



Synthesis and thermal degradation study of polymer blends from polyurethanes of linseed oil and cardanol based dyes with aminophenols

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ABSTRACT

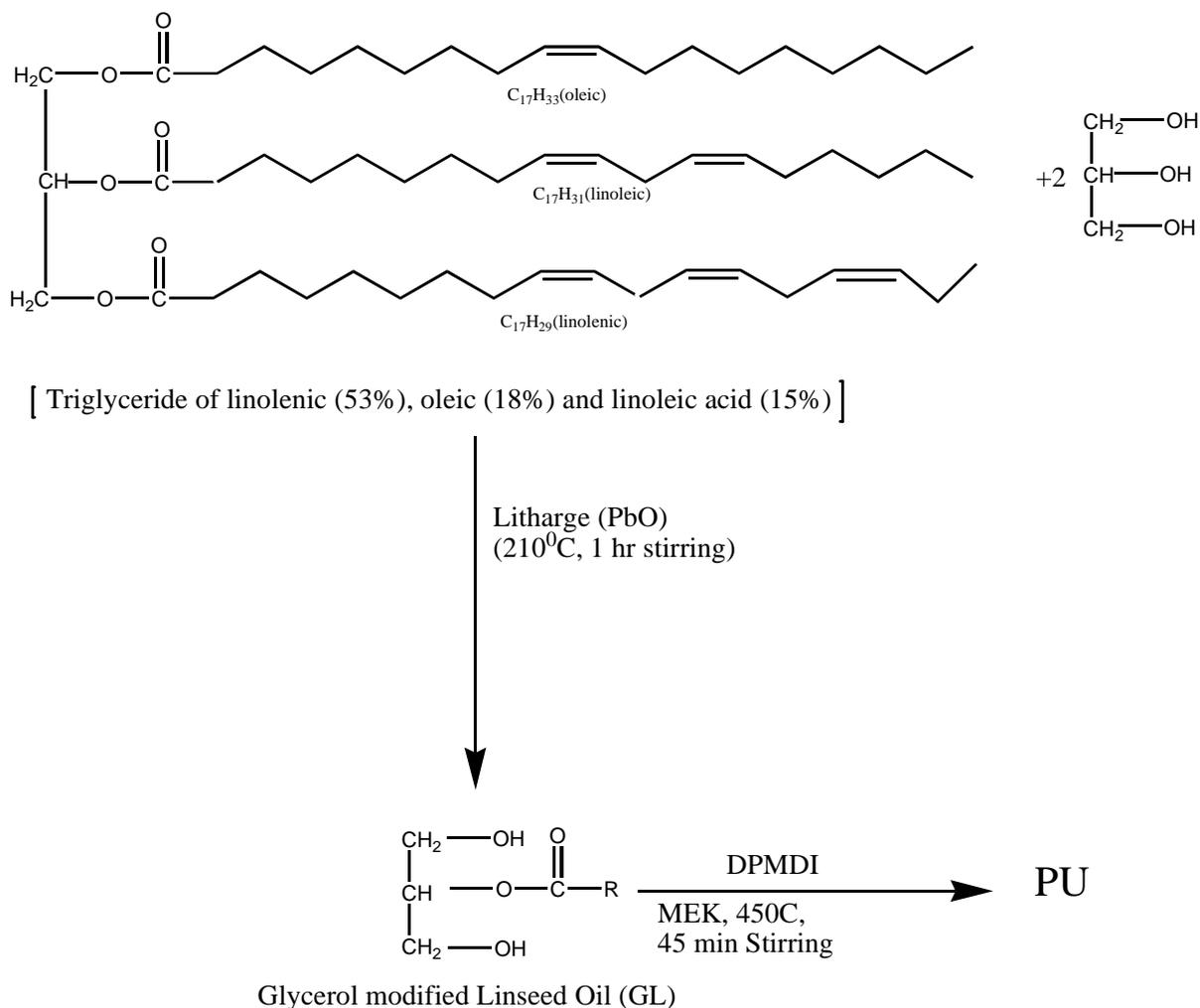
The new biobased polymer blends were synthesized from polyurethanes (PUs) which are derived from glycerol modified linseed oil and diphenyl methane-4, 4'-diisocyanate (DPMDI) and cardanol based dyes with aminophenols. The thermal stability of the polymer blends was investigated by thermogravimetric analysis (TGA), the rate of thermal degradation was determined by derivative thermogravimetry (DTG) and the exothermic and endothermic behavior of thermal degradation was ascertained by differential thermal analysis (DTA). The expected mechanism of the reaction and structure of the polymer blends prepared were investigated by FTIR study. The kinetic parameters such as activation energy and order of reaction of thermal degradation of polymer blends were calculated by Freeman- Anderson's method. Also the significant effect of NCO/OH molar ratio of polyurethanes and the nature of aminophenols on the thermal stability of polymer blends were investigated.

Keywords: Polymer Blends, Thermal Properties, Cardanol, Linseed Oil, Polyurethanes, Dyes.

INTRODUCTION

Now a day the synthesis of new monomers from renewable resources is drawing considerable attention by polymer research community around the globe. Among the various bio-monomers cardanol, a natural meta substituted phenol, obtained from cashew nut shell liquid (CNSL) was chosen for the present study. In the recent past, a very good number of research articles have been published on modification of cardanol using the reactivity of hydroxy phenyl group [1-6]. Now, the CNSL products, in particular cardanol based products are finding greater industrial, pharmaceuticals and medicinal applications as well [7-11]. However, the synthesis of polymer blends using cardanol based dyes which are expected to have better applications than the simple cardanol polymer blends is very limited. In the present work inter-penetrating polymer networks (IPNs) which are a new class of polymer blends in network form in which at least one component is polymerized and/ or cross-linked in the immediate presence of the other were prepared[12-14]. The prepolymers for the present study are polyurethanes with 1.6 and 1.2 NCO/OH molar ratios from glycerol modified linseed oil with diphenyl methane-4, 4'-diisocyanate (DPMDI). The polymer blends were prepared with the prepolymers (PUs) and cardanol based dyes with 2-aminophenol and 4-aminophenol at constant 25:75 weight ratio in presence of benzoyl peroxide (BPO) as initiator and ethylene glycol dimethacrylate (EGDM) as the cross-linker. The derivative thermogravimetry (DTG) curves were studied to know rates of the thermal degradation of the polymer blends. The differential thermal analysis (DTA) technique was used to determine the exothermic and endothermic behavior of thermal degradation of polymer blends at various temperature intervals and also to know whether the processes are one step or two step processes. The structural evaluation of the polymer blends thus prepared was investigated by FTIR study and the expected scheme of the reaction is suggested. The Freeman- Anderson's method is employed to determine the kinetic parameters such as activation energy and order of reaction of thermal degradation of polymer blends. The significant effect of NCO/OH

molar ratio of polyurethanes and the nature of aminophenols were observed on the thermal degradation of polymer blends.



Scheme 1

Scheme 1: Shows reaction between linseed oil and glycerol to obtain glycerol modified linseed oil which produces PU with DPMDI

EXPERIMENTAL SECTION

2.1 Preparation of cardanol

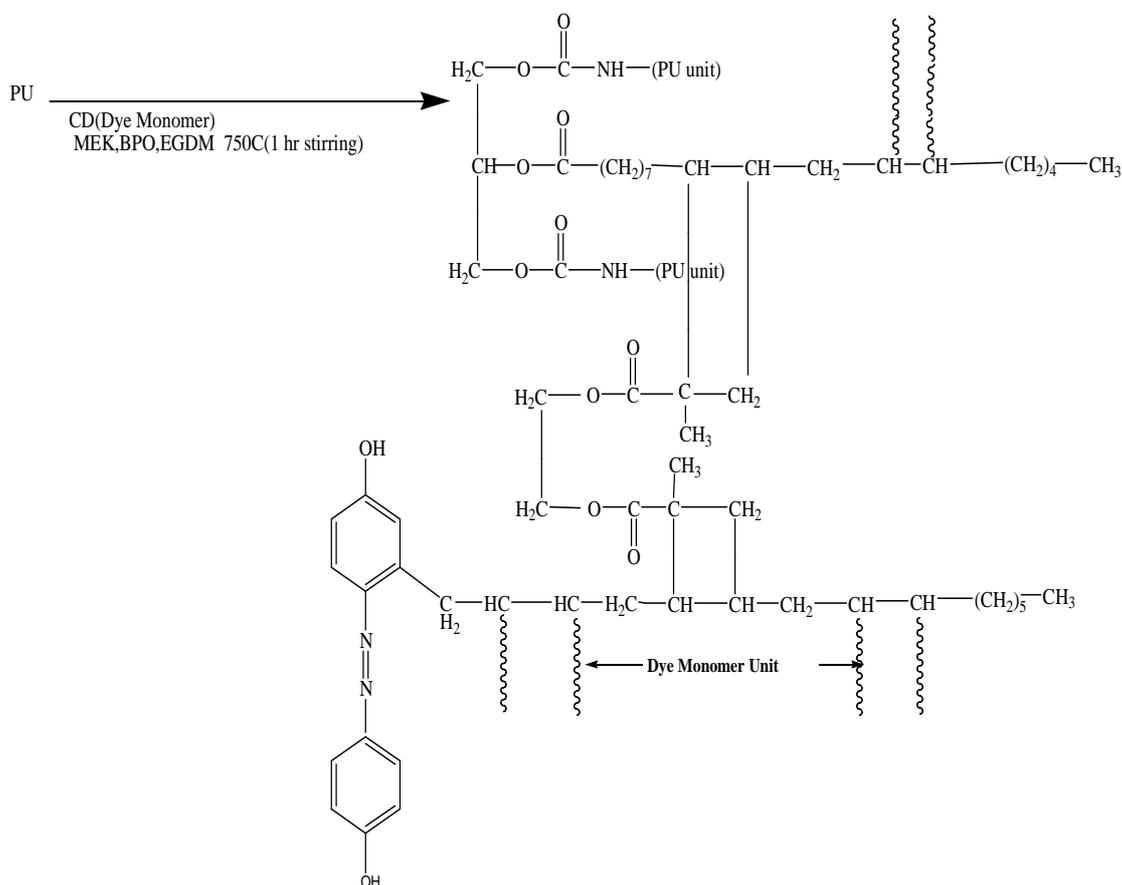
About 300 mL of cashew nut shell liquid was taken in a round bottomed flask fitted with a condenser and a thermometer. Then vacuum distillation was done in the temperature range of 230-240^oC and 3-4 mm Hg pressure. Cold water was circulated through the condenser. Anacardic acid (2-carboxylic -3- pentadecadienylphenol) is decarboxylated to cardanol [15].

2.2 Preparation of Cardanol based Dye (CD)

21.8g (0.2mol) of 2-aminophenol was dissolved in 52 mL (0.6 mol) of conc. hydrochloric acid and 20 mL of water. The solution was cooled to 0-5 ^oC. An ice cold aqueous solution of sodium nitrite of about (0.2mol) 14 g in 72 mL of water was slowly added to it with constant stirring for 3-4 min till a positive test for nitrous acid was obtained. An ice cold alkaline solution of 60 g (0.2 mol) of cardanol in 160 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 (CD) was obtained. Similarly cardanol based dye with 4-aminophenol was also obtained [16].

2.3 Preparation of Glycerol modified Linseed Oil (GL)

Linseed oil was obtained from the local market of southern Orissa, India. About 175 mL of linseed oil taken in a three necked flask fitted with a thermometer, reflux condenser and a mechanical stirrer was heated to 250-260 °C in an inert nitrogen atmosphere. As this temperature range was attained, 0.0784 g of PbO, i.e. 0.05% litharge (oil basis) as catalyst and 40 mL (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 (GL) and thereafter it was dried under vacuum at 80°C for 6 hr.



Scheme 2 : Expected Structure of IPN

Scheme 2: Shows the expected scheme of cross-linking between PU and Dye monomer (CD) in presence of EGDM and BPO to obtain Polymer Blend (Interpenetrating polymer networks)

2.4 Synthesis of Polyurethanes (PUs)

1.416 g of glycerol modified linseed oil was allowed to react with 2.4 g of diphenyl methane-4, 4'-diisocyanate to maintain the NCO/OH molar ratio at 1.2. The reaction was carried out in a small beaker at about 45°C in methyl ethyl ketone (MEK) as solvent with constant stirring for 45 min until a viscous prepolymer of pale yellow colour (polyurethane) separated out. In the same way polyurethane with NCO/OH molar ratio at 1.6 was also prepared from 3.2 g of DPMDI and 1.416 g of glycerol modified linseed oil.

2.5 Synthesis of Polymer Blends

The polyurethane (PU) and cardanol based dye monomer (CD) in 25:75 weight to weight ratio for both 1.6 and 1.2 NCO/OH molar ratios separately was 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 and stirring was continued for about 1hr to get a viscous mass which was poured into a glass mould and kept in an oven at 75°C for 24 hr. The thin film thus formed was

cooled and removed from the mould and labeled for evaluation by FTIR study and thermal analysis (at the Central Research Facility, Indian Institute of Technology, Kharagpur, India). The expected scheme of the reaction and the structure of the polymer blends (IPNs) are given in Scheme 1 and Scheme 2 and the feed composition data of the IPNs are furnished in Table 1.

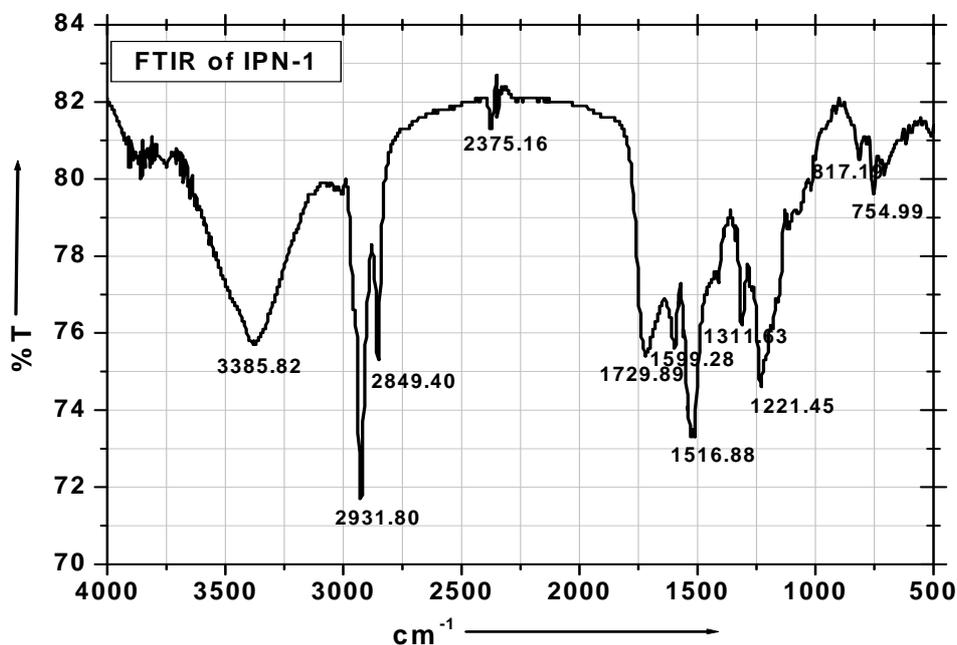


Figure 1: FTIR of IPN-1[GL+ DPMDI+CD of 2- amino phenol]

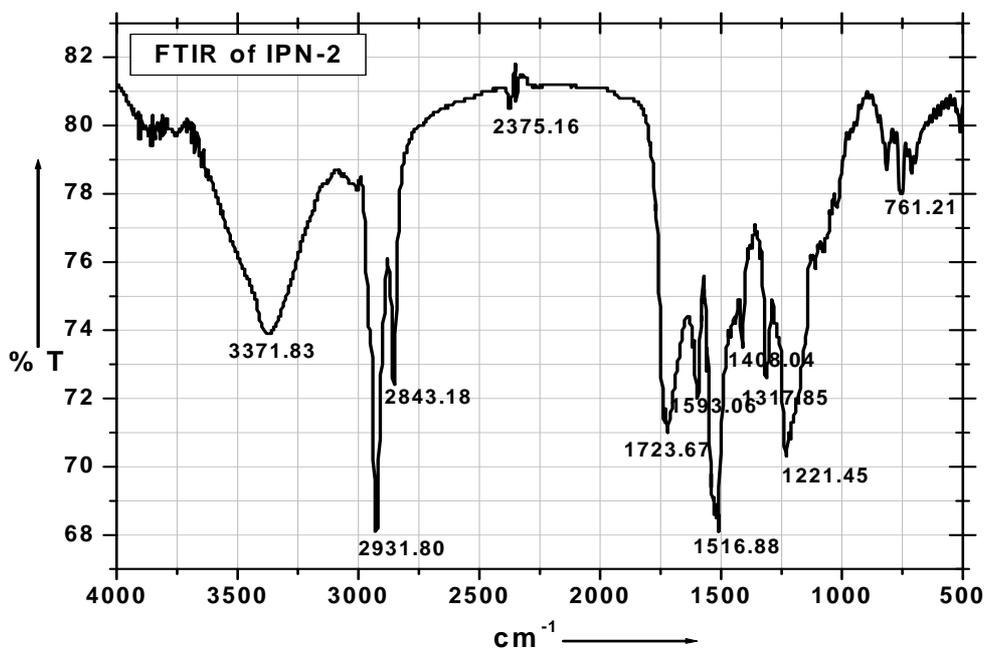


Figure 2: FTIR of IPN-2[GL+ DPMDI+CD of 2- amino phenol]

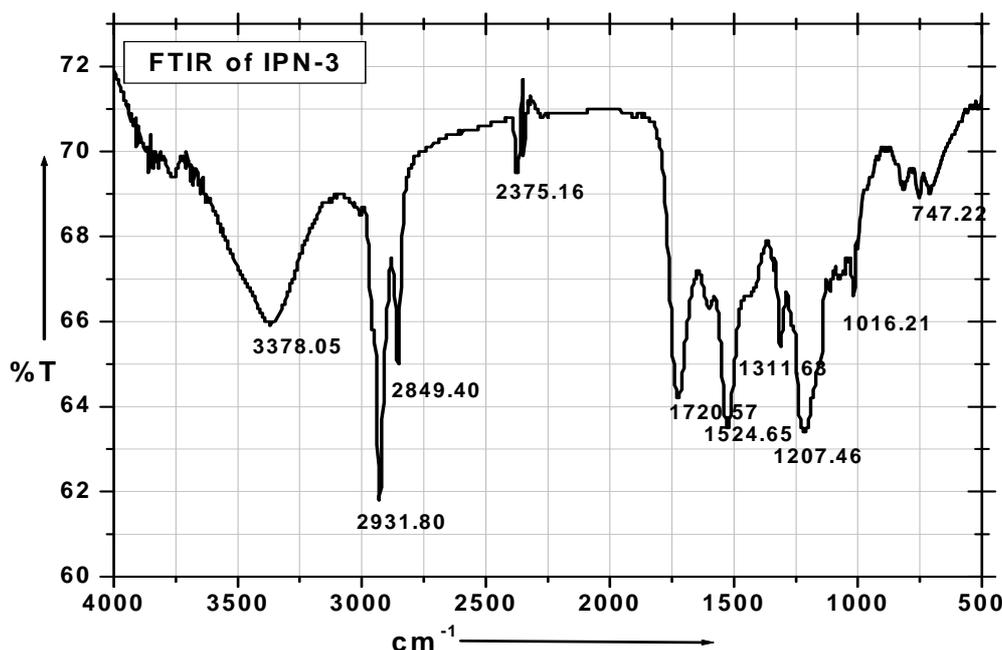


Figure 3: FTIR of IPN-3 [GL+ DPMDI+CD of 4- amino phenol]

3. Characterization and Methods:

3.1 FT-IR Spectra

The infrared spectra of the Polymer Blends (IPNs) were obtained using Perkin Elmer FT-IR spectrometer model paragon 1000. A small amount of the finely powdered sample mixed with about 100 times its weight of powdered potassium bromide (KBr) and pressed into a small disc of about 1mm thick was taken. Elmer FT-IR spectra were analyzed by studying the intensity of the transmittance peaks and comparing with the control spectra. FT-IR spectra of the polymer blends (IPNs) are given in Figure 1, Figure 2 and Figure 3 respectively.

3.2 Thermal Properties Analysis

Perkin Elmer Thermal Analyzer model PYRIS diamond USA was used for TGA, DTG and DTA measurements. 6.506 mg of IPN-1 with 6.0 mg alumina as reference was scanned between 50°C and 650°C at a heating rate of 10°C/min in an inert nitrogen atmosphere (N₂ 100mL/min) given in Figure 4. In the similar way IPN-2 and IPN-3 were scanned for thermo gravimetric analysis (TGA), differential thermogravimetry (DTG) and differential thermal analysis (DTA) measurements given in Figure 5 and Figure 6 respectively.

3.3 Kinetics of thermal degradation

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

The equation used for the Freeman-Anderson method is as follows:

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

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 E is the energy of activation. Freeman-Anderson plots, Figure 5 and Figure 6, for kinetic parameters in the temperature ranges of 200°C to 250 °C and 315°C to 440 °C respectively were obtained by plotting $\Delta \log\left(-\frac{dw}{dt}\right)$ against $\Delta \log \bar{w}$ corresponding to a constant difference in $1/T$.

RESULTS AND DISCUSSION

4.1 FT-IR Spectra analysis

The structural evaluation of the polymer blends (IPNs) were carried out by FTIR spectra to confirm the presence of different functional groups and nature of linkage in the polymers. The characteristic absorptions of IPN-1 corresponding to N-H stretching of >NH group at 3385.82 cm⁻¹, C-H(ss/as) of >CH₂ and -CH₃ groups at 2849.40 cm⁻¹ and 2931.80 cm⁻¹, N≡C(stretching) of -N=C=O for isocyanate terminating PU unit at 2375.16 cm⁻¹, C=O (stretching) of urethane linkage at 1729.89 cm⁻¹, N=N(stretching) of azo group at 1598.25 cm⁻¹, O-H (bending) of -OH group at 1311.63 cm⁻¹ and bending vibration of a chain of >CH₂ groups at 754.99 cm⁻¹ are observed (Fig. 1). Similarly the characteristic absorptions of IPN-2 corresponding to N-H stretching of >NH group at 3371.83 cm⁻¹, C-H(ss/as) of >CH₂ and -CH₃ groups at 2843.18 cm⁻¹ and 2931.80 cm⁻¹, N≡C (stretching) of -N=C=O for isocyanate terminating PU unit at 2375.16 cm⁻¹, C=O (stretching) of urethane linkage at 1723.67 cm⁻¹, N=N(stretching) of azo group at 1593.06 cm⁻¹, O-H (bending) of -OH group at 1317.85 cm⁻¹ and bending vibration of a chain of >CH₂ groups at 761.21 cm⁻¹ are observed (Fig. 2). Finally the characteristic absorptions of IPN-3 corresponding to N-H stretching of >NH group at 3378.05 cm⁻¹, C-H(ss/as) of >CH₂ and -CH₃ groups at 2849.40 cm⁻¹ and 2931.80 cm⁻¹, N≡C (stretching) of -N=C=O for isocyanate terminating PU unit at 2375.16 cm⁻¹, C=O (stretching) of urethane linkage at 1720.57 cm⁻¹, N=N(stretching) of azo group at 1524.65 cm⁻¹, O-H (bending) of -OH group at 1311.63 cm⁻¹ and bending vibration of a chain of >CH₂ groups at 747.22 cm⁻¹ are observed (Fig. 3). The resembles of the peaks of the both the IPNs is because of their similar chemical structures though of different NCO/OH ratios.

4.2 Analysis of Thermal Degradation

Table 1 shows the data of the thermal degradation of the polymer blends (IPNs) at various temperature intervals for the various decomposition processes involved in the degradation. The IPNs as expected exhibit high thermal stability up to 150 °C with 0.7 % weight loss for IPN-1, 0.3 % weight loss for IPN-2 and 0.6 % weight loss for IPN-3. Only 9.8%, 5.5% and 14.9% of weight losses for IPN-1, IPN-2 and IPN-3 respectively in the range of 150 °C to 250 °C which may be due to evaporation of solvent and other volatile matters are observed. The thermal result clearly shows that in the range of 150 °C to 250 °C the IPN-3 is almost 50% less thermal stable than the IPN-1 and 170% less thermal stable than IPN-2 which indicate that in this temperature range IPN-2 exhibits very high thermal stability than the other two. Hence it may be concluded that the polymer blends (IPNs) with 4-aminophenol based dye is about 50% less thermal stable than the polymer blends (IPNs) with 2-aminophenol based dye in the range of 150 °C to 250 °C. Significant 61.7% (IPN-1), 60.7% (IPN-2) and 50.6% (IPN-3) weight losses were recorded in the temperature range of 250 °C - 450 °C which can be attributed to the decomposition of benzene ring as already known that the breakage of main bonds in benzene occurs in the range of 400 °C- 450 °C [17] along with main functional groups such as -OH, >NH, >C=O etc. and due to partial decomposition of cross linking with EGDM between PU unit and CD monomer unit. But in the range of 250 °C - 450 °C, IPN-3 prepared from 4-aminophenol is found to be around 20% thermally more stable than other two IPNs prepared from 2-aminophenol. Finally, 13.6 % (IPN-1), 17 % (IPN-2) and 19.5% (IPN-3) of weight losses were recorded in the range of 450 °C to 600 °C which may be attributed to complete decomposition of crosslinkings with EGDM between PU unit and CD monomer unit i.e., separation of two monomer units. However the results show that in the range of 450 °C to 600 °C IPN-3 is 43% and 12.8% less thermally stable than IPN-1 and IPN-2 respectively. Hence it can be inferred that the polymer blends prepared from 2-aminophenol are about 43% more thermally stable than those blends from 4-aminophenol in the temperature range of 250 °C - 450 °C. On the whole all the polymer blends in the present study are thermally stable, but the thermal degradation in a particular range of temperature is comparatively higher in IPN-1 than that in IPN-2 with constant PU/CD weight ratio and different NCO/OH molar ratios. It may be concluded from this study that the polymer blends (IPNs) with less NCO/OH molar ratio is more thermally stable than those with more NCO/OH molar ratio in the polyurethanes of the prepolymer. Further it is also observed that the polymer blend derived from 4-aminophenol dye is thermally more stable than that derived from 2-aminophenol dye.

Table 1: Feed Composition Data of Polymer Blends and Percentage of Thermal Degradation of the IPNs at various Temperatures

| Sample Code | Composition | NCO/OH (molar ratio) | PU / CD (wt. ratio) | %of weight loss at Temperature /°C | | | | | |
|-------------|-------------------------------|----------------------|---------------------|------------------------------------|------|------|------|------|------|
| | | | | 150 | 250 | 350 | 450 | 550 | 600 |
| IPN-1 | GL+ DPMDI+CD of 2-aminophenol | 1.6 | 25:75 | 0.7 | 10.5 | 55.2 | 72.2 | 85.3 | 85.8 |
| IPN-2 | GL+ DPMDI+CD of 2-aminophenol | 1.2 | 25:75 | 0.3 | 5.8 | 35.6 | 66.5 | 82.7 | 83.5 |
| IPN-3 | GL+ DPMDI+CD of 4-aminophenol | 1.6 | 25:75 | 0.6 | 15.5 | 43.2 | 66.1 | 84.9 | 85.6 |

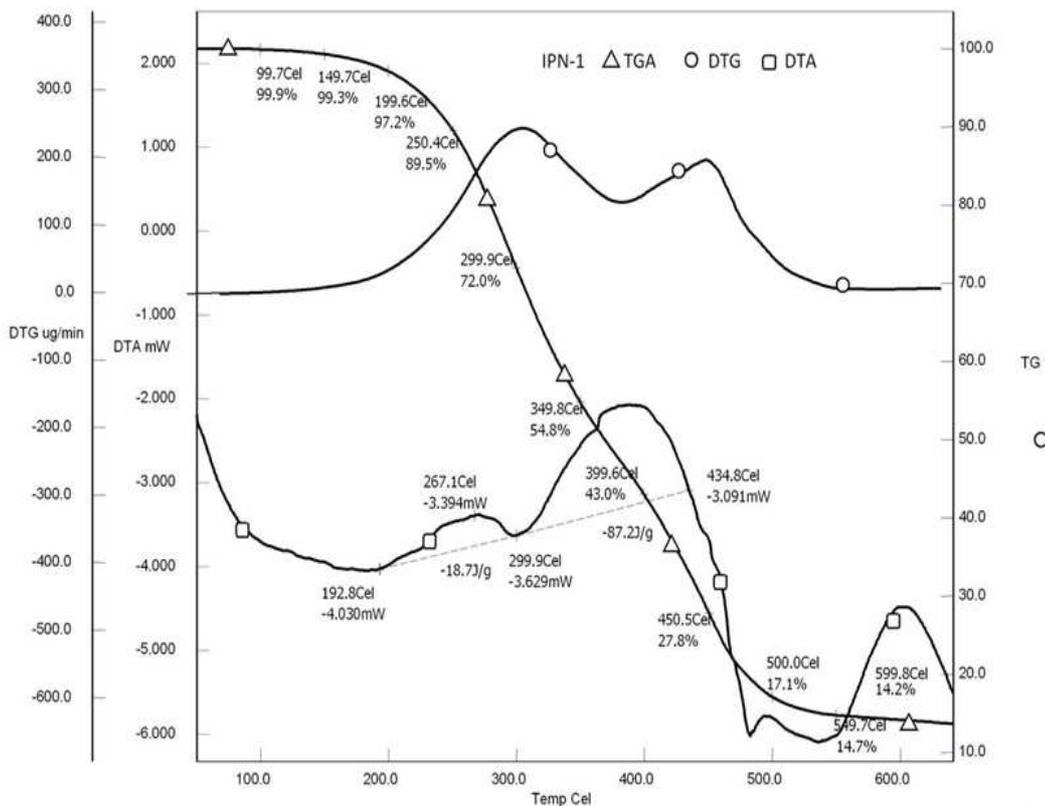


Figure 4: TGA/DTG/DTA of IPN- 1

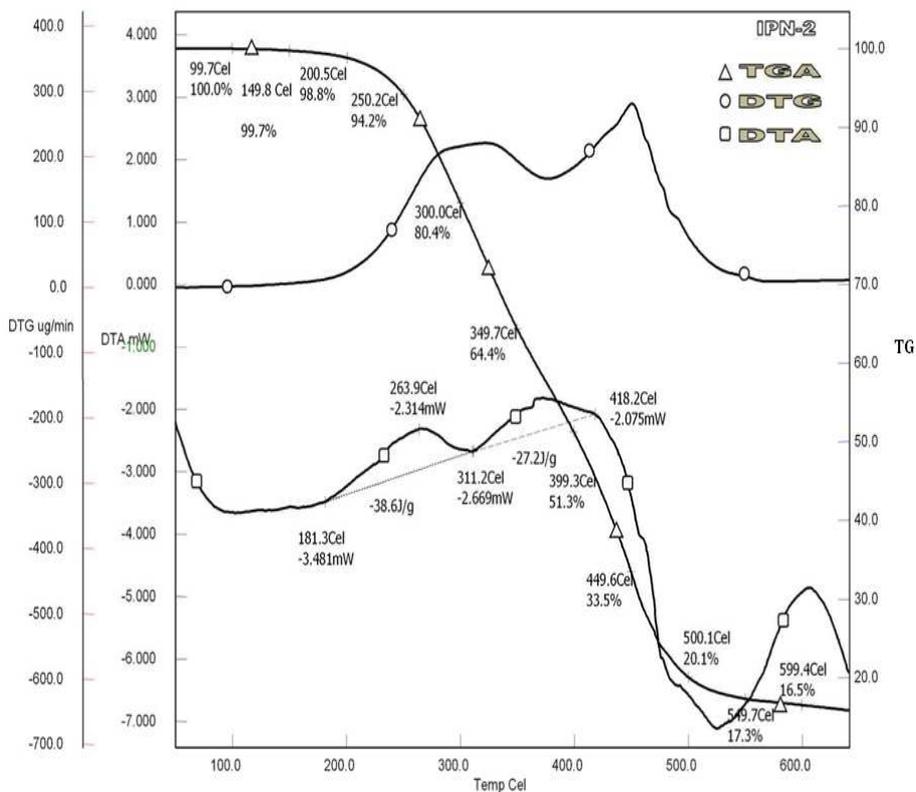


Figure 5: TGA/DTG/DTA of IPN-2

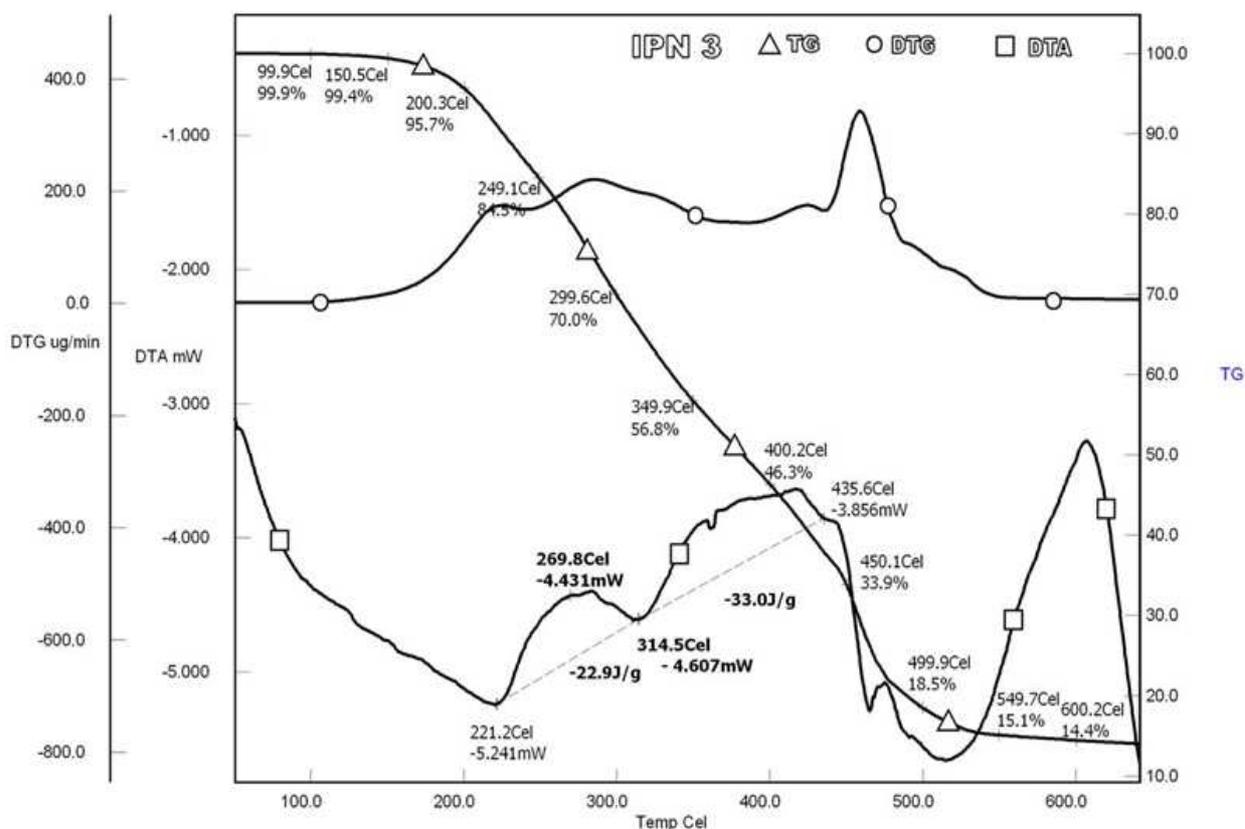


Figure 6: TGA/DTG/DTA of IPN-3

The derivative thermo gravimetric curves show the rate of thermal decomposition ($\mu\text{g}/\text{min}$) with respect to temperature. The DTG curve for IPN-1 (Fig.4) shows two peaks at 299.17°C and 448.85°C corresponding to rates of decomposition $277.08 \mu\text{g}/\text{min}$ and $224.08 \mu\text{g}/\text{min}$ respectively. Similarly the DTG curve for IPN-2 (Fig.5) shows two peaks at 322.98°C and 450.45°C corresponding to rates of decomposition $221.04 \mu\text{g}/\text{min}$ and $281.27 \mu\text{g}/\text{min}$ respectively. Finally the DTG curve of IPN-3 (Fig.6) shows peaks at 285.60°C and 458.74°C corresponding to rates of decomposition $220.21 \mu\text{g}/\text{min}$ and $342.77 \mu\text{g}/\text{min}$ respectively. Among the polymer blends the polymer with 4-aminophenol shows the highest rate of decomposition around 450°C .

Differential thermal analysis was implemented in pure nitrogen atmosphere. Figure 4 shows the recorded DTA curve of the polymer blend, IPN-1, and it suggests and corroborates that the thermal degradation process in nitrogen can be described as two step reaction with an exothermic peak at 393.31°C and an endothermic peak at 482.76°C . Similarly the Figure 5 shows the DTA curve of IPN-2 with an exothermic peak at 368.00°C and endothermic peak at 525.33°C describing that the thermal degradation here also is a two step reaction. But the DTA curve of IPN-3 (Figure 6) clearly shows the thermal degradation process is a three step reaction with two exothermic peaks at 416.87°C and 607.23°C and one endothermic peak at 514.22°C . From these DTA curves it is clear that all the polymer blends show the similar thermal behavior between 180°C to 315°C but in the range of 300°C to 435°C only IPN-2 and IPN-3 exhibit the same behavior. This may be explained by drawing a base line between 180°C and 315°C , and 300°C and 435°C and the enthalpies (ΔH) of the thermal degradation process were calculated from the area under the DTA curves for the above temperature ranges. The enthalpies were found to be -18.7 J/g , -38.6 J/g and -22.9 J/g for the IPN-1, IPN-2 and IPN-3 in the temperature range of 193°C to 300°C , 181°C to 311°C and 221°C to 315°C respectively. The similar enthalpies were observed for the IPN-2 and IPN-3 i.e. -27.2 J/g and -33.0 J/g in the range of 300°C to 435°C , however, IPN-1 showed -87.2 J/g which is about 60 J/g more than IPN-2 and 50 J/g more than PN-3 in the same temperature range. All the three polymer blends showed similar thermal behavior up to 500°C , but above 500°C the polymer blend from 4-aminophenol showed three step reaction with a peak at 607.23°C .

4.5 Kinetic Parameters for the thermal degradation

The thermal degradation of polymers is a complex process. So it becomes very difficult to obtain the exact kinetic parameters of each reaction involved in the decomposition process of the polymer blends because of the complexities in identifying the temperature intervals of the individual reactions due to superposition of different stages of reaction and the shift in temperatures of thermal effects on DTA curve [18]. But such kinetic parameter calculations help to a greater extent in understanding the complexities involved in the thermal degradation of polymers. Thermo gravimetric analysis (TGA) is widely used for the determination of the kinetic parameters of polymer degradation. Table 2 shows the kinetic parameter data such as activation energy and order of reaction for the various decomposition reactions taking place in the thermal degradation of the polymer blends at various temperature ranges using the Freeman-Anderson's approach.

The Freeman-Anderson plots, Figure 7 and Figure 8, for kinetic parameters were obtained by plotting $\Delta \log\left(-\frac{dw}{dt}\right)$ against $\Delta \log \bar{w}$ corresponding to a constant difference in $1/T$ in the temperature range of 200°C to 250°C and 315°C to 440°C.

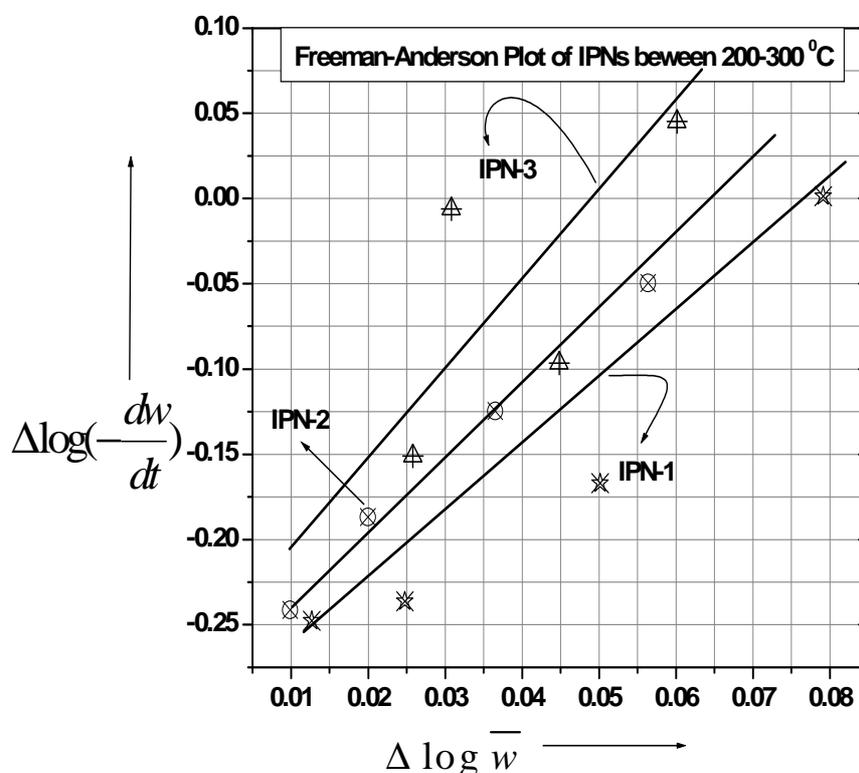


Figure 7: Freeman-Anderson's Plot of the Polymer Blends in the temperature range of 200-300°C

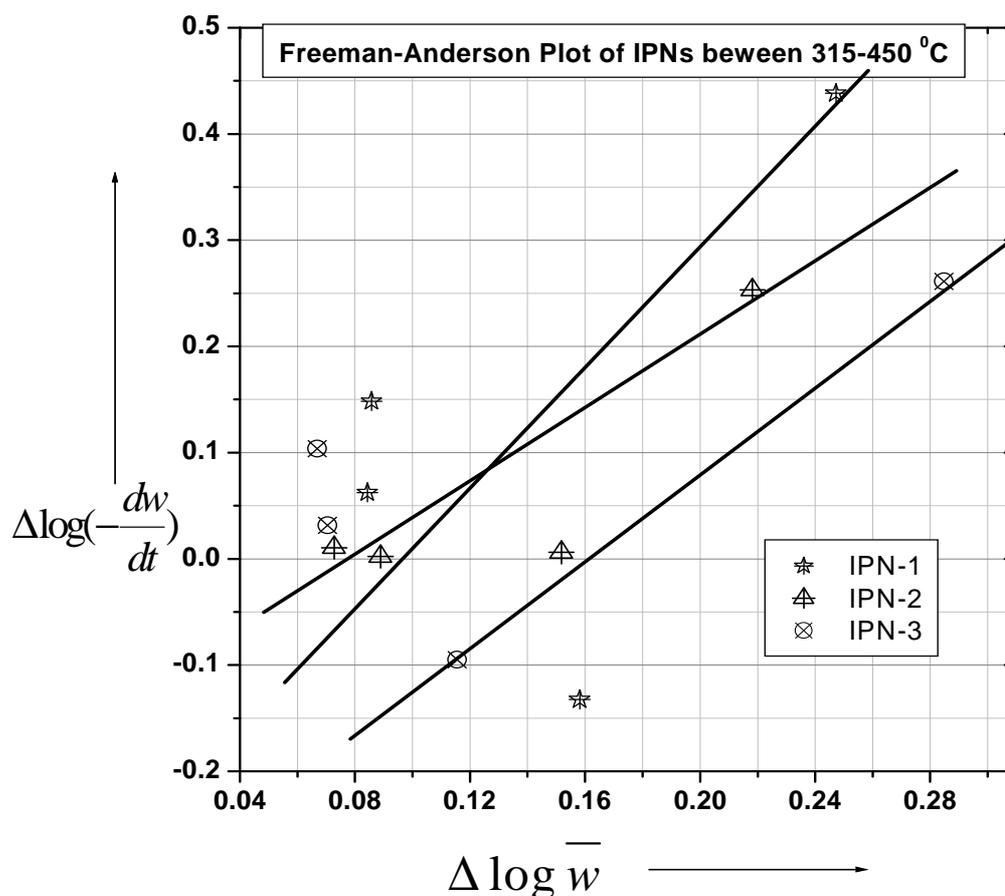


Figure 8: Freeman-Anderson's Plot of the Polymer Blends in the temperature range of 315-450 deg. cel.

Table 2: Kinetic Parameters of Thermal decomposition of Polymer Blends by Freeman-Anderson Method

| Polymer Blends | Temperature Range/ °C | E_a (kJ mol ⁻¹) | n |
|----------------|-----------------------|-------------------------------|------|
| IPN-1 | 200-230 | 43.88 | 2.7 |
| | 230-250 | 50.63 | 0.9 |
| | 250-300 | 77.63 | 5.8 |
| | 400-450 | 202.52 | 6.4 |
| IPN-2 | 200-230 | 64.13 | 2.8 |
| | 230-250 | 74.26 | 6.3 |
| | 250-300 | 87.76 | 8.5 |
| | 400-450 | 189.02 | 6.1 |
| IPN-3 | 200-230 | -32.06 | -1.1 |
| | 230-250 | 194.09 | 0.1 |
| | 250-300 | 84.38 | -0.5 |
| | 400-450 | 57.38 | -0.3 |

Table 2 shows the activation energies (E_a) and order of the reactions (n) of the thermal degradation of the polymer blends at various temperature ranges. The kinetic parameters also agree with the thermal analysis data that the IPN-2 with NCO/OH molar ratio at 1.2 is thermally more stable than the IPN-1 and the IPN-3 with NCO/OH molar ratio at 1.6. The average activation energy between 200°C and 450°C was found to be 93.67, 103.79, 75.95 for the polymer blends IPN-1, IPN-2 and IPN-3 having 3.9, 5.9 and 1.4 as average order of the reactions respectively. From the data it may be inferred that IPN-2 is thermally more stable than the other two IPNs. The Freeman-Anderson method also predicts that the IPN-2 is more cross-linked than the other two IPNs. The nonlinearity of the plots between 300-400 °C in Figure 8 predicts the complex reactions involved in the thermal degradations of the

blends. Overall, the Freeman-Anderson approach is found to be in good agreement with the experimental thermal data with little deviations.

CONCLUSION

Of late, polymers from natural renewable resources are expected to play remarkable roles as far as environmental and energetical concerns are taken into account. Obviously biopolymers derived from sustainable resources like natural oils and the cashew nut shell liquid have many advantages over the polymers synthesized from petrochemicals. The major conclusion from this study is that polymer blends prepared from glycerol modified linseed oil based polyurethane and cardanol based dye are highly cross-linked with high thermal stability and the rate of decomposition of polymer blends depends upon NCO/OH molar ratios and the nature of the dye by considering the suitable composition of the polymer blends it is now possible to design materials for specific purposes.

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