738  $\mu\text{g}/\text{min}$ , 317<sup>0</sup> C with 720  $\mu\text{g}/\text{min}$  and 452<sup>0</sup> C with 872  $\mu\text{g}/\text{min}$  maximum rates of decomposition for IPN – 3.

The DTA thermograms of the IPN – 1 shows two endothermic peaks at 269<sup>0</sup> C and 430<sup>0</sup> C and Exothermic peak at 342<sup>0</sup> C in the temperature range of 250-450<sup>0</sup> C but in the range of 450-650<sup>0</sup> C only two peaks are observed that is exothermic at 474<sup>0</sup> C and endothermic at 590<sup>0</sup> C. Similarly exothermic and endothermic peaks are also recorded for IPN – 2 and IPN – 3 which are listed in the **Table-3**.

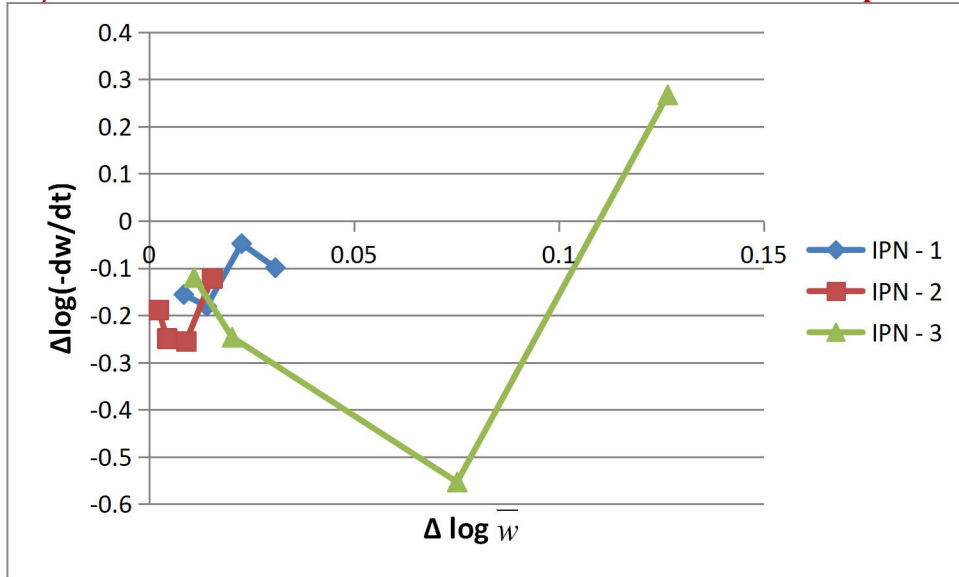
Table – 3: DTA data of IPNs

Sample codes	NCO/OH (molar ratio)	PU/CD (wt ratio)	Temperature ( <sup>0</sup> C)	DTA peak ( <sup>0</sup> C)		Percentage of decomposition
				Endo	Exo	
IPN-1	1.2	36:65	250-450	269 430	342 ---	76.12%
			450-600	590	474	10.03%
IPN-2	1.2	50:50	250-450	420	---	93.78%
			450-600	587	461	3.16%
IPN-3	1.6	50:50	250-450	308 423	352 ---	68.05%
			450-600	498	464	14.48%

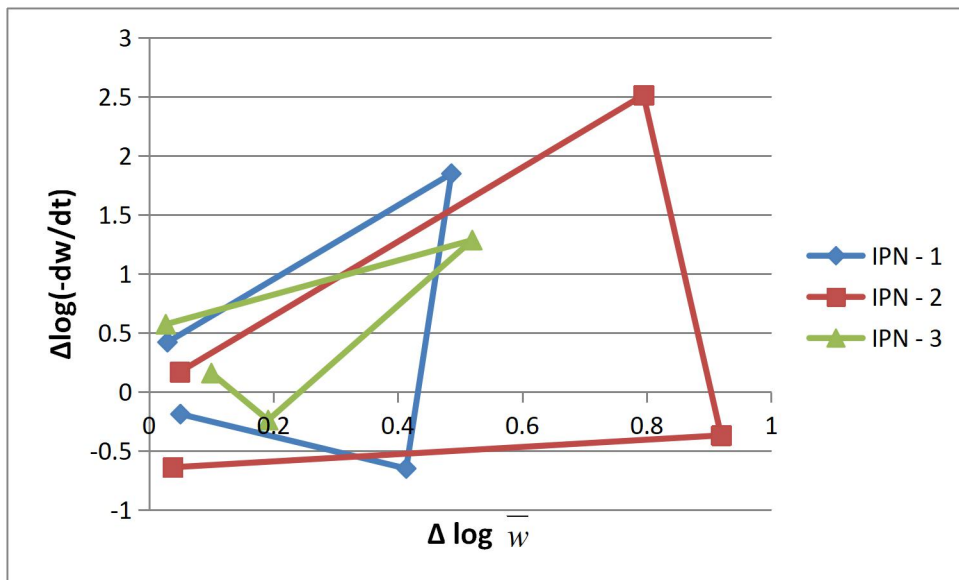
Table – 4: Kinetic parameters of the thermal decomposition of IPNs

Sample Codes	Temperature Range	Slope or Order of Reaction	Intercept	Activation Energy [E <sub>a</sub> ] KJ/mol
IPN – 1	225-320 <sup>0</sup> C	6.906	-0.437	83.67
	350-500 <sup>0</sup> C	6.916	-0.436	83.48
IPN – 2	225-320 <sup>0</sup> C	6.509	-0.344	65.87
	350-500 <sup>0</sup> C	6.519	-0.334	63.95
IPN – 3	225-320 <sup>0</sup> C	3.020	-0.139	26.61
	350-500 <sup>0</sup> C	3.023	-0.138	26.42





IPN-1,  $y = 6.906x + -0.437$ , IPN - 2,  $y = 6.509x + -0.344$ , IPN - 3,  $y = 3.020x + -0.139$   
Fig. 7 Freeman-Anderson Plot of IPN - 1, IPN - 2 and IPN - 3 between 225-320<sup>o</sup> C



IPN-1,  $y = 6.916x + -0.436$ , IPN - 2,  $y = 6.519x + -0.334$ , IPN - 3,  $y = 3.023x + -0.138$   
Fig. 8 Freeman-Anderson Plot of IPN - 1, IPN - 2 and IPN - 3 between 350-500<sup>o</sup> C

### V. KINETIC PARAMETER CALCULATION

In the present work the calculation of kinetic parameters was performed by an approach with the application of the Freeman-Anderson method.

Equation used for the Freeman-Anderson method is as follows:

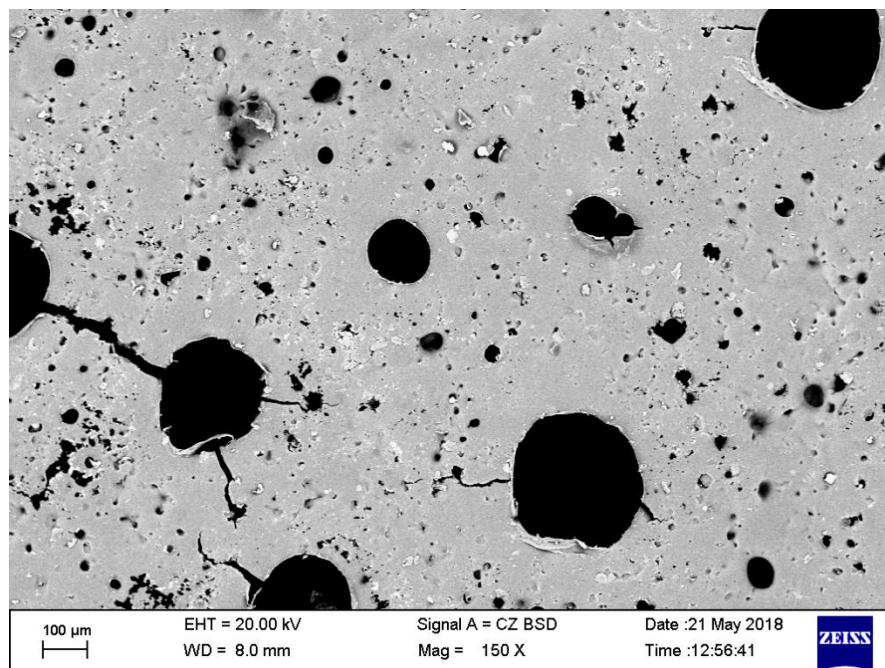
$$\Delta \log \left( -\frac{dw}{dt} \right) = n \Delta \log \bar{w} - \frac{E_a}{2.303R} \Delta \left( \frac{1}{T} \right)$$

Where  $-dw/dt$  is the rate of decomposition (calculated from DTG measurement),  $\bar{w}$  is the residual mass (calculated from TG measurements) at constant difference in  $1/T$  ( $0.1 \times 10^{-3}$ ), 'n' is the order of reaction and  $E_a$  is the energy of activation. Freeman-Anderson plots, **Figs. 7** and **8**, for kinetic parameters in the temperature range of  $226-316^\circ\text{C}$  and  $350-500^\circ\text{C}$  respectively were obtained by plotting  $\Delta \log \left( -\frac{dw}{dt} \right)$  against  $\Delta \log \bar{w}$  corresponding to a constant difference in  $1/T$ .

The kinetic parameters such as activation energy ( $E_a$ ) and order of reaction (n) for the thermal decomposition are given in **Table – 4**. The kinetic data show that the activation energy for the thermal decomposition of IPN-1 in the temperature range of  $350-500^\circ\text{C}$  where major decomposition takes place is appreciably higher than the activation energy for IPN-2 indicating its higher thermal stability which is a good agreement with experimental values. The higher order of reaction of IPN-2 than IPN-3 in the temperature range  $225-320^\circ\text{C}$  shows the higher thermal stability of IPN-2 than IPN-3. The thermal decomposition of IPNs involves complex mechanism which are different at different stages of decomposition in various temperature ranges. Consequently the order of decomposition of polymers are expected to be the higher and different in different ranges of temperatures.

## VI. SCANNING ELECTRON MICROSCOPY (SEM)

Morphological change induced by changes in PU/CD weight ratio were observed using Scanning Electron Microscopy (SEM). The SEM microphotographs of IPN-1 and IPN-3 are shown in the **Fig. 9** and **10** respectively. A binary phase morphology is clearly indicated in the figures. Even though the polymers are chemically the same the morphology of IPNs is controlled by the change in PU/CD weight ratio. It is clear that compatibility and/or interpenetration between the two networks is greatly improved by the increase in PU content of the IPN.



*Fig. 9-a: SEM of IPN-1*

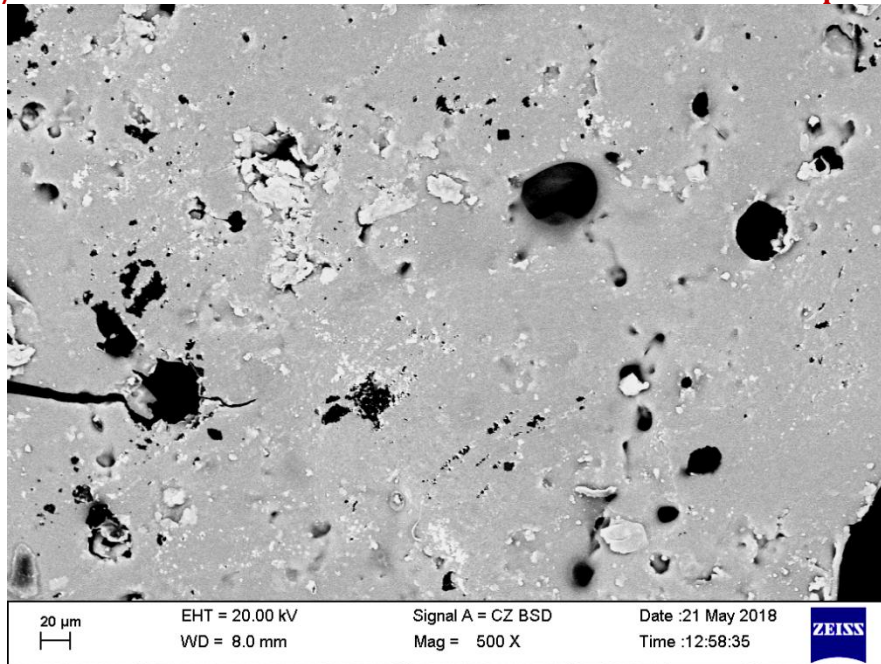


Fig. 9-b: SEM of IPN-1

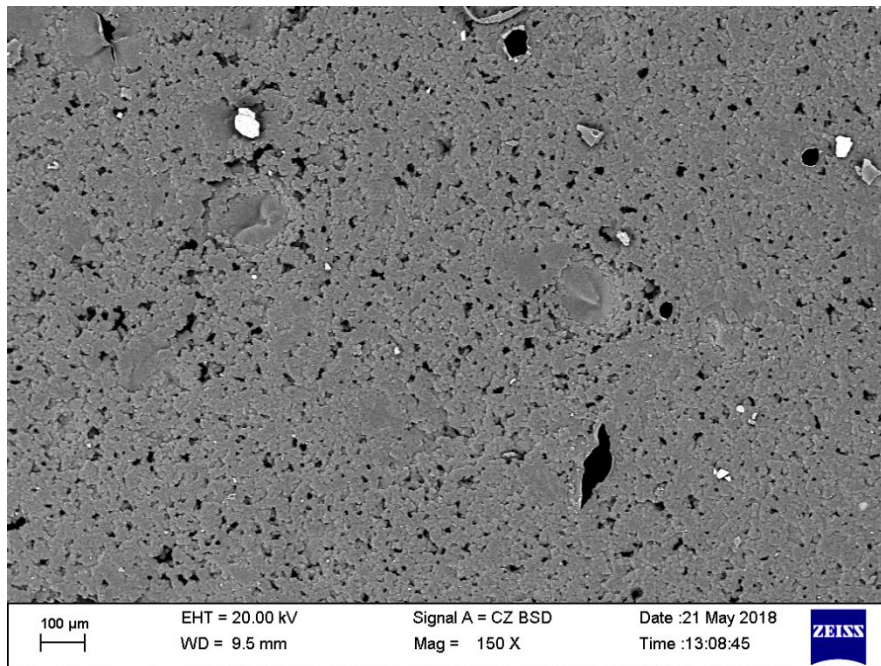


Fig. 10-a: SEM of IPN-3

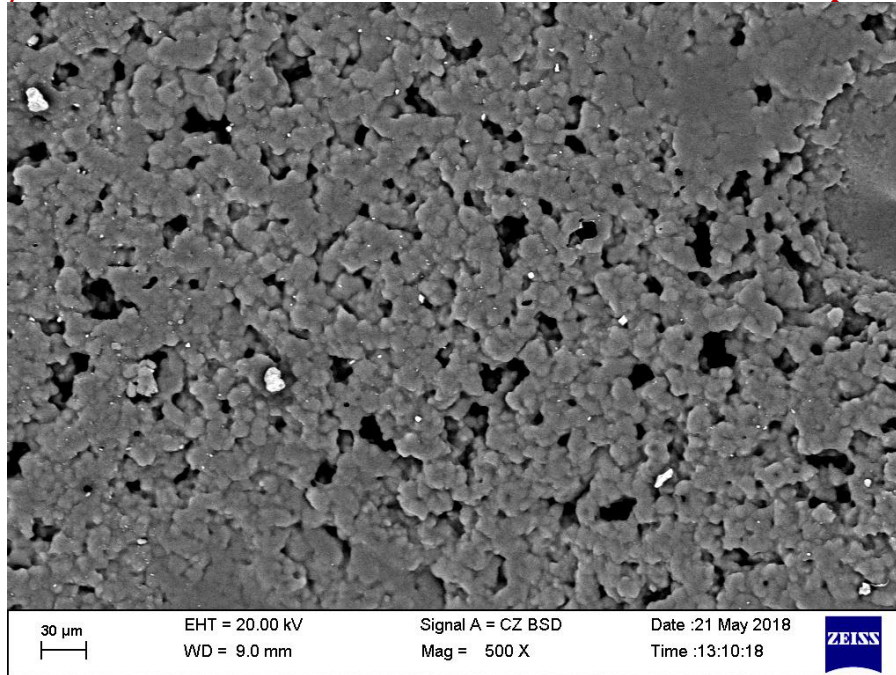


Fig. 10-b: SEM of IPN-3

## VII. ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS, EDXS AND XEDS)

Energy Dispersive X-Ray analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. EDS can be used to determine which chemical elements are present in a sample and can be used to estimate their relative abundance in the samples which is given in the Fig. 11 and 12 of the IPN-1 and IPN-3 respectively.

Table – 5: Element Detection of IPN-1

Element	Weight%	Atomic%
CK	52.28	58.32
NK	27.59	26.40
OK	16.39	13.73

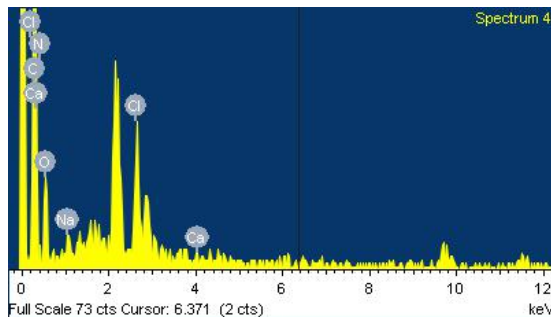


Fig. 11: EDs of IPN-1

Table – 6: Element Detection of IPN-3

Element	Weight%	Atomic%
CK	49.43	55.41
NK	25.25	24.27
OK	23.12	19.45

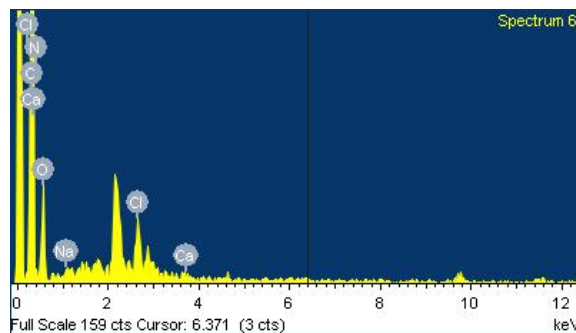


Fig. 12: EDs of IPN-3

From the Table 5 and 6 it is clear that all the IPNs mainly contain these elements (C, N & O) with different percentages.

## VIII. CONCLUSION

As far as environment and energetical concerns are considered, polymers based on natural renewable resources are expected to play a significant role in the present century. The cashew nut shell liquid and triglyceride oils are the important sustainable resources for the production of biopolymers. Oil based biopolymers are expected to be biodegradable and have many advantages over the polymer prepared from petroleum based monomers. The major conclusion of this article is interpenetrating polymer networks prepared from polyol modified castor oil based polyurethanes and cardanol based dye are largely crosslinked. Their thermal stability and mechanical strength are very high with improved morphological property. The final properties of the IPNs depend upon various conditions such as kind of diisocyanate, NCO/OH molar ratio, nature of dye monomer and PU/CD weight ratio. Interpenetrating polymer networks prepared from polyol modified castor oil show improved mechanical and thermal properties over unmodified castor oil.

## IX. ACKNOWLEDGEMENT

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