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Thermally stable and flame retardant brominated polyurethanes

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Abstract

The thermal degradation and fire behaviour of new brominated polyurethanes have been studied by thermogravimetric analysis and by measurement of limiting oxygen index (LOI). It has been shown that the fire retardant incorporated in the prepolymer chain increased LOI. Novel flame retardant polyurethanes was prepared and characterized by FT-IR spectroscopy. Polyurethanes that contained halogen group attached to castor oil were prepared from brominated castor oil, rosinified phenolic resin and diisocyanate by one-step polymerization. The polymers prepared were characterized by FT-IR, thermogravimetric analysis (TGA) and oxygen index (LOI) measurements. The effect of the different percentage weight ratio of brominated castor oil and rosinified phenolic resin on the thermal behavior of the polyurethane was studied. The results indicated that the glass transition temperature (T_g) of the polyurethane increased with the concentration of resin and brominated castor oil content. The brominated containing polyurethanes exhibited slightly higher temperatures of degradation and higher char yields. Moreover, the LOI of the polyurethanes increased with increasing brominated castor oil content. Also studied was the possible mechanism of the flame retardancy.

Keywords: Polyurethanes, Flame Retardant, Thermal Properties.

Introduction

Polyurethanes are particularly versatile polymeric materials and have been extensively applied in various areas, such as construction, automobiles, and biomaterials^[1]. They are synthesized by reactions of polyether based or polyester based diols and diisocyanates, followed by the introduction of chain extenders to form macromolecules. Generally, polyurethanes do not exhibit sufficient flame retardancy and are easily burned. Though the flame retardant polyurethane has halogen and phosphorus compounds^[2-9]. Therefore, studies emphasizing the development of technologies to promote flame retardancy and create flame retardant materials have increased over many years^[10-13]. The literature also indicates that there are few reports regarding the flame retardant polyurethane coating^[14-20]. In extension of the work, we attended to formulate flame retardant polyurethane film. Thus the present commercially comprise studied on flame retardant polyurethanes from brominated castor oil and rosinified phenolic resin. The whole work is scanned in scheme 1.

2. Experimental

2.1 Materials

Bromine, Castor oil was purchased from local market. Rosinified Phenolic Resin (RPR) was purchased from local market. Dibutyltin dilaurate (DBTDL) used as a catalyst which was purchased from himedia. Isophorone diisocyanate (IPDI) and Toluene diisocyanate (TDI) were purchased from the bayer, (Dubai). Xylene used as a solvent was purchased from the S.d. fine chemical limited, (Mumbai).

2.2 Synthesis of brominated Castor oil

The bromination of castor oil was carried out by the reported method in literature^[10]. The method is as follows.

To a solution of 83.5gm (0.1 mole) Castor oil in 350 mL carbon tetrachloride (CCl_4), a solution of 45.5 g Br_2 (0.28 mole) in 75 mL carbon tetrachloride was added drop wise over a period of half an hour. The reaction temperature was maintained at 20 °C during the whole period of reaction. The quantity of the bromine added was in excess of the calculated theoretical amount.

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On completion of reaction, the amount of bromine left unreacted in the reaction mixture was reduced by using 5% aq. sodium sulphite solution. The aqueous layer was then separated from organic layer, which contained the desired product. Anhydrous sodium sulphate was then added and the

solvent was distilled off under vacuum. The structure of the brominated castor oil is shown in figure. The resulting brominated castor oil was designated as BCO. The physical properties of the brominated castor oil given in Table 1.

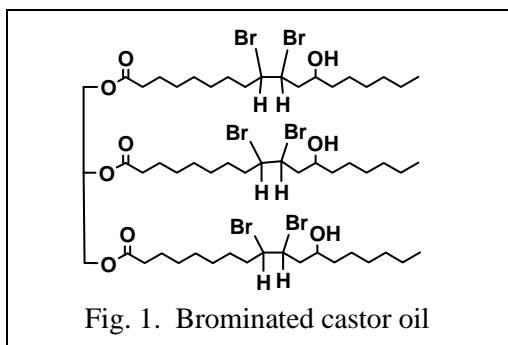
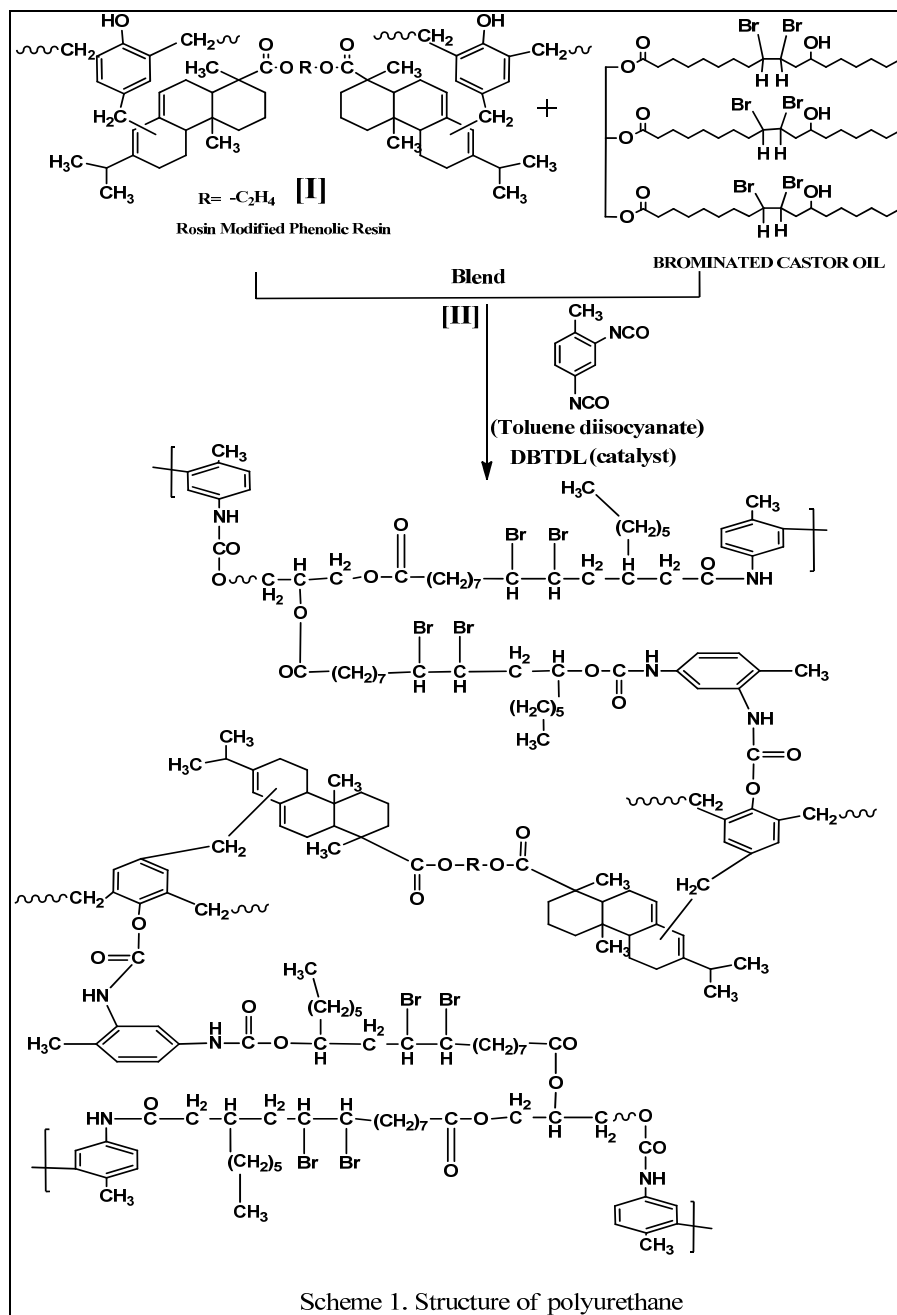


Table 1: Properties of Brominated Castor Oil

Sr. No.	Properties	Values
1	Iodine value	0.98
2	Hydroxyl value	164.26 mg of KOH
3	Hydroxyl equivalent weight	300.88
4	Specific Gravity	0.951-0.966
5	Refractive Index (ⁿ D ₂₀)	1.473-1.480
6	Viscosity (cSt at 37.8)	293.4 secs.
7	Color	Dark brown
8	Melting point	-20 to -10 °C

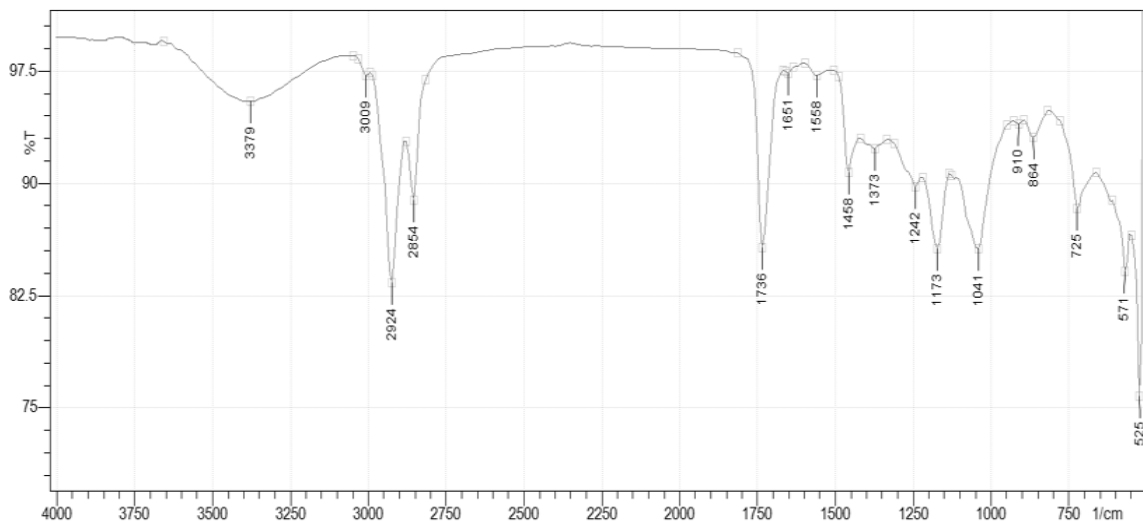


Fig 1: IR Spectra of brominated Castor oil

2.3 Blending of Rosinified phenolic (RPR) resin and Brominated Castor oil (BCO)

To prepare brominated castor oil and rosinified phenolic resin blends, involving a physical mixing of both as described below: Three necked flask equipped with a mechanical stirrer, brominated castor oil was charged and under continuous stirring desired amount of specific rosinified phenolic resin (as shown in Table 1) were added gradually over the period of half an hour. Upon the completion of addition the reaction mixture was stirred for an hour after which it was kept aside in a cylindrical glass container for overnight to check any tendency of separation of the two layers. In neither case separation of the two layers was observed. The physical properties of resultant above different percentage composition blends (RPR-BCO) are given in Table 2.

Table 2: Composition of (RPR: BCO) and Physical Properties

Sr. No.	Composition (RPR+BCO)	Hydroxyl value	OH equivalent Weight
B15	20:80	140.12	410.44
B16	30:70	128.28	452.68
B17	40:60	116.82	494.84
B18	50:50	104.78	553.47
B19	60:40	91.66	663.76
B20	70:30	80.69	716.83
B21	80:20	68.24	843.89

2.4 Synthesis of Polyurethane based on (RMPR-BCO)

Blends of RPR-BCO were taken in three necked flask which was equipped with mechanical stirrer, reflux condenser and thermometer. The stoichiometric amount of isophorone diisocyanate also toluene diisocyanate was added gradually in presence of dibutyl tindilurate (DBTDL) as a catalyst. The reaction was performed at 45-60 °C with continuous stirring for 4-6 hrs. The polymer was isolated as a viscous liquid. As the reaction mixture becomes pourable viscous liquid. It was poured in to the glass cavity. It was kept at room temperature for 24 hrs curing. Other polyurethane with different NCO/OH ratios and using different diisocyanate were prepared through the same procedure and cured in the form of casted films [21-23].

Table 3: Weight of Diisocyanates /10gm of polyol

Sr. No.	Composition (RPR+BCO)	TDI IPDI	
		T1	I1
1	20:80	7.928	8.752
2	30:70	7.426	8.286
3	40:60	6.582	7.339
4	50:50	5.810	6.475
5	60:40	5.040	5.621
6	70:30	4.549	5.277
7	80:20	3.741	4.173

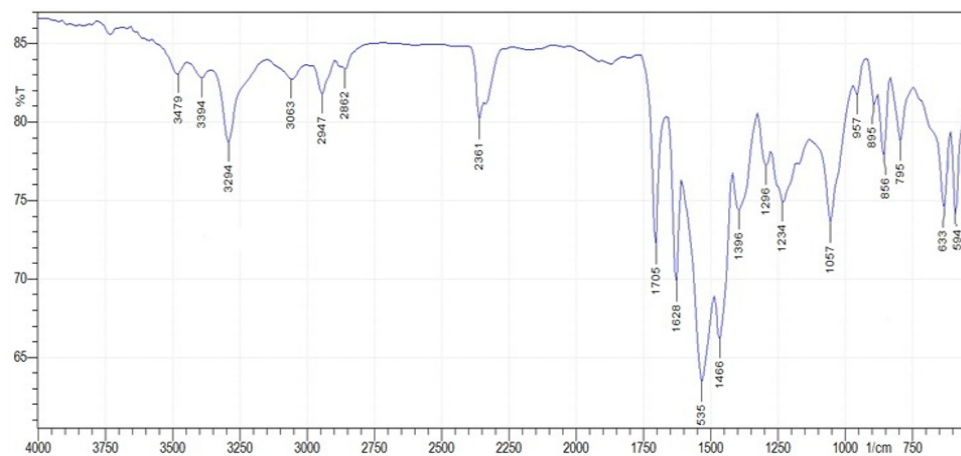


Fig 2: IR Spectra of Polyurethane

3. Thermogravimetric analysis

3.1 Film Casting

Glass plate (10cm×12cm) free from surface imperfections, were cleaned using xylene solvent. The prepared resin was then poured on to one edge of the plate which was left in the vertical position (to spread resin uniformly) at room temperature. Above prepared polyurethane syrups were casted into film form.

3.2 Experimental

TA instrument Model-2960 Thermogravimetric analyzer was used in the present study to record the thermograms of polymer samples. About 5 to 10 mg of the polymer sample was weighed in the boat of a thermo-balance and subjected to heating at a 10 °C/min heating rate in nitrogen atmosphere. The continuous loss in weight of a sample as a function of temperature gave a TG thermogram, which was used for further data analysis. To study effect of variables on thermal stability of polyurethanes prepared for present investigation, Thermogravimetric analysis (TGA) in the range of 0-700 °C was carried out.

Table 4: TGA data of Polyurethane based cured Film

PU Code	% of Weight Loss at Different Temperature (°C)			Decomposition Range (°C)	T max ^a (°C)	T ₅₀ ^b (°C)	IPDT ^c (°C)	Activation Energy ^d (E _a) KJ/Mole ⁻¹
	200	300	400					
B15PUT1	2	17	70	230-580	360	375	366	43
B16PUT1	1	5	65	244-594	372	397	378	50
B17PUT1	1	3	54	256-630	384	435	410	58
B18PUT1	1	9	66	272-676	398	465	442	64
B19PUT1	0	3	49	286-692	416	430	461	67
B20PUT1	1	4	48	295-704	447	461	475	76
B21PUT1	0	2	47	304-715	468	518	496	83
B15PUI1	2	24	77	206-555	354	363	356	39
B16PUI1	1	29	78	222-585	366	475	372	45
B17PUI1	1	12	53	240-598	379	483	435	50
B18PUI1	1	13	53	260-621	394	490	448	59
B19PUI1	1	13	52	269-634	415	495	460	65
B20PUI1	1	10	48	280-680	436	401	460	71
B21PUI1	1	7	49	288-699	458	511	472	77

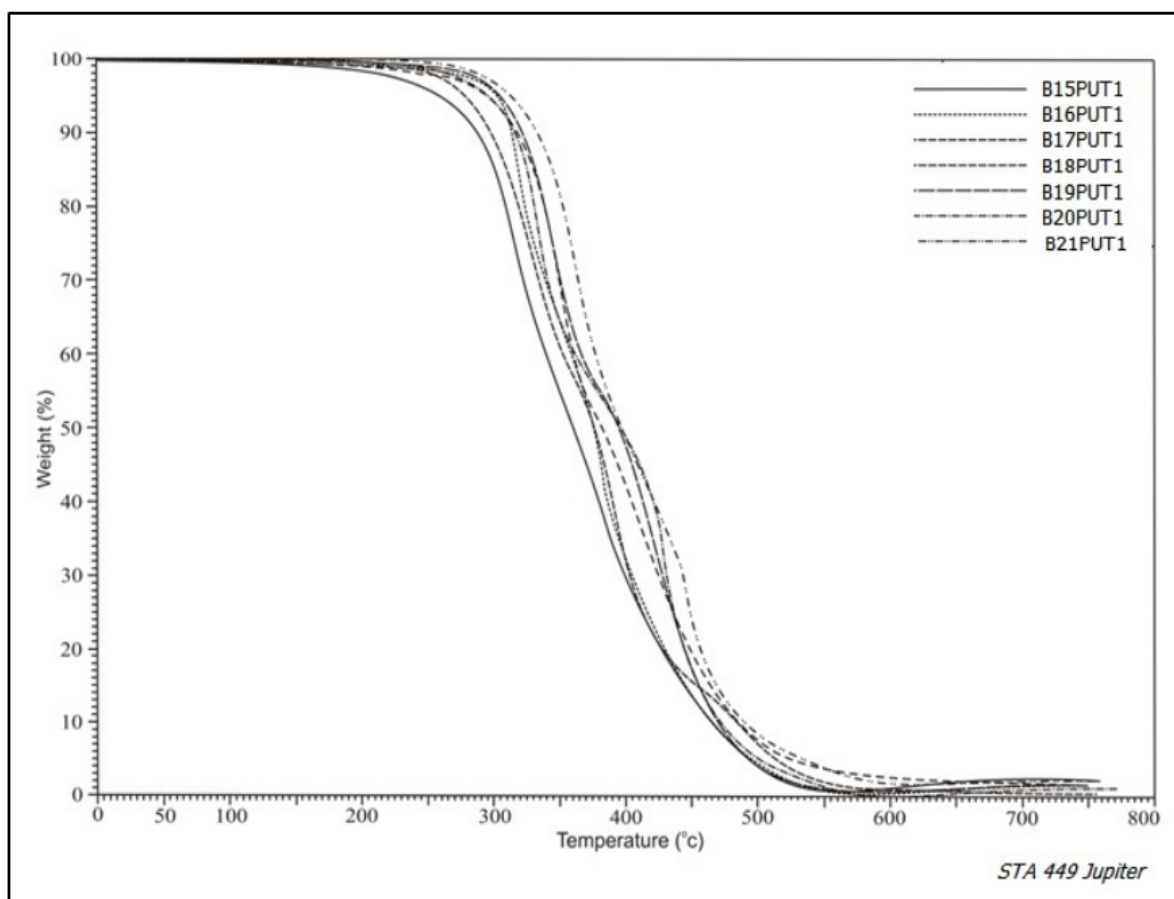


Fig 3: TG Thermogram of polyurethane based on TDI

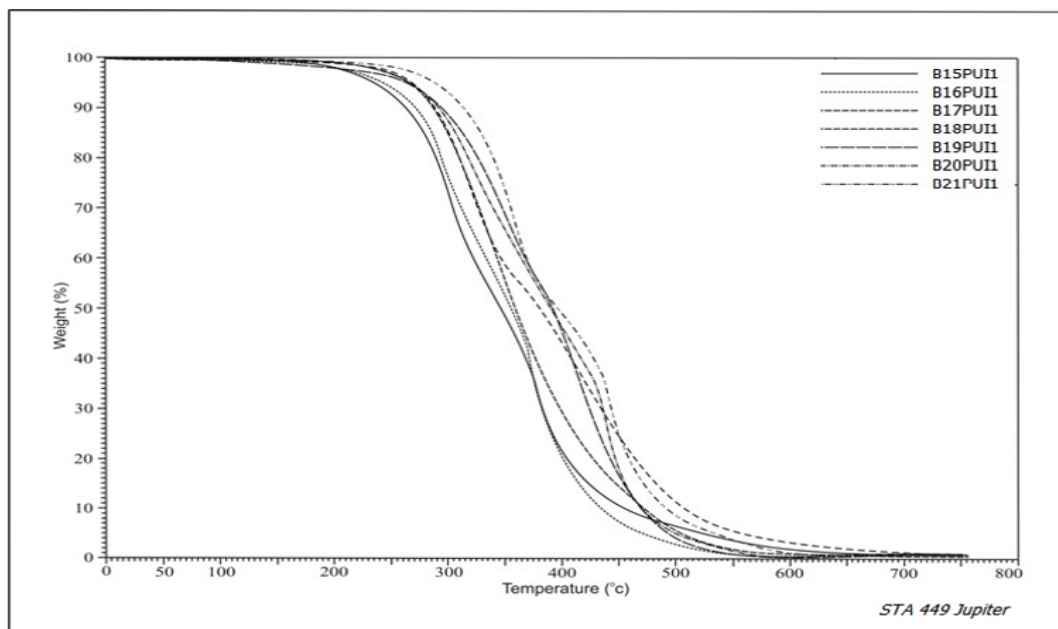


Fig 4: TG Thermogram of polyurethane based on IPDI

4. Flame Retardancy

4.1 Experimental

Flame retardancy of prepared polyurethane syrups based cured films were determined by using ASTM D-2863 procedure (limiting oxygen index, LOI measurement). Analyses were carried out using a Stanton Redcroft analyser. LOI were determined on 10×150 mm specimen with 3 mm thickness. Analyses were conducted at ambient temperature, with a 40 ml/s gas flow in the quartz column. The oxygen ratio variation in the gas was 0.2%. LOI for materials under study are shown in Table 5.

Table 5: Flame Retardant Proprieties of Polyurethane cured Films data

Polyurethane code	LOI	Flammability
B15PUT1	38	F
B16PUT1	37	F
B17PUT1	36	F
B18PUT1	35	F
B19PUT1	34	F
B20PUT1	33	NF
B21PUT1	31	NF
B15PUII	34	F
B16PUII	33	F
B17PUII	32	F
B18PUII	31	F
B19PUII	30	NF
B20PUII	29	NF
B21PUII	28	NF

5. Results and Discussion

FTIR spectroscopic, thermogravimetric and flame retardancy characterization has been performed for the prepared polyurethane films.

FTIR spectra of the prepared polyurethanes were obtained through Perkin Elmer Spectrophotometer. The spectra shows informative results in order to confirm the presence of certain functional groups required for reacting with aromatic diisocyanate for formulating polyurethanes. In all above spectra, the $-N-H$ stretching and bending vibration of urethane linkage is observed at 3479 cm^{-1} and 1535 cm^{-1} respectively.

In the spectrum, bands at 2862 cm^{-1} and 1450 cm^{-1} are observed due to $-C-H$ stretching vibration of alkane chain in the oil. The sharp bands at 1705 cm^{-1} reveal the presence of ester group. The unsaturation present in each can be clearly seen by the sharp $-C=C-$ stretching absorption at 1640 cm^{-1} as well as by out of plane $=C-H$ bending vibration at 900 cm^{-1} and 1010 cm^{-1} . The additional band at 787 cm^{-1} confirms the presence of double bonds ($-C=CH-$). The disappearance of the band at this frequency region is the evidence for the extent of curing. In the spectrum, bands at $500-600\text{ cm}^{-1}$ is observed due to $-C-Br$ stretching vibration of alkane chain in the oil.

The thermal properties of the PUs were studied by TGA. Generally the thermo-stability of polyurethanes depends on the number of aromatic moieties and urethane linkages present in the structure, as they can withstand a considerable amount of heat. Also the presence of secondary interactions increases the thermo stability of the polyurethane. The observed three step degradation of the present polymers in the TGA thermo-grams is supported by the literature report.

Thermograms indicate that all the PU coating films degraded as not well-distinguished three stages. The degradation in the first stage of polyurethanes may correspond to the breaking of urethane bond and leading the formation of CO_2 , alcohols, amines carbon monoxide etc. The second stage at about $250\text{ }^\circ\text{C}$ to $350\text{ }^\circ\text{C}$ may be due to the decomposition of ether and ester links. In the case of PUS cured film from different oil's based Modified Polyol, the main chain degradation may occur with the formation of as evidenced by the thermal degradation of Linoleic acid. In the third step finally this cured product degrades completely at slow rate. The percentage of weight loss up to $250\text{ }^\circ\text{C}$ in aromatic isocyanate based PU coating film is slightly higher compared to aliphatic isocyanate based PU coating films because of the instability of aliphatic moiety and increase the crosslinking density the percentage of weight loss decreases.

As soon as molecules containing bromine atoms have been introduced LOI are clearly improved. The gain on the value of LOI is nearly 2-3 points, which allows oxygen indices greater than 20 to be obtained. Up to a ratio of incorporated brominated castor oil wt. %. When the aliphatic and aromatic

diisocyanate reacts with a blended brominated castor oil-rosinified phenolic resin (wt. %), it is possible to reach a LOI of 39, which becomes very interesting for the fire behaviour of the material. Aromatic polyurethanes have higher LOI than aliphatic polyurethane due to increases the brominated castor oil wt. % and aromatic compound.

6. Conclusions

The brominated PU coats formulation can be easily prepared from modified commercial resin like rosin and renewable oil (i.e. Castor oil). Room temperature curing composition can be prepared easily achieve and give satisfactory results. Drying time of films based on TDI shows faster drying than compared to PU films based on IPDI. Polyurethane films prepared from aromatic Diisocyanates based is more thermally stable than aliphatic Diisocyanates due to aromaticity.

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