IOSR Journal of Engineering (IOSRJEN) **www.iosrjen.org**
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 08, Issue 7 (July. 2018), ||V (II) || PP 41-50

The synthesis and FTIR, Kinetics and TG/DTG/DTA study of Inter Penetrating Polymer Networks (IPNs) of Polyurethanes of polyol modified castor oil and TDI and cardanol based dyes.

M. K. Swain, P.G.R. Achary, Dr N. C. Pal*
Laboratory of polymers and Fibers, Department of Chemistry, Ravenshaw University, Cuttack, Odisha, India
Corresponding Author: M. K. Swain

Abstract: In view of the fast consumption of the petroleum stock and pressing demand for the use of polymeric materials to keep pace with the rate of growth of the world's population the synthesis of polymers from agricultural products has achieved tremendous momentum at present all over the world. A number of Interpenetrating Polymer Networks were synthesized from polyol modified castor oil polyurethanes and cardanol based dyes. Characterizations of these polymers were performed by fourier transform infrared spectra and thermal analysis techniques such as thermogravimetric analysis, derivative thermogravimetry and differential thermal analysis. The kinetic parameters such an activation energies and orders of reactions were determined by using Freeman – Anderson's method. The effect of changes in polyurethane to dye monomer weight ratio and NCO/OH molar ratio of polyurethanes on the properties of such polymer were studied.

Keywords: Cardanol, Cardanol Based Dye, Polyol Modified Castor Oil, Polyurethanes, Interpenetrating Polymer Network.

Date of Submission: 28-06-2018 Date of acceptance: 13-07-2018

I. INTRODUCTION

At present the synthesis of agricultural products based polymers as potential substitute for petroleum based polymers is not only useful to reduce 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 work in this paper is to utilize the available natural and agricultural resources to produce cost-effective and eco-friendly polymers with significantly improved properties to meet the need of the hour. Although, a large number of articles have been published recently on cardanol [7,8], the research work on interpenetrating polymer networks using cardanol based dye monomers and modified castor oil based polyurethanes (PUs) is very limited [9].

Cardanol with an unsaturated side chain at metaposition was obtained from cashew nut shell liquid (CNSL) by decarboxylation of its major component that is anacardic acid [10]. It was then modified into a novel new monomer using an aromatic amino compound by diazotization. The polyol modified castor oil (PC) was allowed to react with toluene di-isocyanate (TDI) in different NCO/OH molar ratios to produce a series of polyurethanes (PUs) by bulk polycondensation polymerization. The cardanol based dye and polyol modified castor oil polyurethane in different weight ratios are allowed to react in presence of benzoyl peroxide (BPO) as initiator and ethylene glycol dimethacrylate (EGDM) as crosslinker to form a number of interpenetrating polymer networks (IPNs) a novel class of polymer blends in network forms in which the cardanol based dye monomer is polymerized and cross linked with the linear prepolymer polyurethanes.

The structural evaluation of the polymers was carried out using Fourier Transform Infra Red (FT-IR) spectral analysis, Thermogravimetric Analysis (TGA), Derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were used to determine the decomposition temperature, temperature of maximum decomposition and relative thermal stability of polymers. Kinetic parameters were determined by the Freeman-Anderson method.

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 ^{0}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 clod alkaline cardanol solution. A brilliant red coloured azo dye was obtained [11].

Table 1 Feed composition data of IPNs

Sample code	Composition	NCO/OH (molar ratio)	PU/CD (weight ratio)
IPN-1	PC+TDI+CD of 2-amino-4chlorobenzoic acid	1.2	35:65
IPN-2	PC+TDI+CD of 2-amino-4chlorobenzoic acid	1.2	50:50
IPN-3	PC+TDI+CD of 2-amino-4chlorobenzoic acid	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 250^0C 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 210^0 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 thereafter dried under vacuum at 80^0 C for 6 hr.

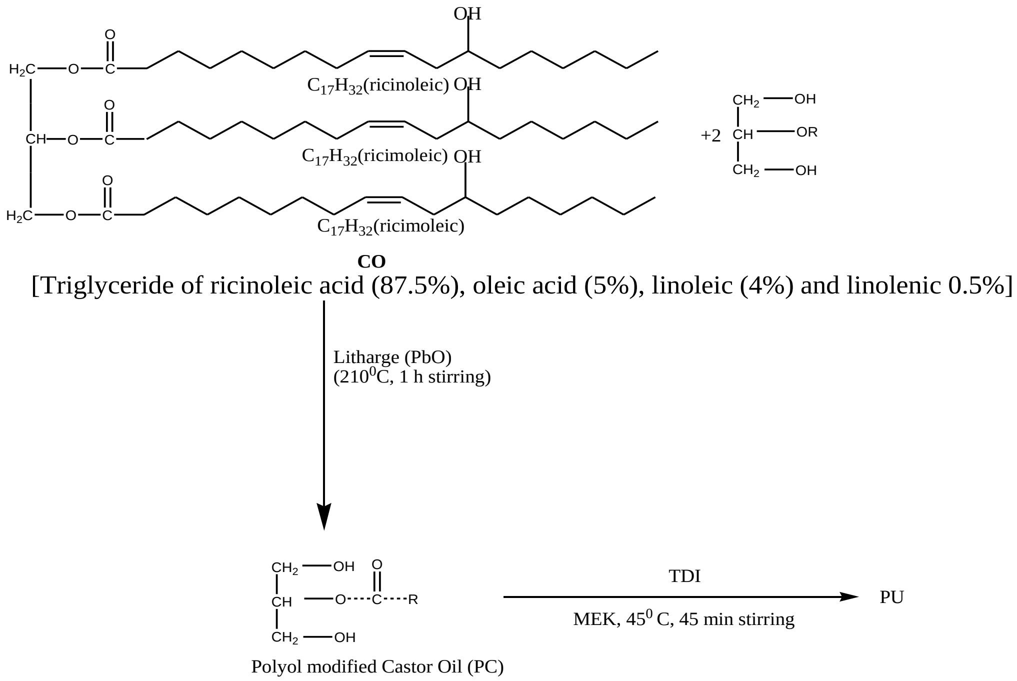
Synthesis of Polyurethanes (PUs)

0.372 g of polyol of modified castor oil was allowed to react with 0.313 g of toluene diisocyanate to maintain the NCO/OH molar ratio at 1.2. The above reaction was carried out in a small reaction vessel at 45^0 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.

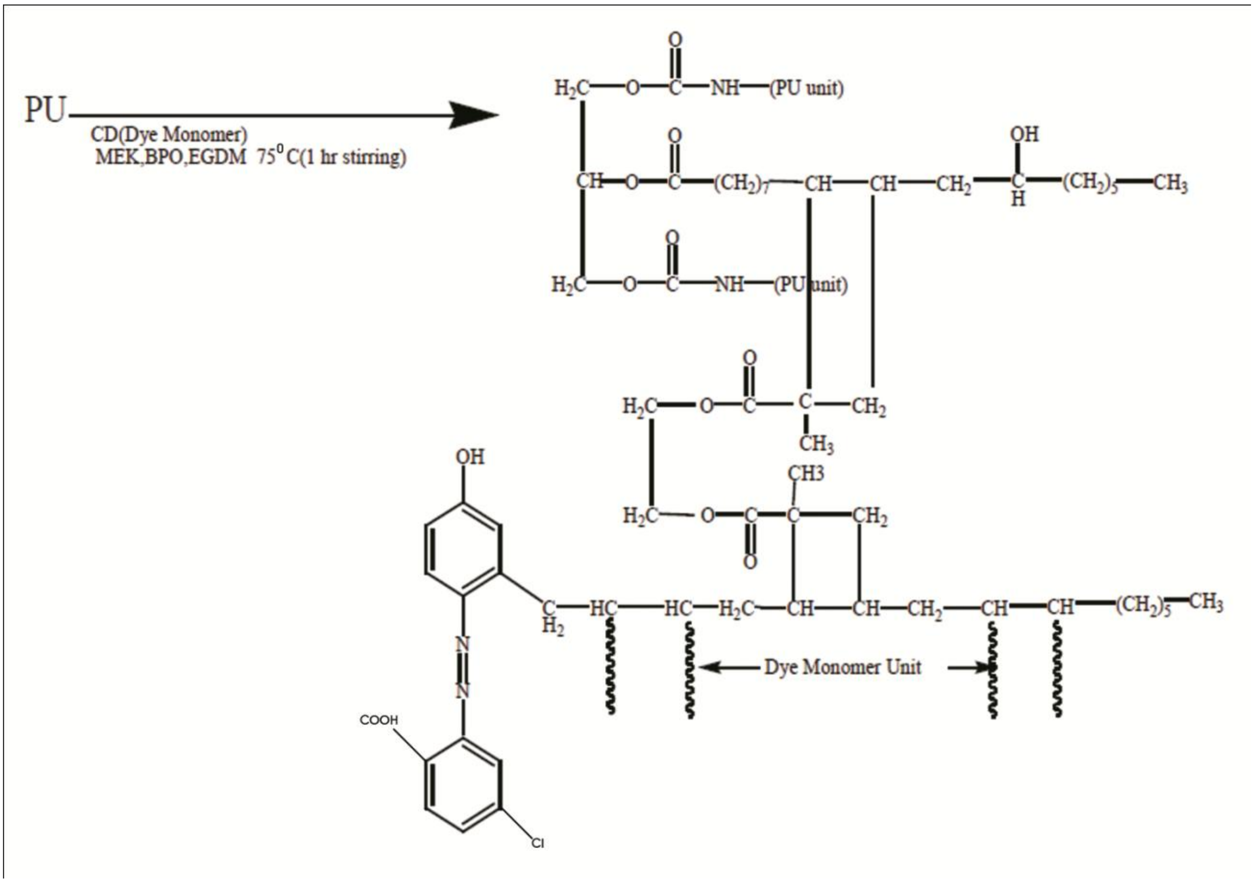
Synthesis of Interpenetrating Polymer Networks (IPNs)

The polyurethanes (PUs) with NCO/OH moral 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 75^0 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 75^0 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 (Structure of IPN)

III. RESULTS AND DISCUSSION

FTIR Spectra

Fourier-Transform Infrared (FTIR) spectra of the interpenetrating polymer network 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. Elmar 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 meterials in the IPNs. FTIR spectra of the IPNs 1, 2 and 3 are given in the figures 1, 2 and 3 respectively.

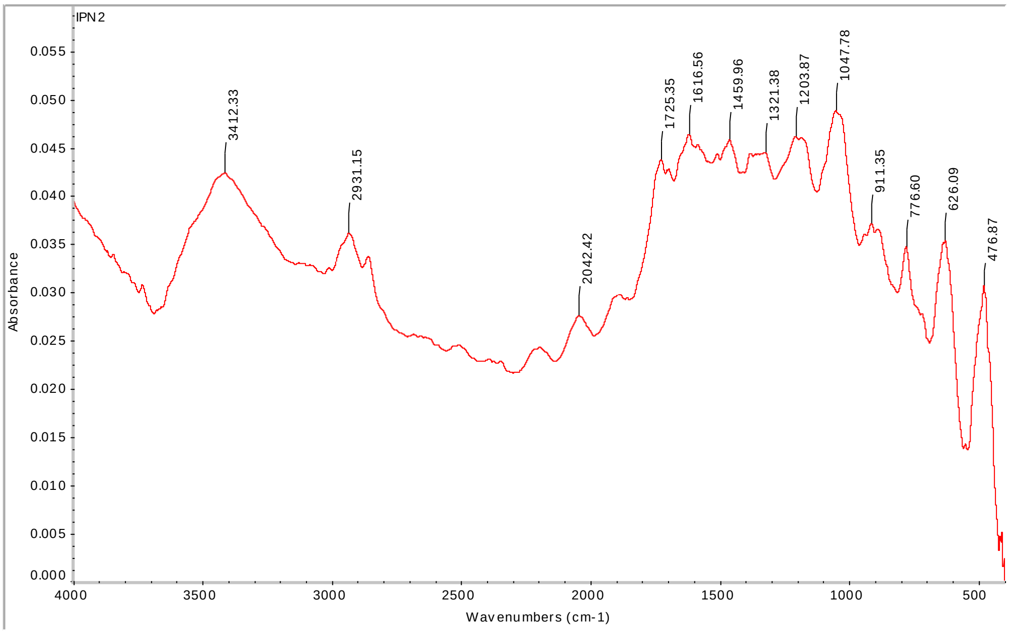


Fig. 1: FTIR spectra [IPN – 1]

Polyol Modified Castor Oil + TDI + CD of 2-amino-4-chlorobenzoicacid

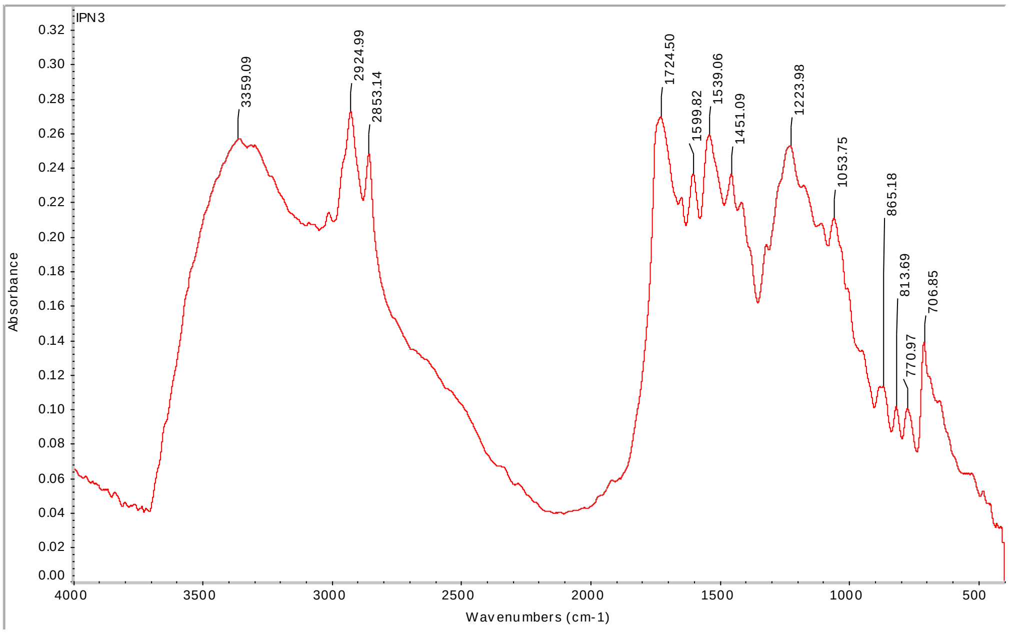


Fig. 2: FTIR spectra [IPN – 2]

Polyol Modified Castor Oil + TDI + CD of 2-amino-4-chlorobenzoicacid

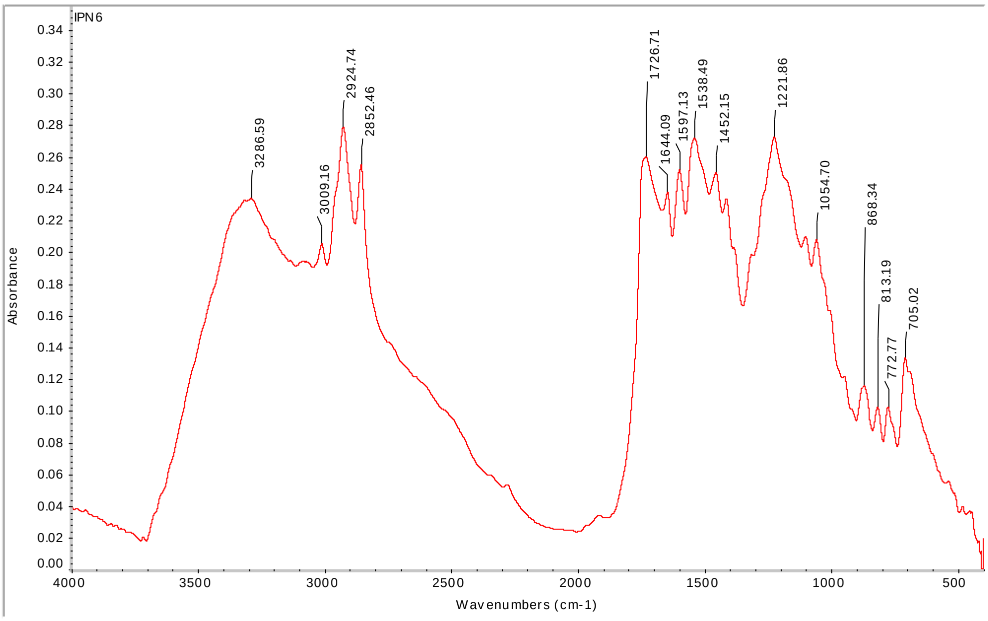


Fig. 3: FTIR spectra [IPN – 3]

Polyol Modified Castor Oil + TDI + CD of 2-amino-4-chlorobenzoicacid

The FTIR spectrum was used mainly to confirm the presence of component materials in IPNs. The characteristic absorptions of IPN-1 corresponding to -OH stretching of hydroxy group at 3412.33 cm^{-1}, C-H stretchings (as/ss) of CH_3 and $>CH_2$ groups at 2931.00 cm^{-1} and 2855.00, C=O stretching of urethane linkage at 1725.35 cm^{-1}, N=N stretching of azo group at 1597.13 cm^{-1}, C-O bending of at 1203.87 cm^{-1} were observed.

The characteristic absorptions of IPN-2 corresponding to N-H stretching of >NH group at 3359.09 cm^{-1}, C-H stretchings (as/ss) of $>CH_2$ and $-CH_3$ group at 2924.49 cm^{-1} and 2853.14 cm^{-1}, C=O stretching urethane linkage at 1724.50 cm^{-1}, N=N stretching of azo group at 1599.82 cm^{-1}, C-O bending at 1223.98 cm^{-1} were observed.

The characteristic absorptions of IPN-3 corresponding to N-H stretching of >NH group at 3286.59 cm^{-1}, C-H stretchings (as/ss) of $>CH_2$ and CH_3 groups at 2924.74 cm^{-1} and 2852.46 cm^{-1}, C=O stretching of urethane linkage at 1726.71 cm^{-1}, N=N stretching of azo group at 1597.13 cm^{-1}, C-O bending at 1221.86 cm^{-1} were observed. Such IPNs are structurally identical.

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 10.45 mg of IPN-1 with 10.5 mg of alumina as reference material was scanned between 50 and 650^0 C at a heating rate of 10^0 C/ min in an inert nitrogen atmosphere [N_2(XL), 100 mL/ min], (Fig. 4). In the same way IPN-2, IPN-3 were scanned for TGA, DTG and DTA measurements (Fig.5 and Fig.6).

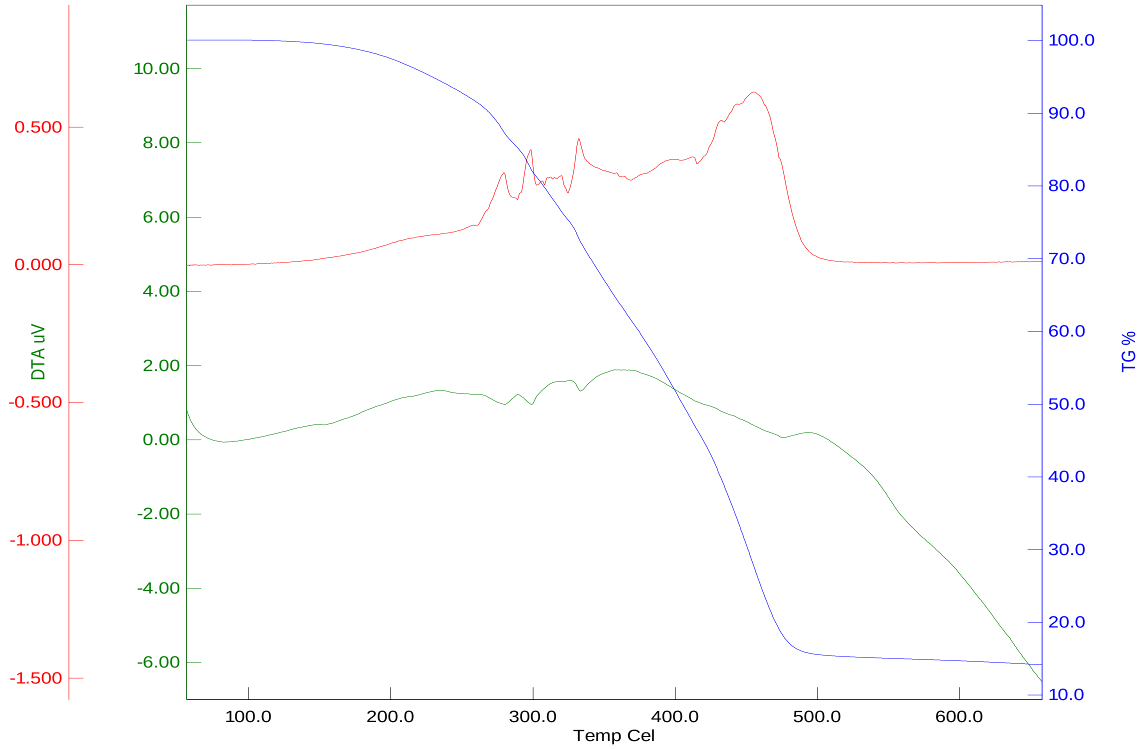


Fig. 4: TG/DTG/DTA of IPN-1

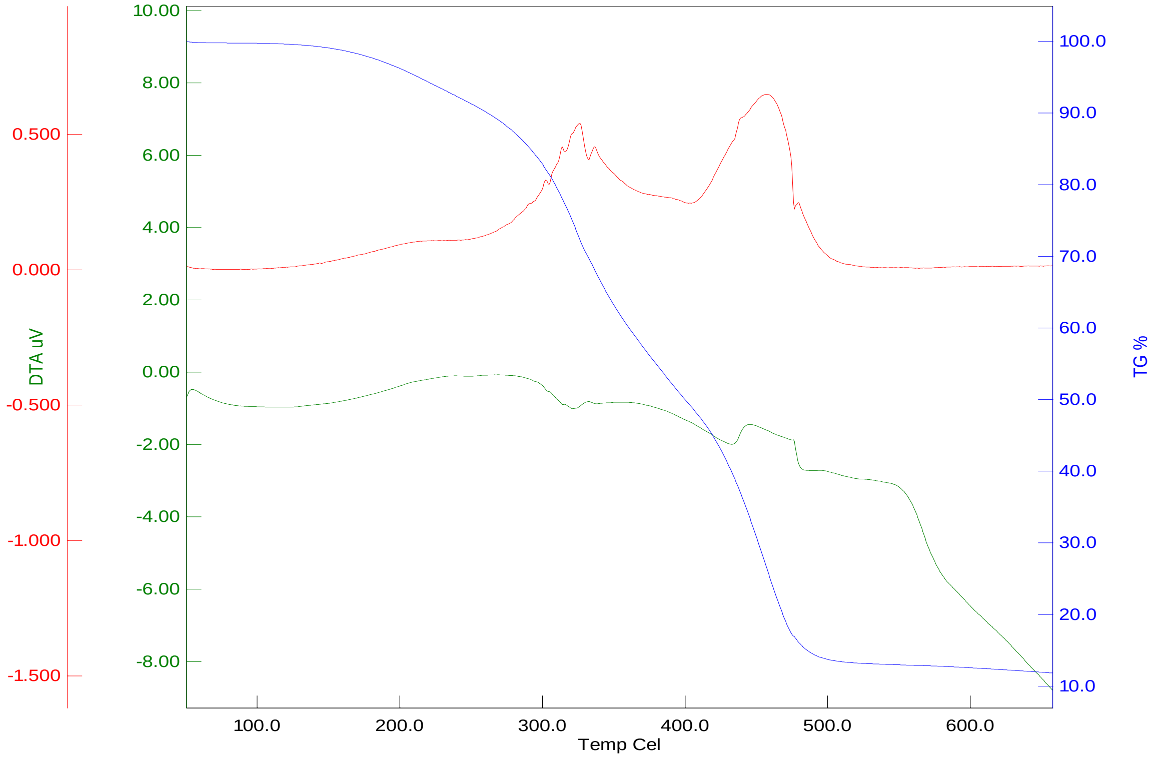


Fig. 5: TG/DTG/DTA of IPN-2

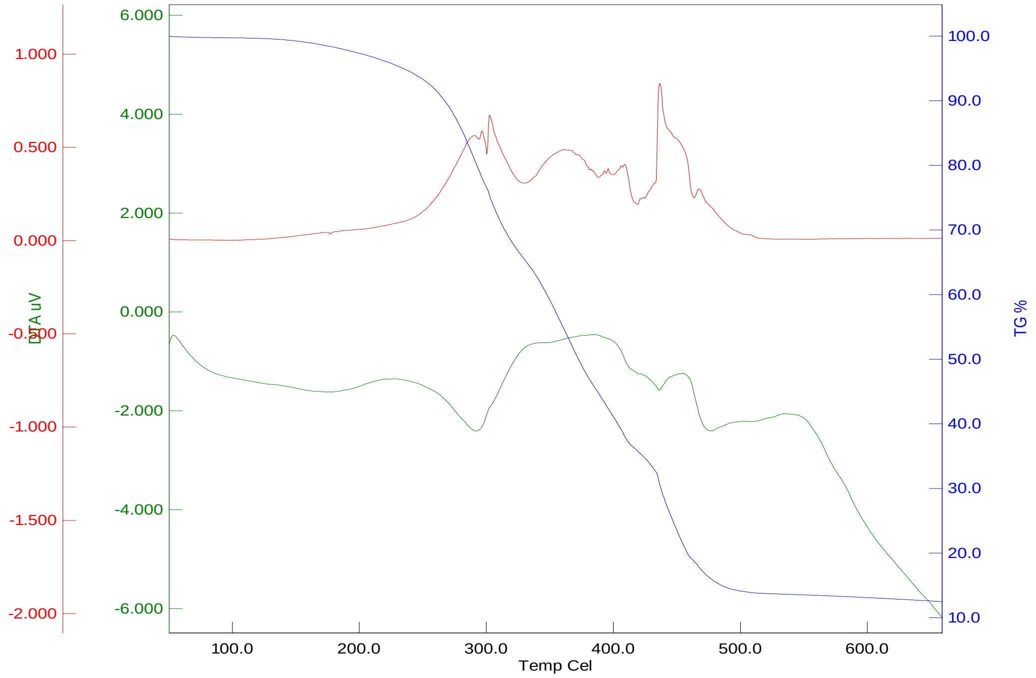


Fig. 6: TG/DTG/DTA of IPN-3

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 mass loss of IPNs at various temperatures (^{0}C)

IPNs/Temp	**100^0 C**	**150^0 C**	**200^0 C**	**250^0 C**	**300^0 C**	**350^0 C**	**400^0 C**	**450^0 C**	**500^0 C**	**550^0 C**	**600^0 C**	**650^0 C**
IPN-1	0.04	0.42	2.49	7.20	18.14	32.94	48.19	69.30	84.41	84.93	85.28	85.74
IPN-2	0.27	0.38	3.27	8.22	16.72	36.44	49.74	68.99	86.19	86.95	87.36	87.99
IPN-3	0.25	0.73	2.65	6.67	23.40	40.85	58.88	76.47	85.85	86.46	86.88	87.39

The **Table – 2** describes the percentages of mass losses of the IPNs at various temperatures at the interval of 50 ^{0}C calculated from TG curves. All the IPNs were found thermally stable up to 150^0 C with only 0.42% (IPN-1), 0.38% (IPN-2) and 0.73% (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^{0}C - 250^{0}C the weight losses are 6.78%, 7.84% and 5.94% 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: Significantly weight losses i.e., about 62.10%, 60.77% and 69.80% for IPN-1, IPN-2 and IPN-3 respectively occur in the temperature range of 250^{0}C - 450^{0}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^{0}C - 600^{0}C the weight losses of 16.44%, 19.00% and 10.92% 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.

Comparing thermal stability of IPN-2 with that of IPN-3 (Table – 2) it is observed that IPN-2 is thermally more stable than IPN-3 up to 450^{0}C where the significant weight losses occur. The enhanced thermal stability of IPN-2 having the same PU/CD weight ratio as that of IPN-3 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 the oil content of the PU component results in greater unsaturation leading to enhanced degree of cross linkings.

The thermal data of IPN-1 and IPN-2 with constant NCO/OH molar ratio at 1.2 and varying PU/CD weight ratio shows that IPN-1 with PU/CD weight ratio at 35:65 is thermally more stable than IPN-2 with PU/CD weight ratio at 50:50. The enhanced thermal stability of IPN-1 with smaller value of PU/CD weight ratio is due to the increased amount of dye monomer content with the same NCO/OH molar ratio. This is because of more unsaturation and hence consequent crosslinkings with increase of dye monomer content.

The DTG curve **(Fig.4)** shows that the IPN-1 has four peaks at 277, 297, 331 and 452^0 C corresponding to maximum rate of decomposition 323 µg/min, 441 µg/min, 451 µg/min and 618 µg/min respectively. **Fig.** 5 and 6 shows similar peaks at 324^0 C with 533.01 µg/min and at 335^0 C with 450 µg/min maximum rate of decomposition for IPN – 2. **Fig. 6** shows peaks at 405^0 C with 396 µg/min and 435^0 C with 833 µg/min maximum rate of decomposition for IPN – 3.

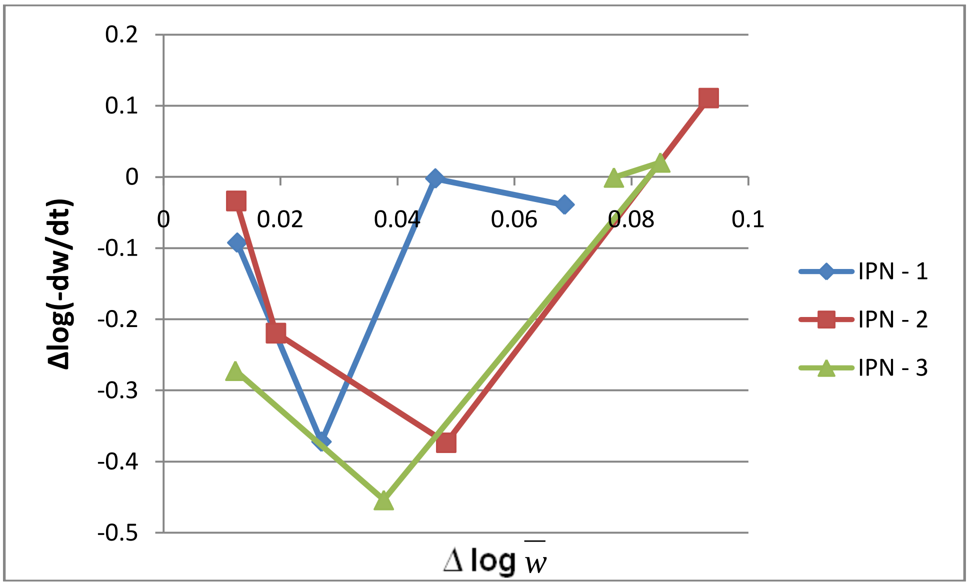
The DTA thermograms of the IPN – 1 shows an endothermic peaks at 286^0 C and Exothermic peak at 312^0 C in the temperature range of 250-450^0 C but in the range of 450-650^0 C only two peaks are observed that is exothermic 484^0 C and endothermic at 460^0 C. Similarly exothermic and endothermic peaks are also recorded for IPN – 2 and IPN – 3 which are listed in the Table-3.

Table – 3: DTA data of IPNs

Sample code	NCO/OH (molar ratio)	PU/DM (wt ratio)	Temperature (^{0}C)	DTA peak (^{0}C)		Percentage of decomposition
				Endo	Exo	
IPN-1	1.2	36:65	250-450	286 330	312 348	62.10%
			450-600	460	484	15.98%
IPN-2	1.2	50:50	250-450	312	256	60.77%
			450-600	479	463	18.37%
IPN-3	1.6	50:50	250-450	285 432	329 370	69.80%
			450-600	470	525	10.41

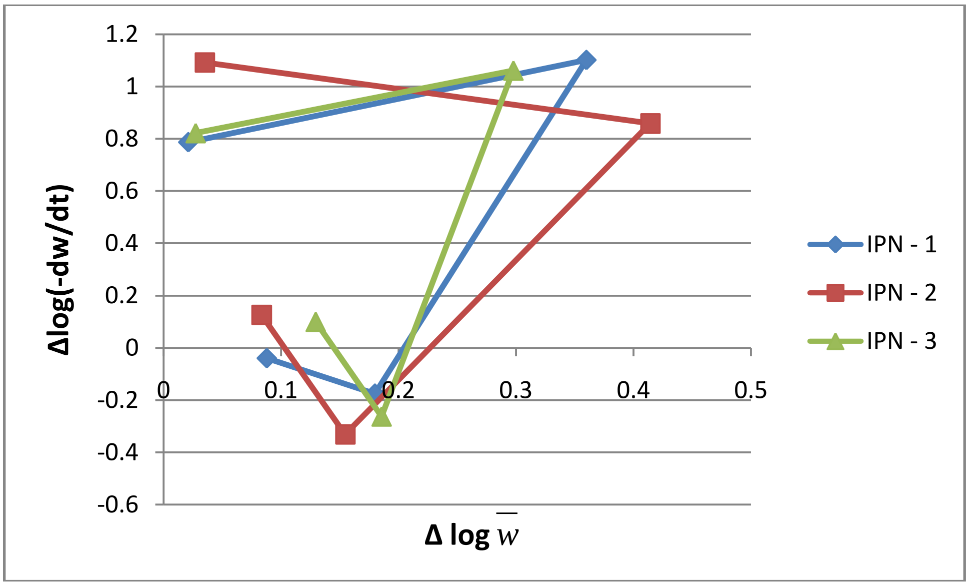
Table – 4: Kinetic parameters of the thermal decomposition of IPNs

Sample Codes	**Temperature Range**	**Slope or Order of Reaction**	**Intercept**	**Activation Energy [E$_a$] KJ/mol**
IPN – 1	226-316^0 C	3.140	-0.247	47.29
	350-500^0 C	0.168	-0.205	39.25
IPN – 2	226-316^0 C	2.465	-0.235	44.99
	350-500^0 C	0.624	-0.328	62.80
IPN – 3	226-316^0 C	5.344	-0.459	87.88
	350-500^0 C	0.715	-0.315	60.31



IPN–1, y = 3.140*x* + -0.247, IPN – 2, y = 2.465*x* + -0.235, IPN – 3, y = 5.344*x* + -0.459

Fig. 7 Freeman-Anderson Plot of IPN - 1, IPN – 2 and IPN – 3 between 226-316^0 C



IPN–1, y = 0.168*x* + -0.205, IPN – 2, y = 0.624*x* + -0.328, IPN – 3, y = 0.715*x* + -0.315

Fig. 8 Freeman-Anderson Plot of IPN - 1, IPN – 2 and IPN – 3 between 350-500^0 C

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:

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

Where – dw/dt is the rate of decomposition (calculated from DTG measurement), $\overline{w}$ is the residual mass (calculated from TG measurements) at constant difference in 1/T (0.1 x 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 226-316^0 C and 350-500^0 C respectively were obtained by plotting $\Delta \log\left(-\frac{dw}{dt}\right)$ against $\Delta \log \overline{w}$ 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 226-316^0 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 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.

IV. CONCLUSION

Polymer synthesized from natural renewable resources play a significant role in the present century as they are expected to be comparatively eco-friendly and cost effective than polymers obtained from petroleum based monomers. The major conclusion from this article is that interpenetrating polymer networks prepared from modified castor oil based polyurethane and cardanol-based dye are largely crosslinked with high thermal stability which not only depends on NCO/OH molar ratios but also on PU/CD weight ratios of the IPNs. Thus, by considering the suitable composition of the IPNs it is possible to prepare improved materials for various specific applications.

ACKNOWLEDGEMENT

The authors are thankful to the authority of the Ravenswah University for providing necessary facility for doing my research work and also thankful to the IIT Kharagpur for characterization of the samples.

REFERENCES

[1]. Suresh KI, Kishanprasa VS (2005) Ind Eng Chem Res 44(13):4504-4512

[2]. Praharaj D, Pal NC, Patra S, Lenka S (2004) Int J Plast Tech 8:172-179

[3]. Achary PGR, Biswal S, Mohapatra S, Pal NC (2010) Polym Plast Tech Eng 49(11):1114-1120

[4]. Yenwo GM, Manson JA, Pulido J, Sperling LH, Conde A, Devia N 91977) J Appl Polym Sci 21:1531-1541

[5]. Hepburn C (1995) In: Klempner D, Frisch KC (eds) Advance in interpenetrating polymer networks. Technomic Publishing AG, Basle

[6]. Kumar PP, Paramashivappa R, Vithayathil PJ, Subba Rao PV, Roa AS 9 (2002) J Agric Food Chem 50:4705-4708

[7]. Sperling LH, Manson JA, Linne MA (1984) J Polym Mater 1(1):54

[8]. Sperling LH, Manson JA, (1983) J Am Oil Chem Soc 60(11):1887-1892

[9]. Barrett LW, Shaffer OL, Sperling LH (1993) J Appl Polym Sci 48:953-968

[10]. Pastukhov AV, Davankov VA, Belyakova LD, Alekseenko NN, Tsurupa MP, Voloshchuk AM (2003) Struct Dyn Mol Syst 10(10):29

[11]. Knill CJ, Kennedy JF (1993) In: Charles G (ed) Biotechnology and polymers. Gebelein Plenum Press, New York

[12]. Sperling LH, (1981) Interpenetrating Polymer Networks and related materials. Plenum, New York.

IOSR Journal of Engineering (IOSRJEN) is UGC approved Journal with Sl. No. 3240, Journal no. 48995.

M. K. Swain " The synthesis and FTIR, Kinetics and TG/DTG/DTA study of Inter Penetrating Polymer Networks (IPNs) of Polyurethanes of polyol modified castor oil and TDI and cardanol based dyes." IOSR Journal of Engineering (IOSRJEN), vol. 08, no. 7, 2018, pp. 41-50.