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RESEARCH ARTICLE OPEN ACCESS

A Study on Biopolymers Synthesized from Soybean oil And Cardanol Based Dye by FTIR, DSC and TG,

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ABSTRACT: Synthetic biopolymers has been synthesized form glycerol modified soybean oil polyurethane and cardanol based liquid amino dyes by the use of benzoyl peroxide (BPO) as initiator and ethylene glycol di-methacrylate (EGDM) as cross linker in different NCO/OH ratios with DPMDI and TDI. The polymer so produced has been characterised by different methods like FTIR, TGA, and DSC. The Synthetic Polymers so produce can be used in different industrial applications in place of petroleum based products.

Keywords: Cardanol, Soybean Oil, Polyurethane, Benzoyl Peroxide, Ethylene glycol di-methacrylate (EGDM), Diphenyl methane di-isocyanate (DPMDI), Toluene 2, 4 di-isocynate (TDI)

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I. INTRODUCTION

The urgent need of today is to develop polymers that are bio-degradable and eco-friendly. As soybean oil is a vegetable oil abundant in supply and relatively low cost, it has become an alternative source to synthesis polyols. About 40% of standard petroleum polyols have now been replaced by soybean oil. The other compound cardanol obtained by vacuum distillation from cashew nut shell liquid (CNSL) is also an agricultural product and an excellent monomer for synthetic polymer. IPNs from renewable resources were initiated by Sperling and Co. [1-3]. A number of articles are published [4-8] in this field with monomers derived from cardanol with other oils like castor oil, lin seed oil etc. Soybean oil is a chemical mixture of glycerides and unsaturated fatty acids. These synthetic polymer can be used in different field like adhesives binders, paints, varnishes coatings of different articles etc. due to its higher thermal stability and mechanical strength. In this paper authors have synthesised the polymer and characterised it by FTIR [9, 10], TGA [12, 13], DSC [14].

II. EXPERIMENTAL SECTION

Materials:

- Refined soybean oil was obtained from market.
- Cardanol was obtained from fractional distillation of CNSL liquid, a by-product of cashew Industry of South India.
- NaOH, MEK, EGDM, $NaNO_2$, HCl, PbO etc. was obtained from M/S BDH. Ltd. (INDIA)
- TDI, DPMDI, 3-amino benzoic acid and 4-amino benzoic acid from E merk (GERMANY).

All chemicals were used as received.

III. METHOD

1. **Spectroscopic analysis- FTIR (Fourier transform infrared):** FTIR spectra of the prepared IPNs samples have been recorded on FTIR Spectrophotometer by Thermo Electric Corporation, USA, and Model: Nicolet 670 FT-IR using KBr pallete in the wavelength range of $500cm^{-1}$ to $4000cm^{-1}$.
2. **Thermal Analysis (DSC and TGA):** DSC and TGA of all IPNs have been performed by use of a Universal v_4.5A.TA instrument (Model SDT Q 600 V20.9 Build 20) at a heating rate of 10^0c/minute.
3. **Morphology study (SEM):** Morphology of samples has been studied by JOEL scanning electron microscope (SEM) Model JSM 500. For this the fractured samples have been coated with a thin layer of gold- platinum alloy by sputtering to provide conductive surface.
4. **Test for biodegradability:** The environmental resistance of the IPNs samples was carried out using soil burial test.

IV. EXPERIMENTAL :-

i. **Preparation of dye monomer:** 6.85g of 4-amino benzoic acid was dissolved in 13mL of conc. HCl acid and 5mL of water was added to it. The solution was cooled 0^0-5^0C, and then a cold solution of sodium nitrite (4g in 20mL of water) was added to it slowly with stirring for 3-4 minutes. A cold solution of cardanol (15g in 45ml) of 10% NaOH solution was prepared. Then cold diazonium solution was added slowly to the alkaline cardanol solution with stirring. A brilliant reddish brown coloured semi liquid dye was formed. The dye was separated by a separating funnel. The same procedure is repeated for 3-amino benzoic acid.

ii. **Preparation of Mixed Ester Polyol (MEP) from Soybean Oil (SO)**: Refined soybean oil (350mL) was heated at 250^0 C in an inert Nitrogen atmosphere taken in three naked flask fitted with a thermometer reflux condensers and a stirrer. At this temperature litherage (0.168g) and glycol (80mL) were added to the reaction mixture with constant stirring. The temperature was maintained at 250^0C until one volume of reaction mixture gave a clear solution in same volume methanol. At this stage the contents were cooled to obtain MEP.

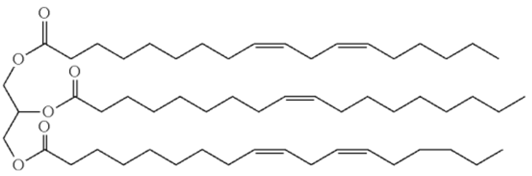
iii. **Synthesis of Polyurethane (PU):** 1 mole of MEP was added to 1.6 mole of TDI to maintain NCO/OH ratio at 1.6. The reaction was carried out at 45^0C with continuous stirring for one hour until a viscous pale yellow colour PU is separated out. The same process was repeated with different NCO/OH ratio (1.2, 1.6, and 2.0) and with other di-isocyanate DPMDI PUs was produced.

iv. **Synthesis of IPNs:** The mixture of PU and diazotised cardanol (with different PU/monomer ratio i.e., (25:75, 35:65, 50:50) and solvent (MEK) were taken in small beaker. Then 5mL of 10% EGDM along with 20mg of Benzoyl peroxide (BPO) were added to each mixture. The total mixture was stirred for 15 minutes with magnetic stirrer in cold to obtain a homogenous solution. Then the temperature was raised to 75^0C and stirred until a thick solution was formed. Then the viscous mass was poured into a petridish in hot condition and kept in an oven at 75^0C for 24 hour.

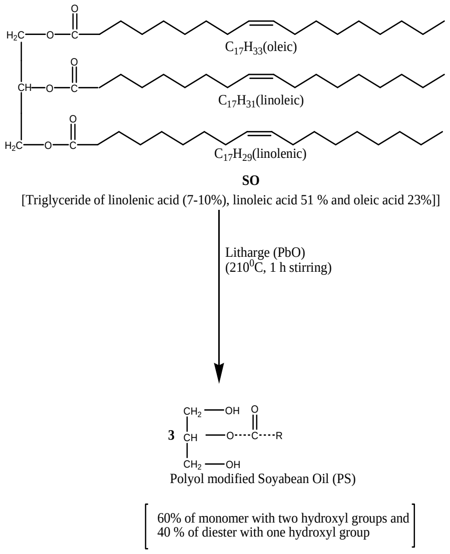
The thin film thus obtained was cooled and removed from the petridish with a sharp blade and sent for characterisation to the Central Instrumentation Facility Pondicherry University, Puducherry, pin-605014.

Soybean oil (SO): Triglyceride of linolenic acid (7-10%), linoleic acid (51%) and oleic acid (23%)

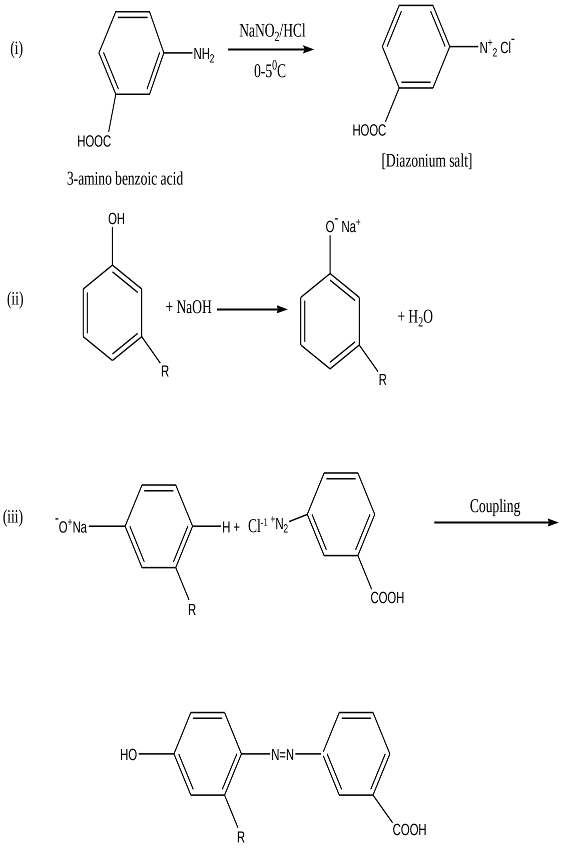
(II)



Scheme-1

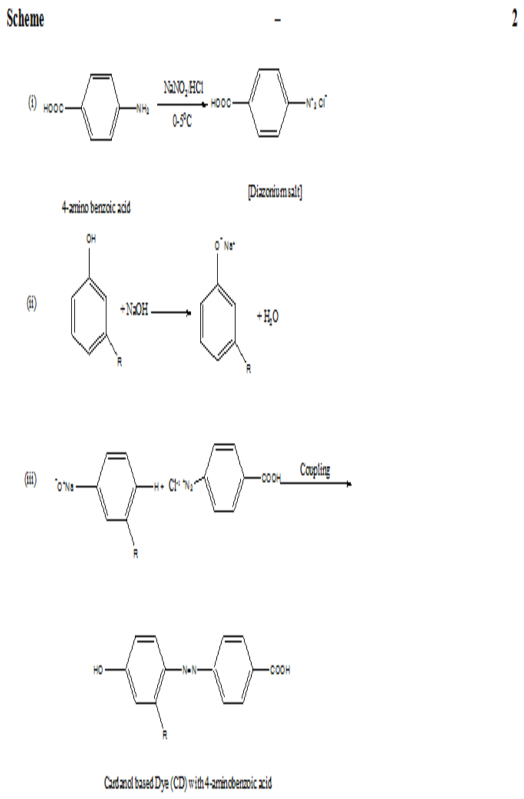


Synthesis of Polyol modified Soybean Oil (PS)
Scheme – 2

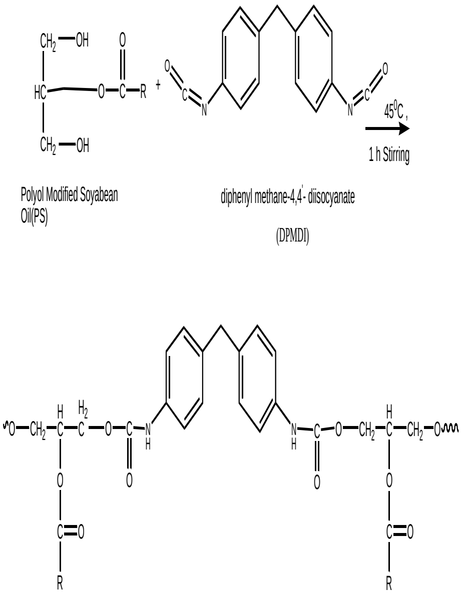


Cardanol based Dye (CD) with 3-aminobenzoic acid

Scheme – 2a

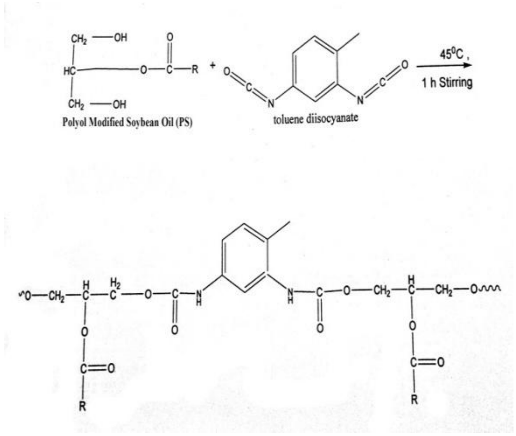


Scheme – 3



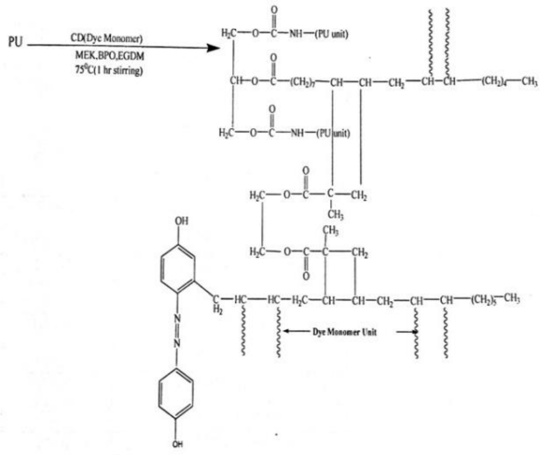
(POLYURATHANE (PU) FROM DPMDI)

Scheme – 3a



[POLYURATHANE (PU) from TDI]

Scheme – 4



Syethesis of IPNs

[Structure of IPN synthesized from Cardonal based dye with 4-aminobenzoic acid and Polyurethane of glycerol modified Soybean Oil with DPMDI]

Same procedure was followed for Polyurathane of Toluene-2,4-diisocyanate with Soybean oil and dye with 4-aminobenzoicacid and Cardanol.

V. ANALYSIS OF THE SAMPLE:

1. Ftir – The FTIR spectra of the IPNs 6, 10, 12, 14 and 24 are presented in figs 1-a to 1-e

The presence of component materials in the macromolecules was confirmed by the study of FT-IR spectra if the prepared samples.

Ftir Of Ipn-6

The characteristic absorption of **IPN-6** corresponding to IPN-6 to O-H stretching of >OH groups shifted to lower value by hydrogen bonding at 3677.1 cm^{-1} and 3607.6 cm^{-1}. N-H stretching of >NH group at 3333.5 cm^{-1}, C-H stretching (ss/as) of >CH_2 and > CH_3 groups at 2857.7 cm^{-1} and 2926.4

cm^{-1}, N≡C stretching of -N=C=O group for the isocyanate terminating PU unit at 2341.8cm^{-1} , C=O stretching of urethane linkage at 1662.8 cm^{-1} , N=N stretching of azo group at 1605.7 cm^{-1}, C-O bending at 1164.2 cm^{-1}, C=C stretching at 1531.2 cm^{-1}, C-C stretching at 1453.1 cm^{-1}, out of plane C-H bending at 708.6 cm^{-1} and out of plane C-C bending at 506.3 cm^{-1}.were observed.

Ftir Of Ipn-10

The characteristic absorption of **IPN-10** corresponding -OH stretching of >OH groups shifted to lower value by hydrogen bonding at 3837.7 cm^{-1}. N-H stretching of >NH group at 3441.2 cm^{-1}, C-H stretching (ss/as) of >CH_2 and > CH_3 groups at 2855.4 cm^{-1} and 2924.7 cm^{-1}, N≡C stretching of -N=C=O group for the isocyanate terminating PU unit at 2334.8 cm^{-1} , C=O stretching of urethane linkage at 1665.0 cm^{-1} , N=N stretching of azo groupat 1589.8 cm^{-1}, C-O bending at 1055.2 cm^{-1}, C=C stretching at 1390.3 cm^{-1}, C-C stretching at 1342.8 cm^{-1}, out of plane C-H bending at 723.3 cm^{-1} and out of plane C-C bending at 450.5 cm^{-1} were observed.

FTIR OF IPN-12

The characteristic absorption of **IPN-12** corresponding -OH stretching of >OH groups shifted to lower value by hydrogen bonding at 3834.8 cm^{-1}. N-H stretching of >NH group at 3402.4 cm^{-1}, C-H stretching (ss/as) of >CH_2 and > CH_3 groups at 2926.5 cm^{-1} and 2857.2 cm^{-1}, -N≡C stretching of -N=C=O group for the isocyanate terminating PU unit at 2374.3 cm^{-1} , C=O stretching of urethane linkage at 1727.6 cm^{-1} , -N=N stretching of azo groupat 1604.0 cm^{-1}, -N=N stretching of aromatic rings at 1542.4 cm^{-1}, C-O bending at 1164.2 cm^{-1}, C=C stretching at 1531.2 cm^{-1}, C=C stretching of aromatic rings at 1232.2 cm^{-1}, C-O stretching of ester at 1160.7 cm^{-1}, out of plane C-H bending at 869.6 cm^{-1} and out of plane C-C bending at 713.8 cm^{-1} were observed.

FTIR OF IPN-14

The characteristic absorption of **IPN-14** corresponding to N-H stretching of >NH group at 3456.9 cm^{-1}, C-H stretching (ss/as) of >CH_2 and > CH_3 groups at 2925.4 cm^{-1} and 2856.5 cm^{-1},- N≡C stretching of -N=C=O group for the isocyanates at 2354.0 cm^{-1} and 2546.0 cm^{-1}, C=O stretching of urethane linkage at 1691.5 cm^{-1}, -N=N stretching of azo groupat 1596.3 cm^{-1}, -N=N stretching of aromatic rings at 1542.4 cm^{-1}, C=C stretching at 1393.2 cm^{-1}, C=C stretching of aromatic rings at 1244.8 cm^{-1}, C-O stretching of ester at 1166.6cm^{-1}, out of plane C-H bending at 784.4 cm^{-1} and out of plane C-C bending of p-substituted benzene ring at 695.2 cm^{-1} and 543.1 cm^{-1} were observed.

FTIR OF IPN-24

The characteristic absorption of **IPN-24** corresponding to -OH stretching of >OH groups shifted to lower value by hydrogen bonding at 3590.8 and 3452.4 cm^{-1}. N-H stretching of >NH group at 3349.2 cm^{-1}, C-H stretching (ss/as) of >CH_2 and > CH_3 groups at 2921.1 cm^{-1} and 2861.8 cm^{-1},- N≡C stretching of -N=C=O group for the isocyanides at 2771.5 cm^{-1}, 2619.9 cm^{-1}, 2365.4 cm^{-1}, C=O stretching of urethane linkage at 1984.0 cm^{-1} , -OH bending due to –COOH group at 1306.7 cm^{-1} , -N=N stretching of azo group at 1605.5 cm^{-1}, C-O bending at 1154.8 cm^{-1}, C-C stretching of aromatic rings at 1399.7 cm^{-1}, C=C stretching of aromatic rings at 1518.6 cm^{-1}, C-O stretching of ester at 1160.7 cm^{-1}, out of plane C-H bending at 811 cm^{-1} and out of plane C-C bending of p-substituted benzene ring at 634 cm^{-1} and 481 cm^{-1} were observed.

Findings

From the fig.1a to 1e correlation with the peak of the authentic compound helps to identify the structure of the polymer sample. Thus it is concluded that the polymer sample contains azo based compound which contain –COOH, -OH, -CH_2, -CH_3, -C-O-C stretching of –OCH_3, azo groups, urethane linkage and benzene rings.
The probable structure of IPN is as in Scheme 4.

VI. THERMOGRAVIMETRIC ANALYSIS

Thermal stability of IPNs was determined by the use of Universal V_4 5ATA instrument at a rate of 10^0C/min from room temperature to 700^0C, again it is cooled from 700^0C to room temperature. The percentage of mass left with temperature was recorded as shown in figure 2a to 2e.
In this paper we have compared the thermal stability of different IPNs with varied NCO/OH ratio and different amino acid compounds.

Findings

$IPN_{12\ is}$ less stable than IPN 6, IPN 10, IPN 14, IPN 24 having 0.50/0.50 PU/CD ratio. IPN 14 is the most stable of the five IPNs. IPNs are stable upto 180^0C after which they decompose. In general it is observed that IPNs undergo degradation in three steps. In the first step, there is an initial weight loss which is attributed to the loss of moisture retained in the samples and elimination of smaller groups. In the second step, there is a gradual weight loss which is due to the decomposition of the urethane linkage and volatilization of low molecular weight products. In this step, the unreacted unsaturated parts (=bonds) get activated due to the presence of excess benzoyl peroxide in the macromolecules. So, in the IPN cross linking, which makes the system more rigid, occurs and the new cross links formed inside the macromolecules develop a strain in the macromolecular chain resulting the release of small groups outside the macromolecular structure. In the third step, it is seen that the major portion of the samples decompose because of the random scission of the cardanol backbone. In this step, the strained macromolecules suffer depolymerisation (unzipping) leading to segmental release of larger groups and leaving a charred residue as shown in Table 1 & 2.

Kinetics of IPNs is determined by Freeman Anderson method as per the following equation

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

Where n= order of reaction

E_a= Activation Energy

These values are determined from the plot of $\Delta \log\left(-\frac{\mathrm{dw}}{\mathrm{dt}}\right)$vs $\Delta \log \overline{\mathrm{w}}$. The slope gives us order of reaction n and intercept is related to activation energy (Ea) which is given by $\mathrm{Ea} = \frac{-\mathrm{Intercept}\ \ \mathrm{X}\ 2.303\ \mathrm{R}}{\Delta(\frac{1}{\mathrm{T}})}$

(As shown in fig. 3a(i) to Fig 3e (ii) and table 5.

VII. D.S.C. (DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS)

In this instrument heat capacity of a sample is measured as the function of differential heat flow rate between the sample and reference material.

The instrument directly gives a recording of heat flow rate against temperature. Heat flow rate undergoes a change during transition. T_g, T_c and Tm values can be computed from the table-3.

T_g: Glass transition temperature

T_c: Curie temperature or crystallization temperature

$T_{m:}$ The temperature at which change of state occurs

T_f: The flow point

T_g = (Pre transition temperature + Post transition temperature)/2

Findings

IPN 24 has more Tg, Tc and Tm value than IPN 14 because it contains more amount of PU and more crystalline.

VIII. BIODEGRADABILITY:

The IPN samples synthesized were tested for environmental resistance by use of soil burial test. The samples were buried in soil for sixty days. The samples were removed from the soil once in fifteen days to access the changes in their weight loss, mechanical strength and surface damage if any as shown in Table 4.

Findings

From this observation (table-4) it is seen that these samples are not biodegradable, only a small amount of it decomposes with the bacteria and virus present in the soil which is very negligible but can be recycled.

IX. CONCLUSION

These synthetic biopolymers highly cross linked and thermally stable, hence can be used in place of petroleum based polymers and exhibit excellent performance in various applications than the copolymers derived from simple cardanol.

ACKNOWLEDGEMENT

The authors are thankful to the Registrar,Ravenshaw University, Odisha for his kind permission to provide the laboratory facility and help to publish this paper. The authors are thankful to the Registrar, Utkal University, Bhubaneswar to publish the paper. The authors are also thankful to the Dean, Pondicherry University, Puducherry for characterisation of the samples.

Figure 1a: FTIR of IPN 6

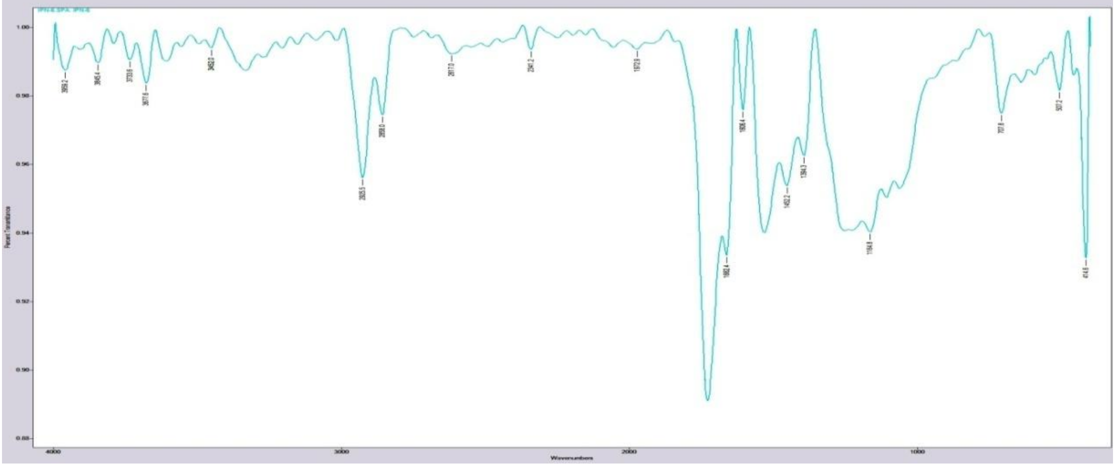


Figure 1b: FTIR of IPN 10

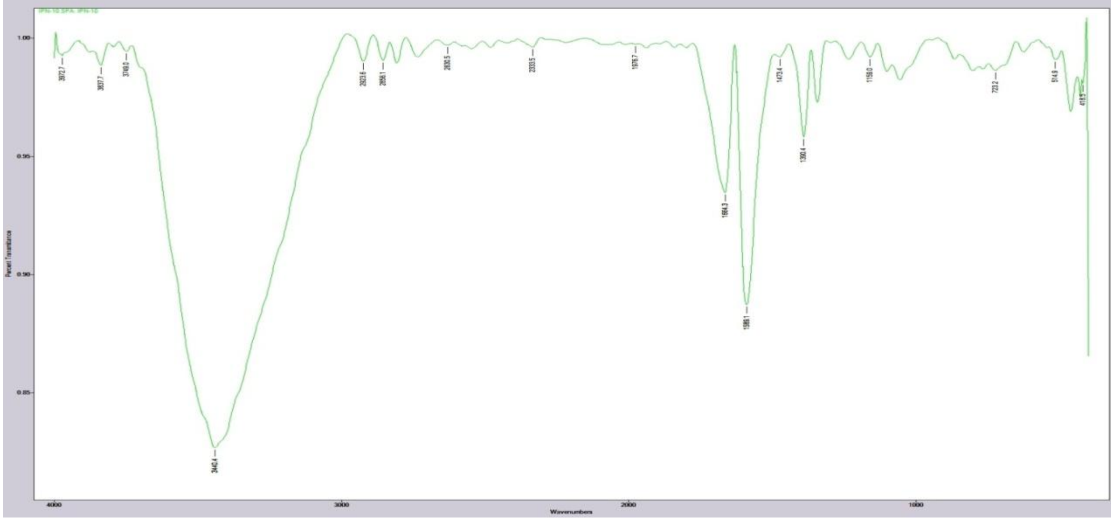


Figure 1c: FTIR of IPN 12

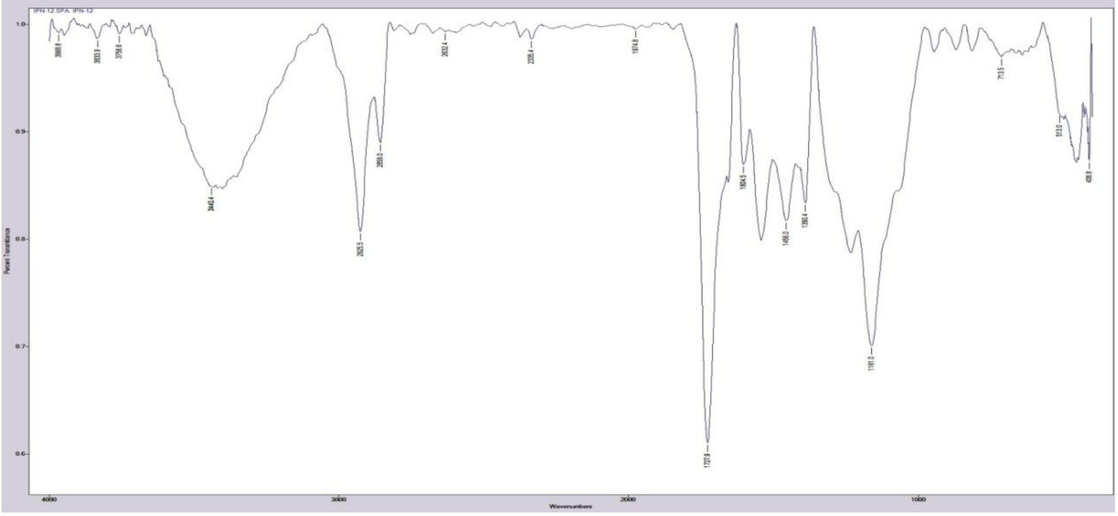


Figure 1d: FTIR of IPN 14

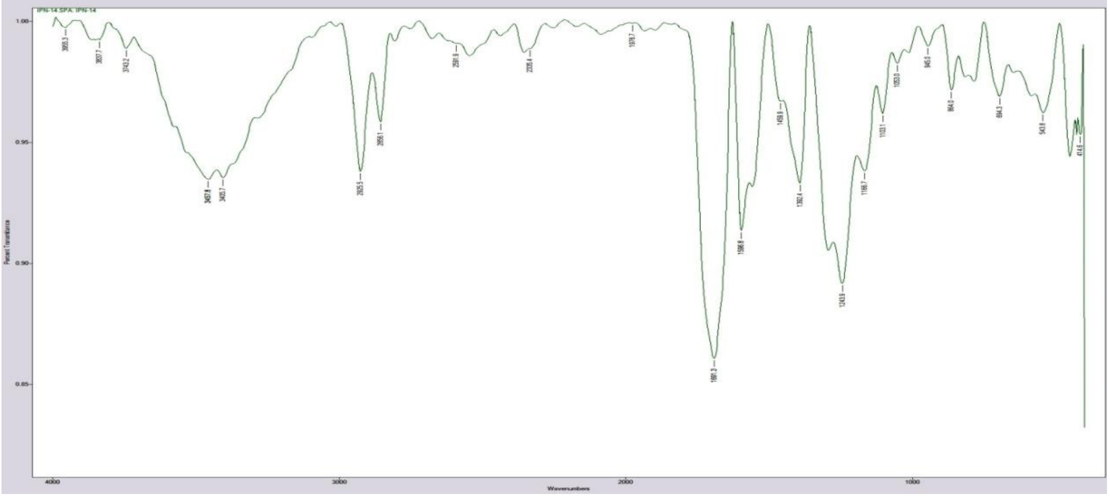


Figure 1e: FTIR of IPN 24

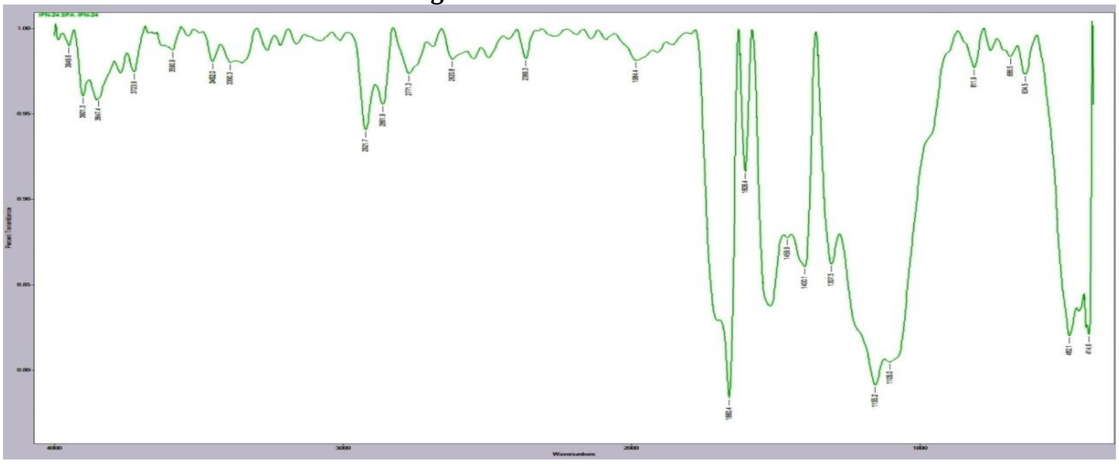


Fig2a: DSC-TGA OF IPN-6

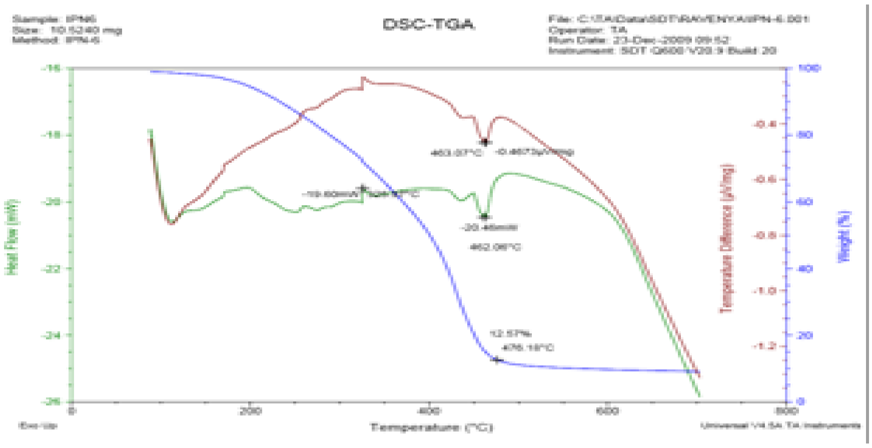


Fig 2b:DSC-TGA OF IPN-10

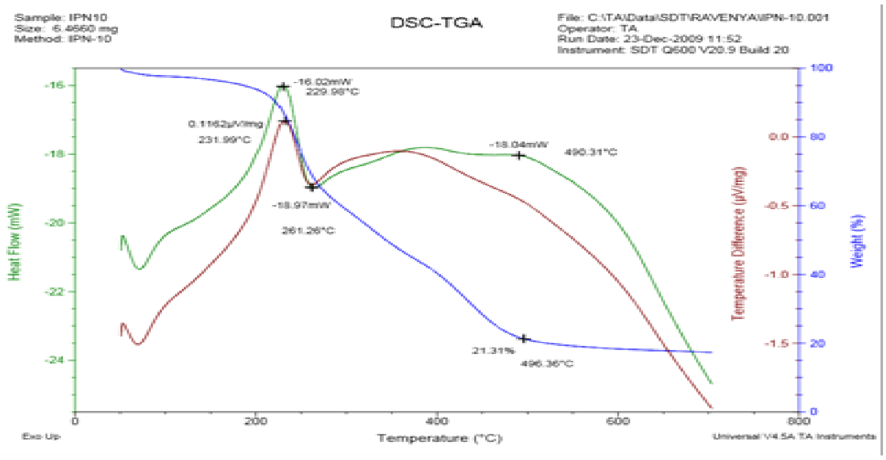


Fig2c: DSC-TGA OF IPN-12

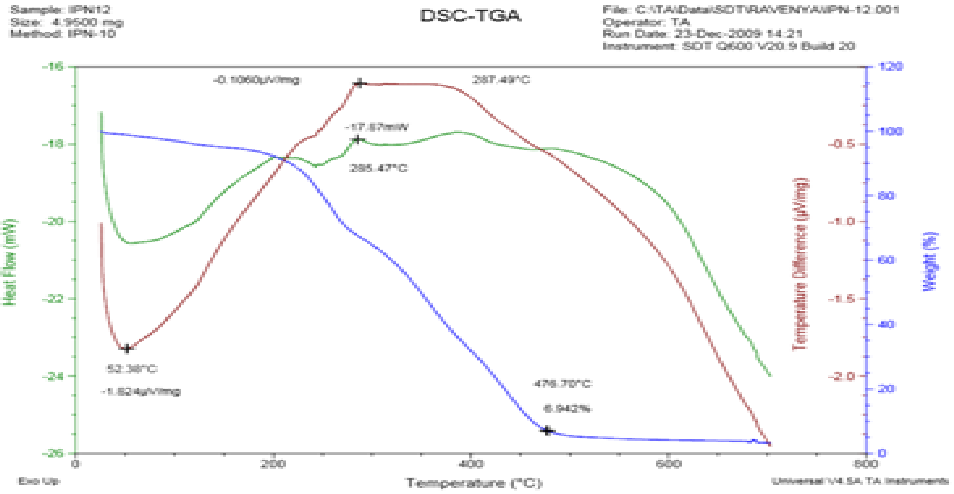


Fig2d: DSC-TGA OF IPN-14

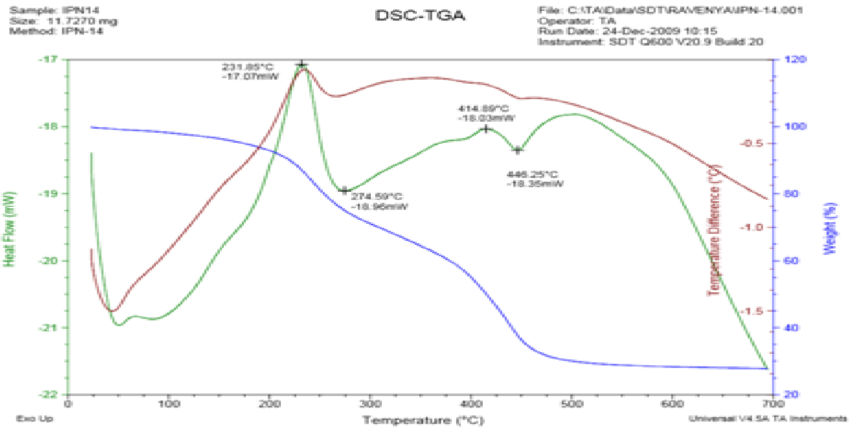


Fig2e: DSC-TGA OF IPN-24

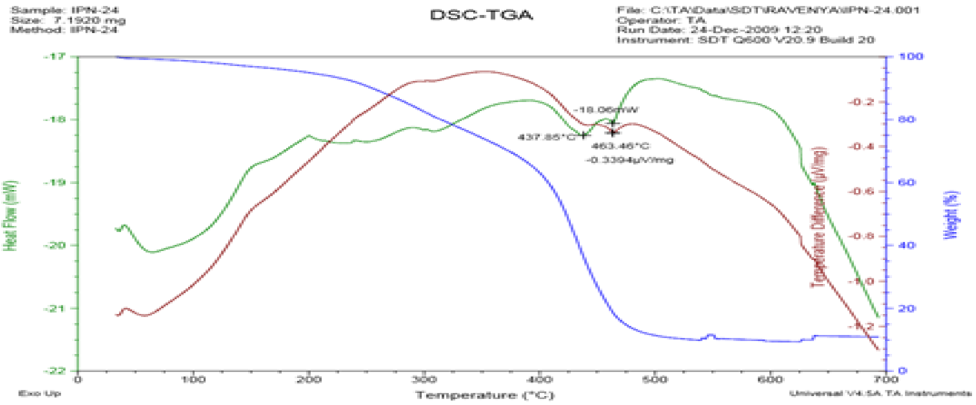


Fig 3a(i) showing kinetics of IPN-6

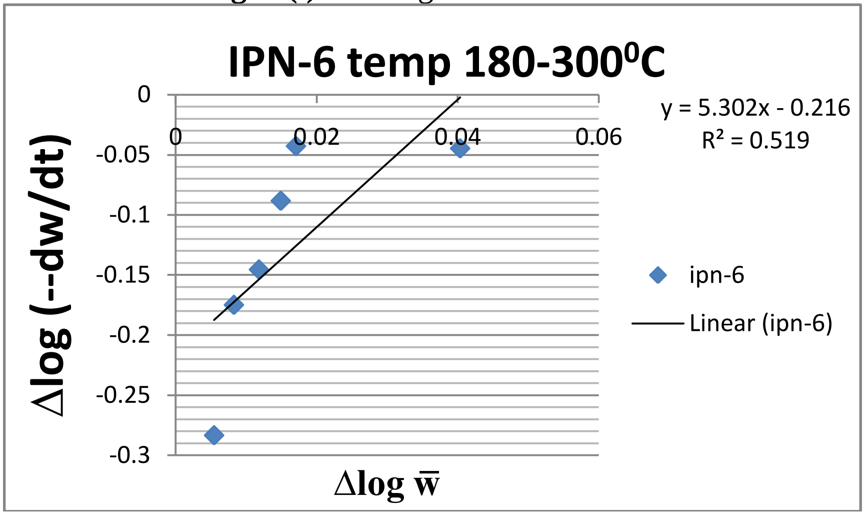


Fig 3a(ii) showing kinetics of IPN-6

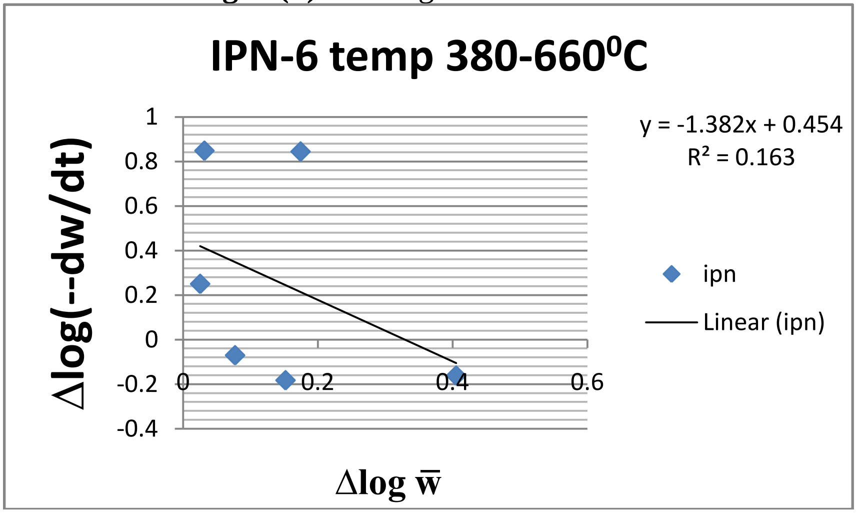


Fig 3b(i) showing kinetics of IPN-10

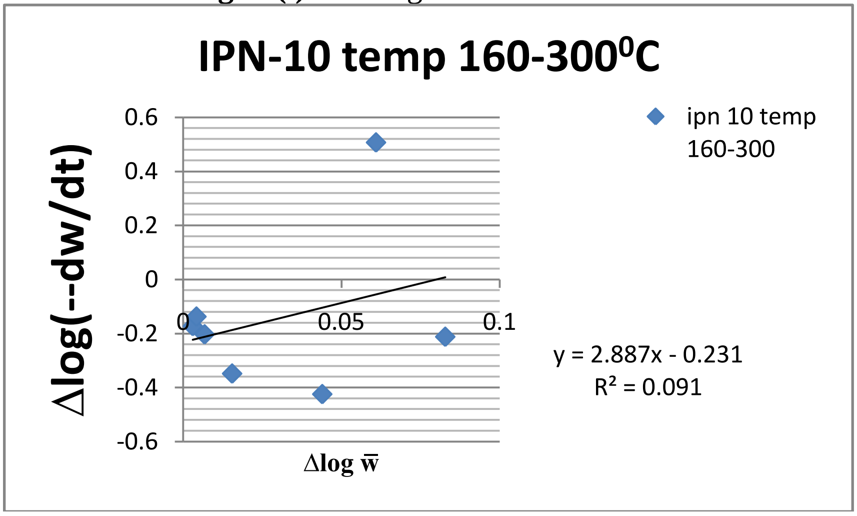


Fig 3b(ii) showing kinetics of IPN-10

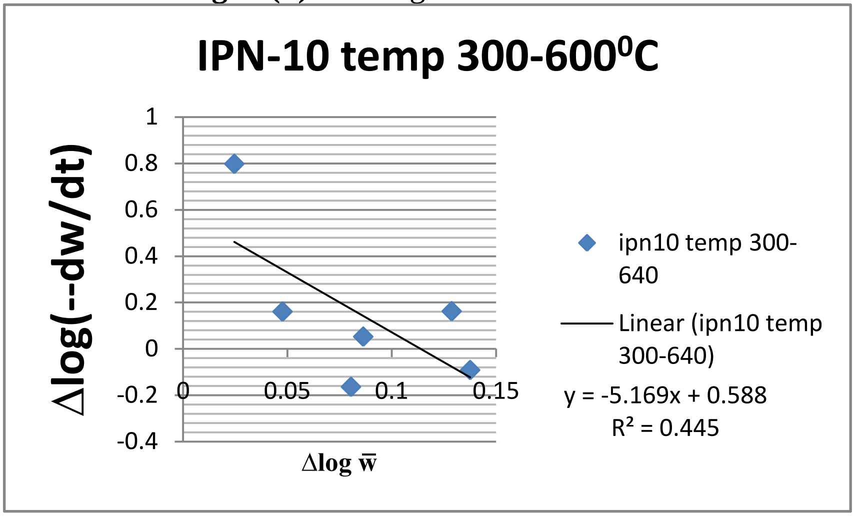


Fig 3c(i) showing kinetics of IPN-12

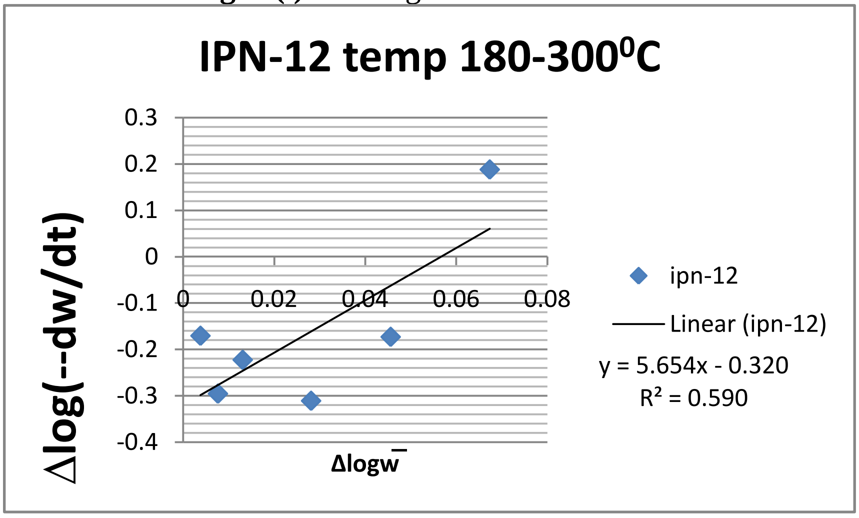


Fig 3c(ii) showing kinetics of IPN-12

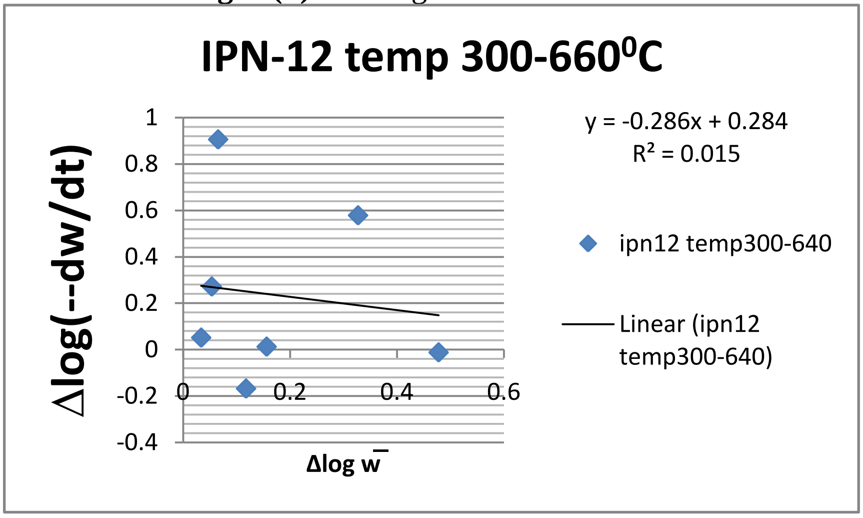


Fig 3d(i) showing kinetics of IPN-14

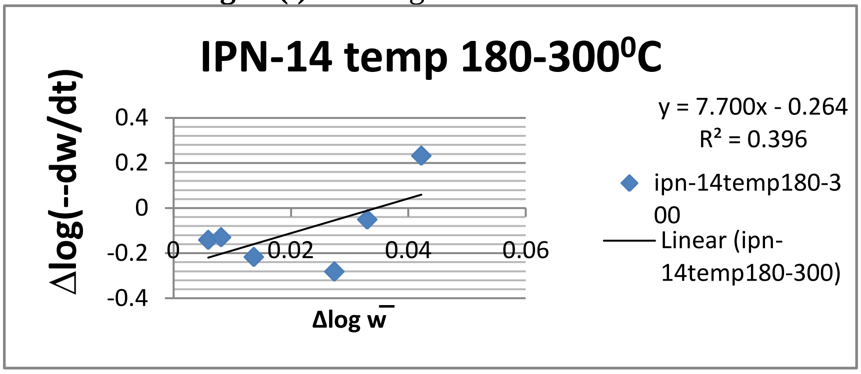


Fig 3d(ii) showing kinetics of IPN-14

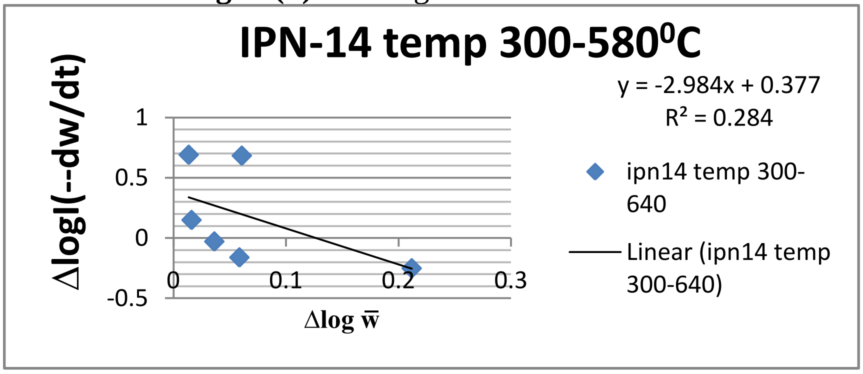


Fig 3e(i) showing kinetics of IPN-24

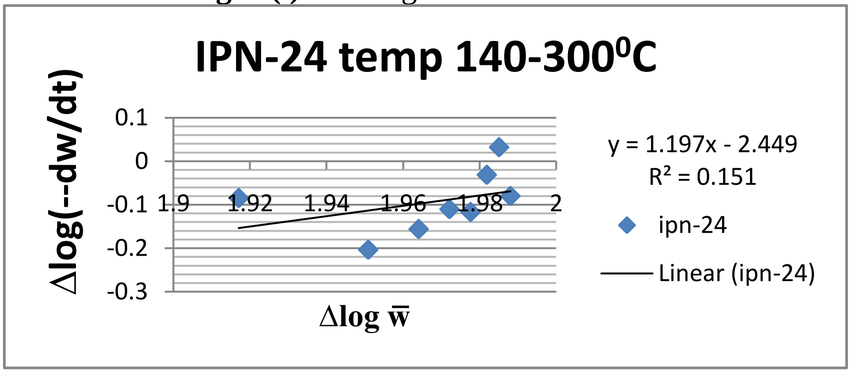


Fig 3e(ii) showing kinetics of IPN-24

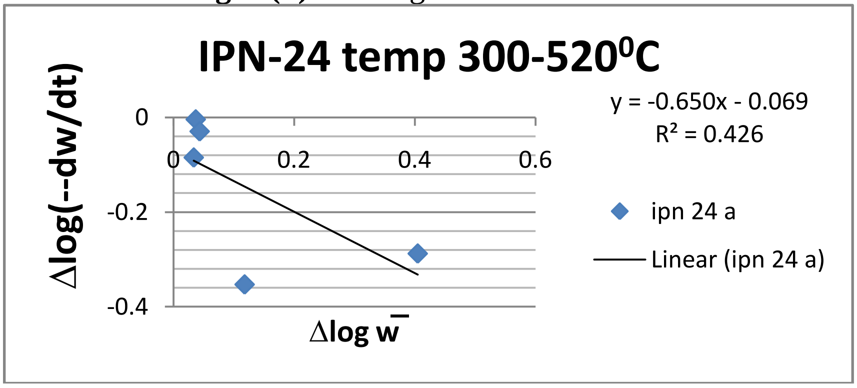


Table 1. Percentage of residual mass left with temperature

Sl No.	Sample code	100^{0}C	200^{0}C	300^{0}C	400^{0}C	500^{0}C	600^{0}C	700^{0}C
1	IPN 6	98.89	94.89	77.85	50.01	11.13	9.73	9.12
2	IPN10	97.66	93.92	58.84	4.9	20.99	18.37	17.36
3	IPN12	97.04	92.29	64.73	31.91	5.48	4.16	3.27
4	IPN14	98.18	92.88	70.94	54.78	30.05	28.34	27.76
5	IPN 24	98.58	94.48	82.6	63.09	11.44	9.61	9.12

Table 2. Feed composition data

Sl. No.	Sample code	Composition	NCO/OH	PU/CBD
1	IPN 6	PS+TDI+CD of 3-amino benzoic acid	1.6	0.50/0.50
2	IPN 10	PS+TDI+CD of 3-amino benzoic acid	1.2	0.25/0.75
3	IPN 12	PS+TDI+CD of 4-amino benzoic acid	1.2	0.50/0.50
4	IPN 14	PS+TDI of 4-amino benzoic acid	1.6	0.35/0.65
5	IPN 24	PS+TDI of 4-amino benzoic acid	1.6	0.50/0.50

Table 3. DSC parameter of IPNs

Sl. No.	Sample Code	Composition	NCO/OH	PU/CD	Tg	Tc	Tm
1	IPN 6	PS+TDI+CD of 3-amino benzoic acid	1.6	50:50	170.65	325.97	462.06
2	IPN10	PS+TDI+CD of 3-amino benzoic acid	1.2	25.75	200.11	231.1	490.31
3	IPN12	PS+TDI+CD of 4-amino benzoic acid	1.6	50:50	172.91	285.47	496.11
4	IPN14	PS+TDI of 4-amino benzoic acid	1.6	35:65	172.1	231.85 414.89	446.25
5	IPN24	PS+TDI+CD of 3-amino benzoic acid	1.6	50:50	195.02	310.05 437.03	472.25

Where, T_g: Glass transition temperature
T_c: Curie temperature or crystallization temperature
T_m: The temperature at which change of state occurs

Table 4 Decomposition of IPNs by bacteria:

Sl No.	Sample code	Initial mass in mg	Mass after 15 days in mg	Mass after 30 days in mg	Mass after 45 days in mg	Mass after 60 days in mg
1	IPN 6	10.52	10.46	10.23	10.1	10.06
2	IPN 10	10.31	10.26	10.21	10.1	10.09
3	IPN 12	9.52	9.47	9.41	9.32	9.29
4	IPN 14	9.98	9.89	9.57	9.43	9.4
5	IPN 24	9.76	9.64	9.56	9.41	9.32

Table 5. Kinetic parameters of different IPNs

Sample Codes	Temperature Range in ^0C	Slope or Order of reaction (n)	Intercept	Activation Energy (Ea) Jule/Mole
IPN6	380-660	1.3821	- 0.454	867.81
	18-300	5.3028	-0.2163	413.45
IPN10	160-300	2.8877	-0.2314	442.31
	300-600	5.1696	0.5886	1125.10
IPN 12	180-300	5.654	-0.3203	612.25
	300-600	0.2861	- 0.2845	543.81
IPN14	180-300	7.7004	- 0.2649	506.35
	300-580	2.9846	- 0.3778	722.16
IPN 24	140-300	1.1974	-2.4496	4682.38
	300-520	0.6507	-0.0692	132.27

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