



Research Article

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## The synthesis and FTIR, kinetics and TG/DTG/dta study of biopolymers derived from polyurethanes of glycerol modified linseed oil and cardanol based dyes

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### ABSTRACT

Agro based raw materials such as glycerol modified linseed oil polyurethanes and cardanol based dyes were used to synthesize Interpenetrating Polymer Networks. Such biopolymers prepared using benzoyl peroxide as initiator and ethylene glycol dimethacrylate as cross-linker and not studied extensively were characterized by FTIR study and various thermal techniques 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. In addition to the effect of change in PU/CD weight ratio and NCO/OH molar ratio of polyurethane, the effect of change in nature of diisocyanate (DI) and cardanol based dye monomer (CD) on thermal properties of such polymers was also studied.

**Keywords:** Cardanol; cardanol based dyes; glycerol modified linseed oil; polyurethanes, interpenetrating polymer networks.

### INTRODUCTION

Now a days conventional methods of using petroleum raw materials may not be the suitable methods for the synthesis of polymeric materials. Scientists are worried about the fact that by 2050 AD petroleum itself will be a rare commodity and also it is not a renewable resource. Moreover, primary petrochemicals are very prone to oxidation to produce carbon dioxide, the main green house gas responsible for global warming. So, to find out an alternative, renewable resources for the production of cost effective interpenetrating polymer networks are the urgent need of the hour. The work with interpenetrating polymer networks from renewable resources was initiated by Sperling and co-workers [1-6].

The present study aims at utilizing agro based renewable resources to prepare cost effective and relatively eco-friendly polymers for specific uses. A good number of articles have been published recently on cardanol [7 – 8] but the research on polymers using cardanol based dye monomers (CDs) and modified linseed oil based polyurethanes (PUs) is very limited.

Linseed Oil (LO) was modified with glycerol and the glycerol modified linseed oil (GL) so obtained was allowed to react with diisocyanates such as hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI) in different NCO/OH molar ratios to give a series of polyurethanes (PUs). Cardanol, a monomer, was obtained from the cashew nut shell liquid [9]. It was allowed for diazoreaction with aromatic amino compounds to convert it into a number of new dye monomers (CDs) [10]. The glycerol modified linseed oil polyurethanes were allowed to react with these dye monomers in different weight ratios in presence of Benzoyl Peroxide (BPO) as initiator and ethylene glycol dimethacrylate (EGDM) as cross-linker to give a number of interpenetrating polymer networks (IPNs), an exotic

class of biopolymers in network forms in which the cardanol based dye monomer is polymerized and cross-linked with the linear prepolymer polyurethane [11].

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 activation energy (Ea) were calculated by using Freeman – Anderson's method [12]. With regard to thermal stability, the kinetic constants are found in good agreement with the results obtained from the study of experimental thermal data for the IPNs with different feed compositions [13] but constant parameters i.e. NCO /OH molar ratios or PU/CD weight ratios. The effect of variation in nature of diisocyanate and dye monomer on thermal properties of polymers was also studied.

## EXPERIMENTAL SECTION

### Preparation of Cardanol Based Dye Monomer (CD)

7.20 g (0.05 mol) of 2-amino-4-chlorophenol was dissolved in 13 mL of conc. hydrochloric acid and 10 mL of water. The solution was cooled to 0-5°C. An ice cold aqueous solution of sodium nitrite of about (0.05 mol) 3.45 g in 72 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 isolated from vacuum distillation of Cashew Nut Shell Liquid (CNSL) 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 colored azo dye (CD) was obtained. Similarly 6.37g (0.05 mol) of 2-chloroaniline was taken and the same procedure was followed to prepare another brilliant red coloured azo dye.

### Preparation of Glycerol Modified Linseed Oil (GL)

About 350 mL of linseed oil obtained from local market of Southern Odisha was taken in a three-necked flask fitted with a thermometer, reflux condenser and a mechanical stirrer. The oil was heated to 250-260°C in an inert nitrogen atmosphere. As the required temperature range was obtained, 0.1575 g of PbO i.e., 0.05% litharge (oil basis) as catalyst and 80 mL of (1.5 times stoichiometric quantity) of glycerol were 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 glycerol modified linseed Oil and thereafter it was dried under vacuum at 80°C for about 6 h.

### Synthesis of Linseed Oil Based Polyurethane (PU)

0.354 g of glycerol modified linseed Oil was allowed to react with 0.278 g of toluene diisocyanate (TDI) to maintain the NCO/OH molar ratio at 1.6. The reaction was carried out in a small beaker at about 45°C in methyl ethyl ketone (MEK) with constant stirring for 45 min until a viscous prepolymer of pale yellow color polyurethane separated out. In a similar way 0.354 g of glycerol modified linseed oil was allowed to react with 0.201 g and 0.268 g of hexamethylene diisocyanate to maintain NCO/OH molar ratios at 1.2 and 1.6 respectively.

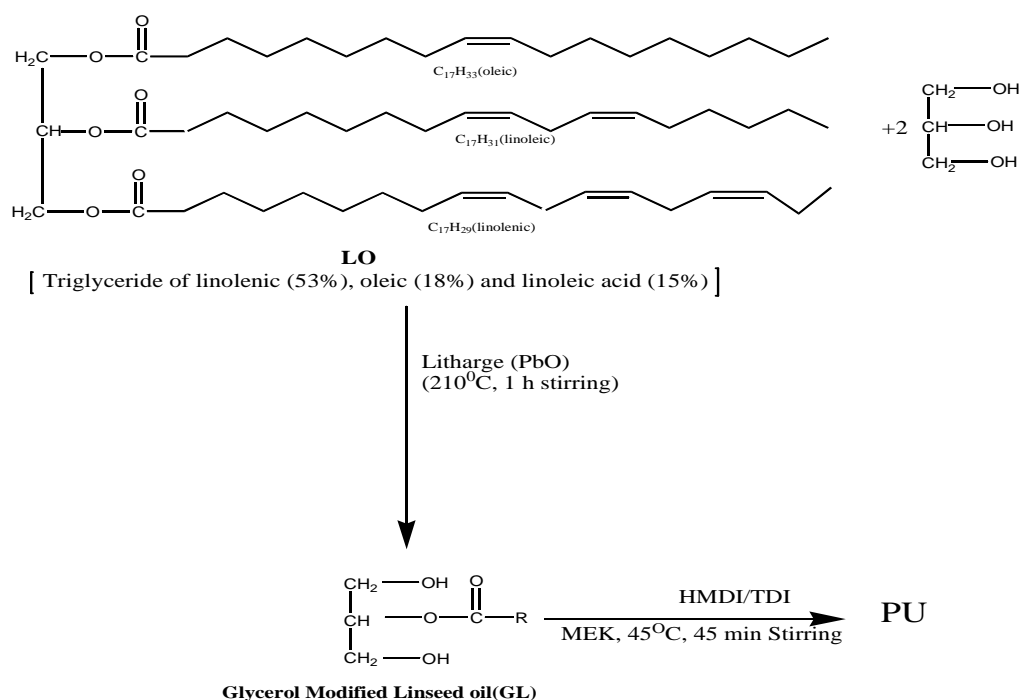
### Synthesis of Interpenetrating Polymer Network (IPN)

The polyurethane (PU) and cardanol based dye monomer (CD) in different weight to weight ratios (35:65, 50:50) were separately taken in methyl ethyl ketone (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. Thereafter, the temperature was increased to 75°C with constant stirring 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 labeled for characterization at the central research facility, IIT, Kharagpur, India. The feed composition data of IPNs are furnished in the **Table 1**.

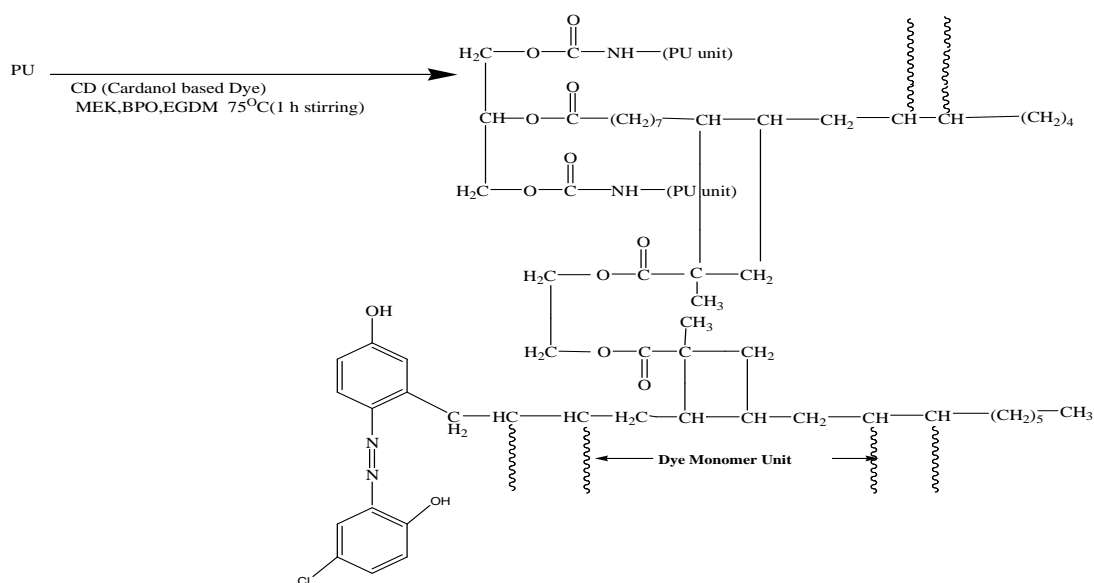
TABLE – 1 FEED COMPOSITION DATA OF IPNs

Sample Code	Composition	NCO/OH molar Ratio	PU/CD Weight Ratio
IPN-1	GL+TDI+CD of 2-chloroaniline	1.6	35 : 65
IPN-2	GL+HMDI+CD of 2-chloroaniline	1.2	35 : 65
IPN-3	GL+HMDI+CD of 2-chloroaniline	1.6	50 : 50
IPN-4	GL+HMDI+CD of 2-chloroaniline	1.6	35 : 65
IPN-5	GL+HMDI+CD of 2-amino- 4 – chlorophenol	1.6	35 : 65

The probable schemes of reaction involved in the synthesis of interpenetrating polymer networks are given in **Schemes 1 and 2**.



Scheme 1



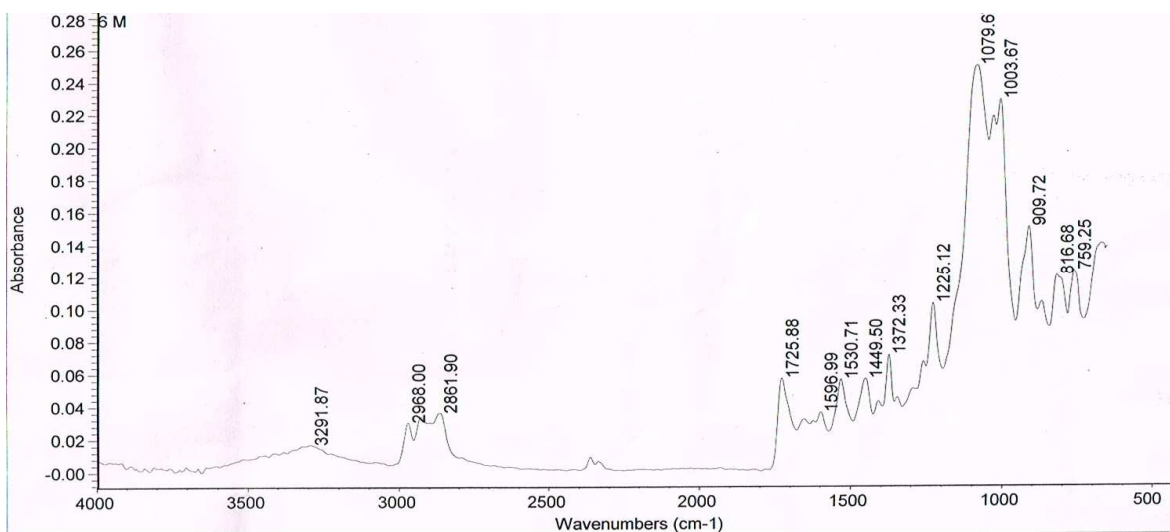
Scheme 2 : Expected Structure of IPN

## RESULTS AND DISCUSSION

### FT-IR Spectra

The FT-IR spectra of the interpenetrating polymer networks were obtained using a Perkin Elmer FT-IR Spectrophotometer, model paragon 1000. A small amount of the finely powdered sample was mixed with about 100 times its weight of powdered potassium bromide (KBr) and pressed into a small disc of about 1 mm thick. Elmer FT-

IR spectra were analyzed by studying the intensity of the absorbance peaks and comparing with the control spectra. FT-IR spectra of the IPNs were found to be identical, given in **Figure 1** for the PIN-2.



**Figure 1 : FTIR OF IPN-2**

The presence of component materials in the macromolecules was confirmed by the study of FT-IR spectra of the prepared samples. The characteristic absorptions of IPN-1 corresponding to N-H stretching of  $>NH$  group at  $3306.42\text{ cm}^{-1}$ , C-H stretchings (ss/as) of  $>CH_2$  and  $-CH_3$  groups at  $2855.81\text{ cm}^{-1}$  and  $2924.01\text{ cm}^{-1}$ ,  $N\equiv C$  stretching of  $-N=C=O$  group for the isocyanate terminating PU unit at  $2361.71\text{ cm}^{-1}$ , C=O stretching of urethane linkage at  $1723.59\text{ cm}^{-1}$ , N=N stretching of azo group at  $1593.53\text{ cm}^{-1}$ , O-H bending of  $-OH$  group at  $1372.50\text{ cm}^{-1}$ , C-O bending at  $1223.72\text{ cm}^{-1}$ , out of plane C-H bending at  $816.91\text{ cm}^{-1}$  and out of plane O-H bending at  $754.40\text{ cm}^{-1}$  were observed.

The characteristic absorptions of IPN-2 corresponding to N-H stretching of  $>NH$  group at  $3291.87\text{ cm}^{-1}$ , C-H stretchings (ss/as) of  $>CH_2$  and  $-CH_3$  groups at  $2861.90\text{ cm}^{-1}$  and  $2968.00\text{ cm}^{-1}$ , C=O stretching of urethane linkage at  $1725.88\text{ cm}^{-1}$ , O-H bending of  $-OH$  group at  $1372.33\text{ cm}^{-1}$ , C-O bending at  $1225.12\text{ cm}^{-1}$ , out of plane C-H bending at  $812.62\text{ cm}^{-1}$  and out of plane O-H bending at  $760.60\text{ cm}^{-1}$  were observed (**Figure 1**).

The characteristic absorptions of IPN-3 corresponding to  $>N-H$  stretching of  $=NH$  group at  $3293.49\text{ cm}^{-1}$ , C-H stretchings (ss/as) of  $>CH_2$  and  $-CH_3$  groups at  $2865.77\text{ cm}^{-1}$  and  $2968.62\text{ cm}^{-1}$ , C=O stretching of urethane linkage at  $1726.38\text{ cm}^{-1}$ , N=N stretching of azo group at  $1593.53\text{ cm}^{-1}$ , O-H bending of  $-OH$  group at  $1372.38\text{ cm}^{-1}$ , C-O bending at  $1224.90\text{ cm}^{-1}$ , out of plane C-H bending at  $817.03\text{ cm}^{-1}$ , out of plane O-H bending at  $759.18\text{ cm}^{-1}$  were observed.

Similar peak values are obtained for the IPN – 4 and IPN – 5. Such IPNs are structurally identical.

### Thermal Analysis

Perkin Elmer Thermal Analyzer model PYRIS diamond USA was used for TGA, DTG and DTA measurements. The samples were scanned for TGA, DTG and DTA between  $50^\circ\text{C}$  and  $650^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in an inert nitrogen atmosphere ( $N_2$  100 ml/min) (**Figures 2-6**).

### TG Analysis

The thermogravimetric analysis of IPN-1, IPN-2, IPN-3, IPN-4 and IPN-5 was carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  in the nitrogen atmosphere. The samples have been analyzed with respect to the following variations taking into consideration.

- |                                    |                                |
|------------------------------------|--------------------------------|
| a. NCO/OH molar ratio              | b. Nature of diisocyanate (DI) |
| c. Nature of Dye monomer unit (CD) | d. PU/CD weight ratio          |

The **Table 2** exhibits the percentage of the mass loss of IPN-1, IPN-2, IPN-3, IPN-4 and IPN-5 at various temperatures calculated from TG curves (**Figures 2-6**). The IPNs as expected, are thermally stable upto  $150^\circ\text{C}$  with

1.14%, 0.78%, 0.76%, 1.00% and 1.00% of weight losses for IPN -1, IPN- 2, IPN -3, IPN -4 and IPN -5 respectively due to loss of moisture retained in the samples. Mass losses increase slowly and occur in three steps.

i) In the temperature range of 150<sup>0</sup>C —250<sup>0</sup>C the weight losses are 16.71%, 3.02%, 5.21%, 6.15% and 9.65% for IPN -1, IPN -2, IPN -3, IPN -4 and IPN -5 respectively which may be due to evaporation of solvent and other volatile matters, if any.

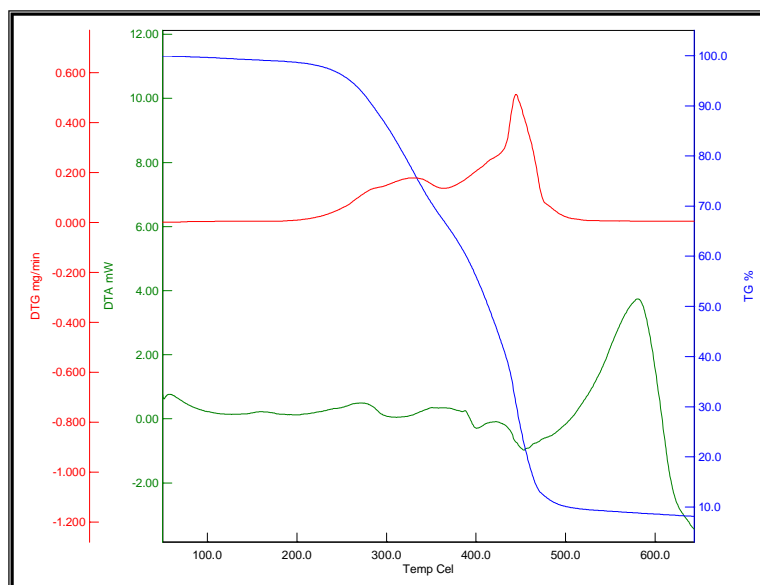
ii) Significant weight losses i.e about 53.02%, 70.66%, 69.07%, 68.27% and 48.25% for IPN -1, IPN -2, IPN -3, IPN -4 and IPN -5 respectively occur in the temperature range of 250<sup>0</sup>C -450<sup>0</sup>C, which can be attributed to the decomposition of the benzene ring along with main functional groups such as –OH, >NH and >C=O etc and also due to partial decomposition of cross linkings with EGDM between PU and CD units.

iii) Finally in the temperature range of 450<sup>0</sup>C -600<sup>0</sup>C the weight losses of 9.62%, 16.95%, 16.66%, 16.74% and 16.02% for the IPN- 1, IPN- 2, IPN- 3, IPN- 4 and IPN- 5 respectively may be due to complete decomposition of the cross linkings with EGDM between PU unit and CD monomer unit i.e separation of two monomer units.

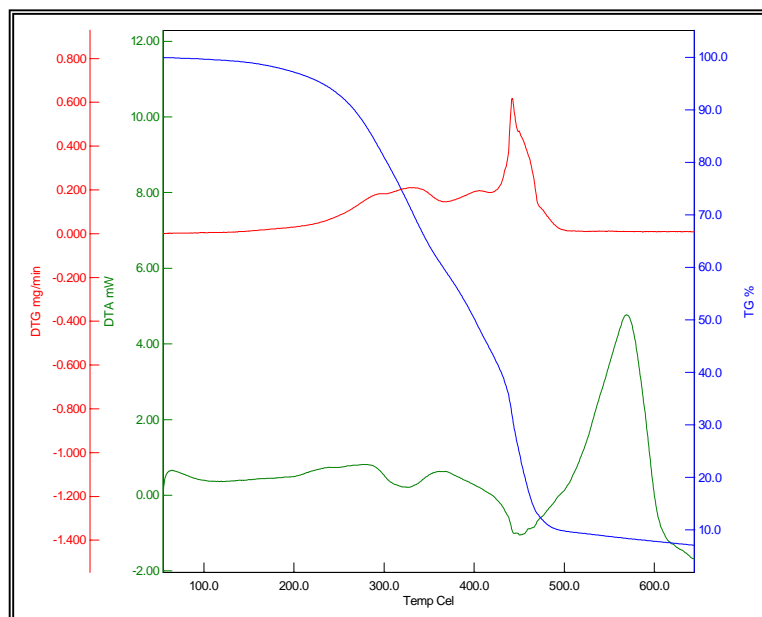
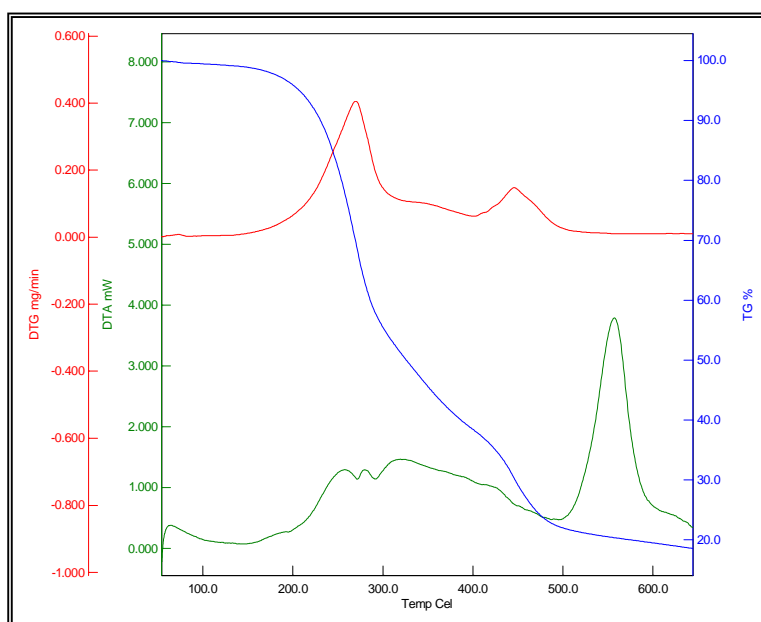
a) Comparing the thermal stability of IPN 2 with that of IPN 4 (**Table 2**) it is observed that IPN- 2 is thermally more stable than IPN- 4. The enhanced stability of IPN- 2 having same PU/CD weight ratio as that of IPN- 4 but with less value of NCO/OH molar ratio is due to the increase in oil content of the PU unit in the IPN- 2. The increase in oil content of the PU component results in greater unsaturation leading to enhanced degree of crosslinkings.

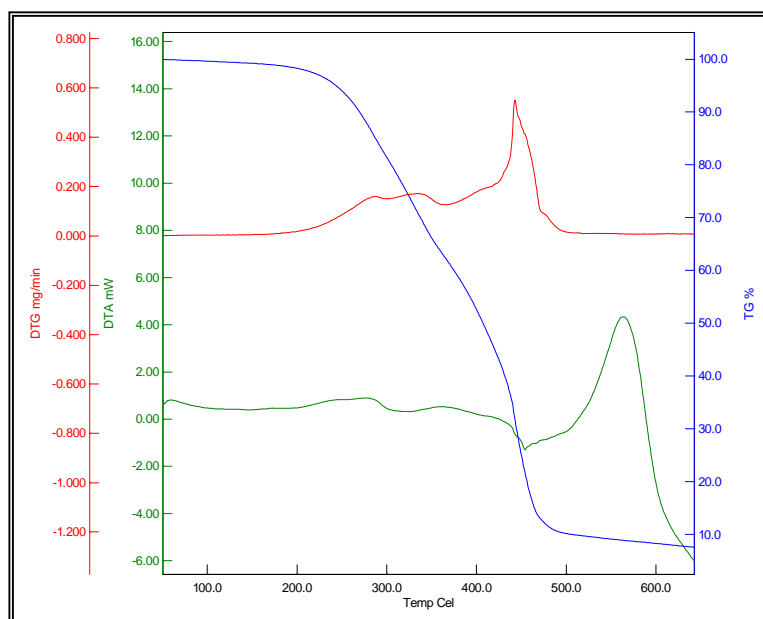
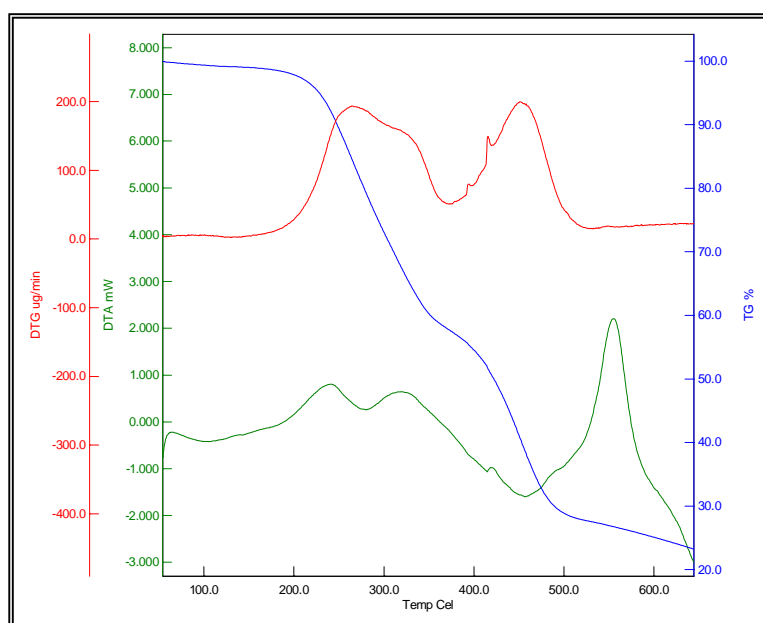
**TABLE – 2 Percentage of Mass Loss of IPNs at Various Temperature (<sup>0</sup>C)**

Samples/ Temp ( <sup>0</sup> C)	100	150	200	250	300	350	400	450	500	550	600
IPN-1	0.56	1.14	4.08	17.85	44.52	54.41	61.56	70.87	78.01	79.48	80.49
IPN-2	0.32	0.78	1.30	3.80	13.93	29.31	44.04	74.46	89.90	90.84	91.41
IPN-3	0.35	0.76	1.70	5.97	18.59	33.81	47.42	75.04	89.83	90.88	91.70
IPN-4	0.35	1.00	2.82	7.15	19.02	35.83	49.78	75.42	90.22	91.25	92.16
IPN-5	0.64	1.00	2.14	10.65	26.93	39.76	55.48	58.90	1.13	73.09	74.92



**Figure 2: TGA/DTG/DTA of IPN-1**

**Figure 3: TGA/DTG/DTA of IPN-2****Figure 4 : TGA/DTG/DTA of IPN-3**

**Figure 5 : TGA/DTG/DTA of IPN-4****Figure 6 : TGA/DTG/DTA of IPN-5**

b) The effect of nature of diisocyanate component in the IPNs on the thermal stability is observed in IPN- 1 and IPN-4. The thermal data of IPN- 1 (TDI) and IPN-4(HMDI) for constant NCO/OH molar ratio at 1.6 and constant PU/CD weight ratio at 35:65 for the same 2-chloroaniline component show that IPN-4 is thermally more stable than IPN-1 upto 400°C. So, IPNs with aliphatic diisocyanate like HMDI are thermally more stable than IPNs with aromatic diisocyanate like TDI. However, at the still higher temperatures IPN-1 is thermally more stable than IPN-4, i.e., IPNs with aromatic diisocyanates are more stable than the IPNs with aliphatic diisocyanates may be due to the presence of benzene ring.

c) The effect of nature of cardanol based dye (CD) component present in the IPNs on the thermal stability can also be observed in the IPN-4 and IPN-5. The thermal data of IPN-4 and IPN-5 with constant NCO/OH molar ratio at 1.6 and constant PU/CD weight ratio at 35:65 and for a given diisocyanate (HMDI) show that IPN-4 with 2-chloroaniline is more stable than IPN-5 with 2-amino-4-chlorophenol upto 350°C. However, at the still higher temperature the IPN-5 is thermally more stable than the IPN-4.

d) The thermal data of IPN-3 and IPN-4 with constant NCO/OH molar ratio at 1.6 and varying PU/CD weight ratio show that IPN-3 with PU/CD weight ratio at 50:50 is more stable than IPN-4 with PU/CD weight ratio at 35:65. The enhanced stability of IPN-3 with greater value of PU/CD weight ratio is due to increased amount of the PU content leading to increased degree of crosslinkings in the IPN-3.

### DTG Study

The DTG curves (**Figures 2-6**) show the rate of thermal decomposition in g/min. The **Table-3** shows the peak data of the thermograms of the IPNs.

**TABLE – 3 DTG Data of the IPNs**

Sample Code	NCO/OH Molar ratio	PU/CD Weight Ratio	Temperature Range (°C)	Peaks (mg/min)	Temp. (°C)
IPN-1	1.6	35 : 65	200 – 350	389.7	265.1
			351 - 550	126.2	436.7
IPN-2	1.2	35 : 65	200 – 350	163.8	310.5
			351 - 550	501.3	442.6
IPN-3	1.6	50 : 50	200 – 350	558.5	313.0
			351 - 550	535.8	442.0
IPN-4	1.6	35 : 65	200 – 350	192.6	311.0
			351 - 550	596.6	441.0
IPN-5	1.6	35 : 65	200 – 350	188.8	257.6
			351 - 550	192.6	444.8

- The DTG curve of IPN-1 shows two peaks at 265.19°C and 436.7°C corresponding to maximum rates of decomposition 389.7 mg/min and 126.2 mg/min respectively.
- The DTG curve of IPN-2 shows two peaks of 310.5°C and 442.6°C corresponding to maximum rates of decomposition 163.8 mg/min and 501.3 mg/min respectively.
- The DTG curve of IPN-3 shows two peaks at 313°C and 442°C corresponding to maximum rates of decomposition 558.5 mg/min and 535.8 mg/min respectively.
- The DTG curve of IPN-4 shows two peaks at 311°C and 441°C corresponding to maximum rates of decomposition 192.6 mg/min and 596.6 mg/min respectively.
- The DTG curve of IPN-5 shows two peaks at 257.6°C and 448.8°C corresponding to maximum rates of decomposition 188.8 mg/min and 192.6 mg/min respectively.

It is observed that IPN-1 to IPN-5 undergo two steps thermal degradation with respect to rate of decomposition.

### DTA study

Exothermic and endothermic behaviour of the reactions associated with the thermal decomposition can be studied from differential thermal analysis (**Figure 2-6**). The DTA data of IPNs are given in **Table-4**.

**TABLE – 4 DTA Data of the IPNs**

Sample Code	NCO/OH Molar ratio	PU/CD Weight Ratio	Temperature Range (°C)	DTA Peak	
				Exo	Endo
IPN-1	1.6	35 : 65	200 – 400	304.82	479.99
			400 - 600	552.07	
IPN-2	1.2	35 : 65	200 – 400	254.88	461.59
			400 - 600	376.83	
IPN-3	1.6	50 : 50	200 – 400	--	461.24
			400 - 600	556.26	
IPN-4	1.6	35 : 65	200 – 400	272.93	440.82
			400 - 600	562.84	
IPN-5	1.6	35 : 65	200 – 400	224.29	462.63
			400 - 600	550.76	

### Calculation of kinetic Parameters

The kinetic parameters of thermal decomposition process such as energy of activation ( $E_a$ ) and order of reaction ( $n$ ) in the temperature range from 160°C -300°C and from 300°C -450°C were calculated from thermograms obtained by the Freeman-Anderson method (**Figures 7-11**). The equation used for Freeman-Anderson's method is

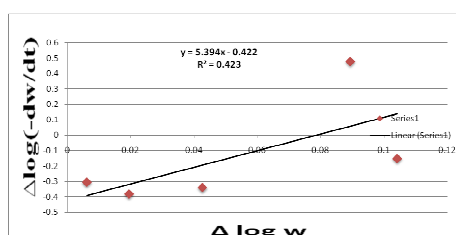
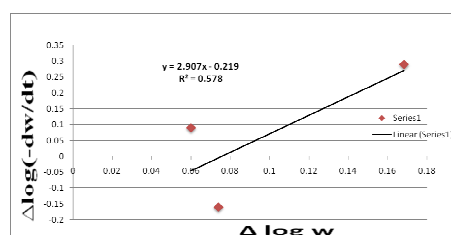
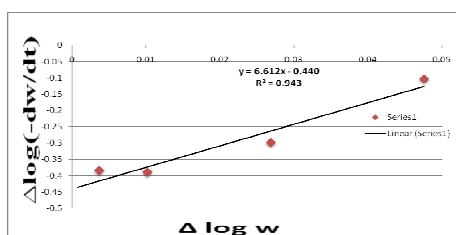
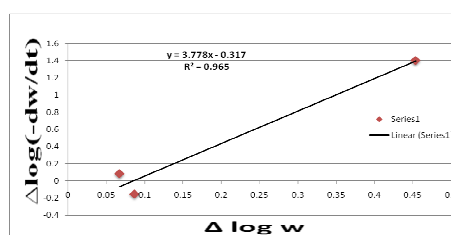
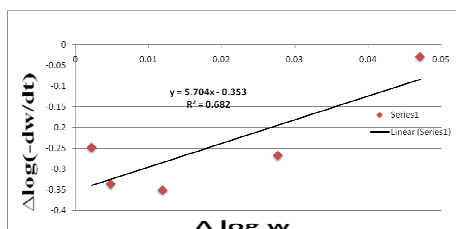
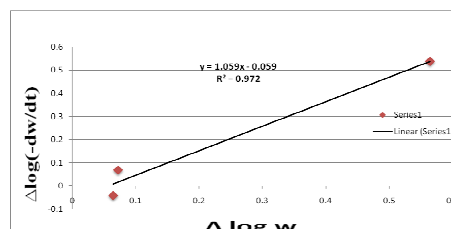
$$\Delta \log \left( -\frac{dw}{dt} \right) = n \Delta \log W - (E_a / 2.303R) \Delta \left( \frac{1}{T} \right)$$
 where  $-\frac{dw}{dt}$  is rate of decomposition (calculated from DTG measurements), 'w' is the residual mass (calculated from TG measurements) at constant differences in



$\frac{1}{T}$  ( $0.1 \times 10^{-3}$ ), 'n' is the order of reaction and  $E_a$  is the activation energy. The kinetic parameters such as activation energy ( $E_a$ ) and order of reaction (n) for the thermal decomposition are given in **Table 5**. The order of thermal degradation process 'n' indicates the complexity of the degradation process. The kinetic data clearly show that the activation energy values for the decomposition process of all the IPNs except IPN-4 are high indicating their high thermal stability. The higher is the activation energy, the slower is the rate of thermal degradation process and the higher is the stability of the IPNs. The kinetic parameters of the IPN-2 and IPN-4 show that IPN-2 has higher activation energy than IPN-4 indicating that IPN-2 is more stable than IPN-4. Similarly comparing the stability of IPN-3 and IPN-4, IPN-3 has high activation energy than IPN-4 upto  $300^\circ\text{C}$ . So IPN-3 is more stable than IPN-4. The kinetic parameters of IPN-1, IPN-2, IPN-3, IPN-4 and IPN-5 given in **Table-5** are almost in good agreement with experimental thermal data (**Table-2**).

TABLE – 5 Kinetic Parameters of the Thermal Decomposition of IPNs

Sample Code	Temperature Range ( $^\circ\text{C}$ )	$E_a/k_J$	n
IPN-1	160 – 300	80.93	5.4
	300 – 450	42.06	2.9
IPN-2	160 – 300	84.3	6.6
	300 – 450	60.8	3.7
IPN-3	160 – 300	67.6	5.7
	300 – 450	11.34	1.1
IPN-4	160 – 300	38.81	1.4
	300 – 450	32.51	3.5
IPN-5	160 – 300	89.32	8.5
	300 – 450	111.36	3.2

Figure 7a : IPN-1 Temp (160-300 $^\circ\text{C}$ )Figure 7b : IPN-1 Temp (300-450 $^\circ\text{C}$ )Figure 8a : IPN-2 Temp (160-300 $^\circ\text{C}$ )Figure 8b : IPN-2 Temp (300-450 $^\circ\text{C}$ )Figure 9a : IPN-3 Temp (160-300 $^\circ\text{C}$ )Figure 9b : IPN-3 Temp (300-450 $^\circ\text{C}$ )

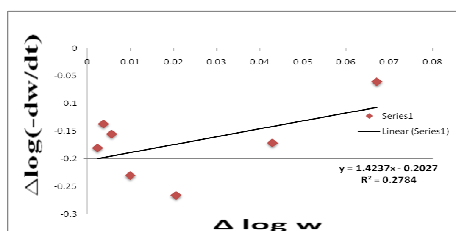


Figure 10a : IPN-4 Temp (160-300°C)

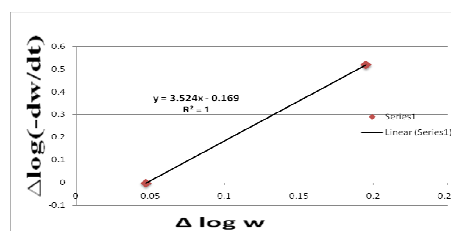


Figure 10b : IPN-4 Temp (300-450°C)

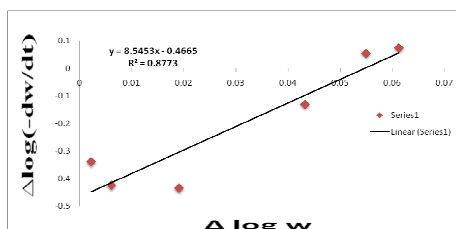


Figure 11a : IPN-5 Temp (160-300°C)

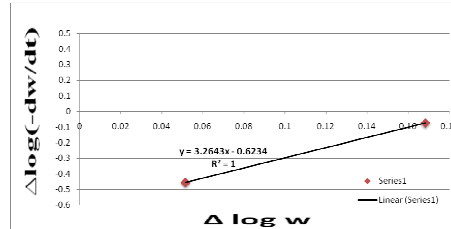


Figure 11b : IPN-5 Temp (300-450°C)

## CONCLUSION

Polymers based on natural renewable resources are expected to be comparatively more eco-friendly and cost effective than the petroleum based polymers. The cashew nut shell liquid and triglyceride oils are the renewable resources for the production of bio-polymers. These oil-based bio-polymers are expected to be bio-degradable. Interpenetrating polymer networks (IPNs) prepared from glycerol modified linseed oil based polyurethanes and cardanol-based dyes are highly crosslinked with high thermal stability which depends on NCO/OH molar ratios, PU/CD weight ratios, nature of diisocyanate and nature of dye monomer unit of the IPNs. The present study is aimed at synthesizing cost effective, eco-friendly and thermally stable polymers from agricultural products for various specific applications by considering the suitable composition of the IPNs.

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