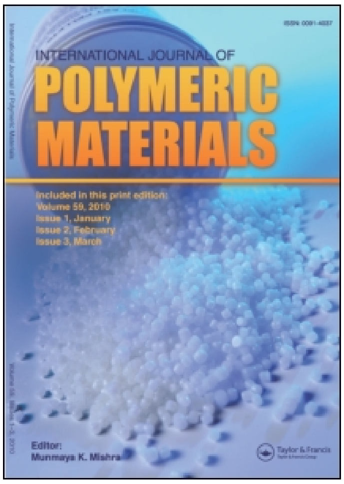

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Two Pack Polyurethane Coating System Based on Styrenated Polyols from Renewable Resource

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A series of styreneated polyols have been prepared from unsaturated glycol glycoside and argemone oil. Upto 50% by weight. styrene was loaded by generating free radical onto hydroxyl functionalised polyester, using AIBN as initiator.

The extent of unsaturation in styrenated polyols was determined by its Iodine Value. its molecular weight was determined by Gel Permeation Chromatogram (GPC) and functional group by Infrared Spectroscopy. A series of such prepared styrenated polyols was mixed with an aromatic adduct based on toluene di isocyanates (TDI) in different ratios of their equivalents (OH : NCO) to form Two Pack Polyurethane. Polyurethane resin thus prepared was coated on test panel and were compared with a set of unstyreneated polyols and isocyanate adduct admixtures for Flexibility. Scratch hardness, Impact resistance, % Adhesion and Chemical resistance. Structure of the polyurethane was confirmed by FTIR. Thermal stability of styreneated polyurethane was determined and compared with unstyreneated polyurethane by TGA.

Keywords: Polyurethane; Styrenated polyol; Argemone oil coatings

INTRODUCTION

In 1946, Hewitt and Armitage [1], reported a process of reacting styrene with drying oil, specially, with linseed and castor oil. The venture of synthesizing of styrenated polyurethane was carried out with the aim to have polyurethane of better mechanical and chemical properties compared to unstyrenated polyurethane synthesized from

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*Corresponding author.

liquid polyester polyol derived from renewable resources using reported method [2]. S. A. Harrison and Tolberg has reported that it is possible to bind the styrene onto nonconjugated polyester. The union occurs through "chain transfer" *i.e.*, by generating the free radical. Films derived form these compositions have shown all the qualities to be used as protective coating for metals [3].

Styreneated oil, polyesters and alkyd resins made form variety of drying oils have been known for many years [4, 5]. Some of the advantages claimed are fast drying with improved durability, Excellent water and alkali resistance, light color, and improved scratch resistance [6]. Preparation of styrenated polyurethane seems. to be logical because such polymers show improved properties over the unstyrenated polyurethane.

EXPERIMENTAL

Materials

Styrene, AIBN, and other chemicals used were of laboratory grade. Prior to use, styrene was made inhibitor free with 5% solution of sodium hydroxide to remove inhibitors followed by washing it with distilled water until it becomes free form alkali. It was then dried with anhydrous Na_2SO_4. An aromatic isocyanate adduct based on TDI was procured from Marigold Coating Pvt. Ltd. V. U. Nagar Gujarat. India (Bayer's Desmodur 175, %NCO = 13.5).

A liquid polyol used for the styrenation was prepared by transesterification of glycol glycosides and argemone oil, according to the reported method [2]. The Analytical data of the unstyrenated liquid polyol are as follows:

Molecular Weight($\overline{Mw}$):	2257
Viscosity Average($\overline{Mv}$):	2524
Iodine Value	120
Conjugated Diene	31.2%
Acid Value	6.0 mg of KOH/gms
Hydroxyl Number	333.3

Moisture content of Styrenated liquid polyol was determined by Karl Fischer Method and it was found to be in the range 0.03–0.2%.

Synthesis of Styreneated Polyol

Liquid polyol was charged into a three-necked flask, equipped with an efficient water condenser, mechanical stirrer, a thermometer pocket and a nitrogen inlet. The reaction mixture was heated and brought to reaction temperature *i.e.*, 60°C. AIBN (2.5% by weight of liquid polyol) was previously dissolved in styrene. It was then added to the reaction flask over the period of 4.0 hours. After the addition was complete, the reaction was stirred further for 2.5 hour to stabilize the reaction product.

Samples were withdrawn periodically from reaction flask and checked for viscosity and clarity. Reaction was stopped when no significant increase in the viscosity was observed between two consecutive samples. Resin was thinned down with xylene to 60% non-volatile content. Styrenation of liquid polyol was carried out under identical condition using different ratios of Polyol : Styrene.

Styrenated Polyol

To establish the formation of Styrenated polyol the infrared analysis were carried out. The representative IR of Styrenated polyol is as shown in Figure 1. A broad band around $3350\,\mathrm{cm}^{-1}$ is attributed by hydroxyl linkage present in the polyol. A sharp peak around $1750\,\mathrm{cm}^{-1}$ indicates the presence of ester linkage within the polyol. The presence of styrene can be felt by the band around $700\,\mathrm{cm}^{-1}$ which indicating the band of aromatic ring. The band around $3022\,\mathrm{cm}^{-1}$ shows the presence of vinyl group —(CH)— present due to styrene, within the polyol.

Gel Permeation Chromatography (GPC)

Number average molecular weight of liquid polyol was determined by Gel Permeable Chromatography (Fig. 2). It was found to be in the range of 1742–2041 and weight average was found to be in the range of 4300–7084. The conclusive evidence of the formation of the copolymer of styrene with liquid polyol is attained by sharp and narrow chromatogram. The polydispersity ranges from 2.46–3.47. Representative GPC is displayed in figure.

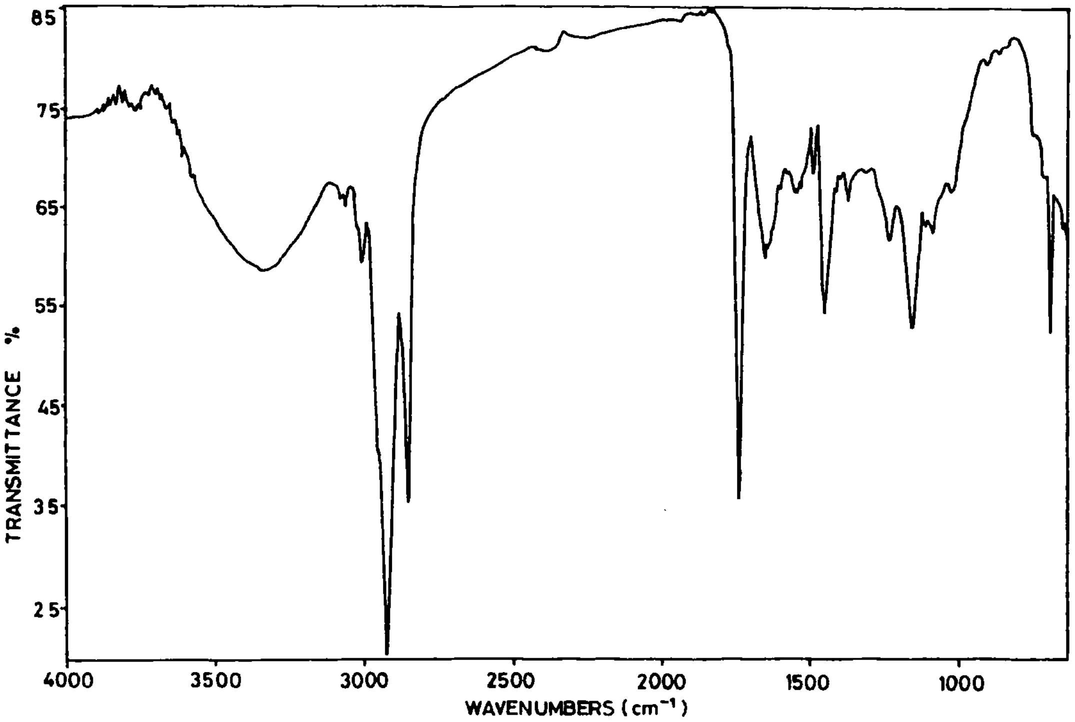

FIGURE 1 IR spectra of styrenated polyol.

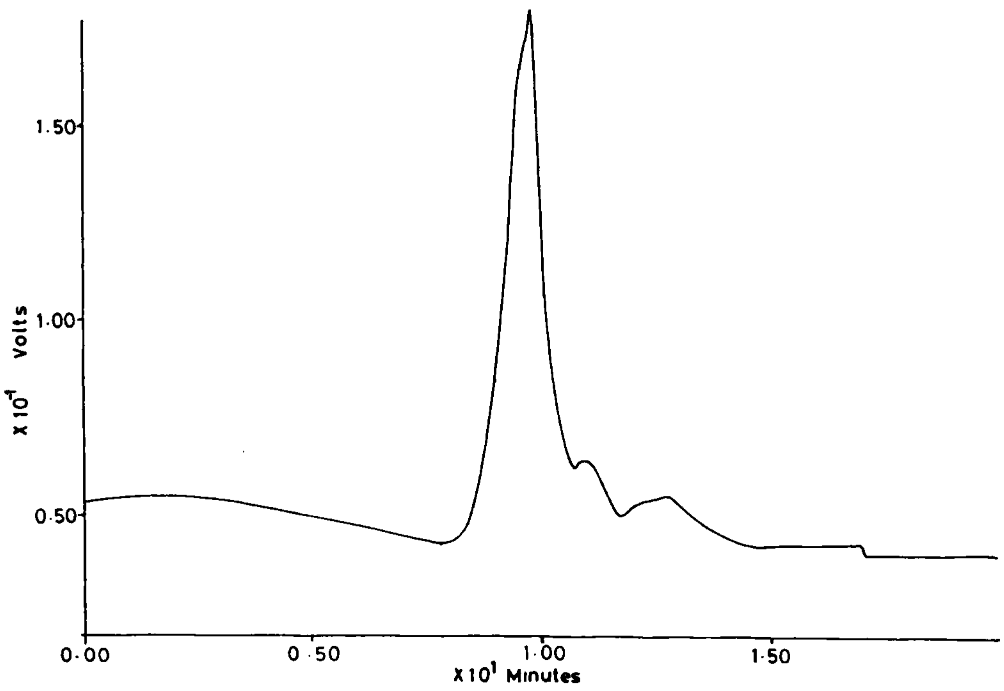

FIGURE 2 Gel permeation chromatogram of styrenated polyol.

Iodine Value

Iodine value of the styrenated polyol was determined by Hoffman and Green method using 2.5% solution of mercuric acetate in acetic acid as the catalyst with the Wij's solution [8]. The iodine value of the series of Styrenated polyol is tabulated in Table I. With the increase in the styrene content in liquid polyol the iodine value decreases, indicating that styrene is attached to the conjugation in unsaturated liquid polyol. From the Table I, it indicates that iodine value ranges from 120-56.69. Thus iodine value signifies that more than 50% of styrene can be loaded onto unsaturation of liquid polyol.

Synthesis of Polyurethane

After determination of hydroxyl value of the styrenated polyol, it was mixed with Aromatic Isocyanate adduct of TDI of different ratios of OH : NCO on equivalent basis. The mixed material were thinned with

TABLE I Mechanical properties of polyurethane derived from styrenated polyol

% Styrene loaded on polyol	*NCO/OH*	*Iodine value*	*Scratch resistance Kgs.*	*Impact hardness lbs./inch*	*Flexibility 1/8″*	*Adhesion %*
	1.0		0.80	300	P	88
	1.1		1.00	275	P	77
0%	1.2	120.000	1.30	250	P	88
	1.3		1.70	250	P	89
	1.4		1.80	250	P	91
	1.0		1.00	275	P	89
	1.1		1.32	250	P	77
10%	1.2	109.750	1.50	250	P	88
	1.3		1.75	250	P	91
	1.4		1.90	225	P	90
	1.0		1.60	250	P	84
	1.1		1.75	225	P	92
20%	1.2	98.360	1.80	225	P	95
	1.3		2.00	175	P	91
	1.4		2.25	175	P	89
	1.0		1.80	150	P	92
	1.1		2.00	125	F	96
50%	1.2	65.275	2.25	125	F	95
	1.3		2.30	100	F	93
	1.4		2.40	100	F	95

P = Passes the 1/8 inches conical mandrel flexibility test.
F = Fails the 1/8 inches conical mandrel flexibility test.

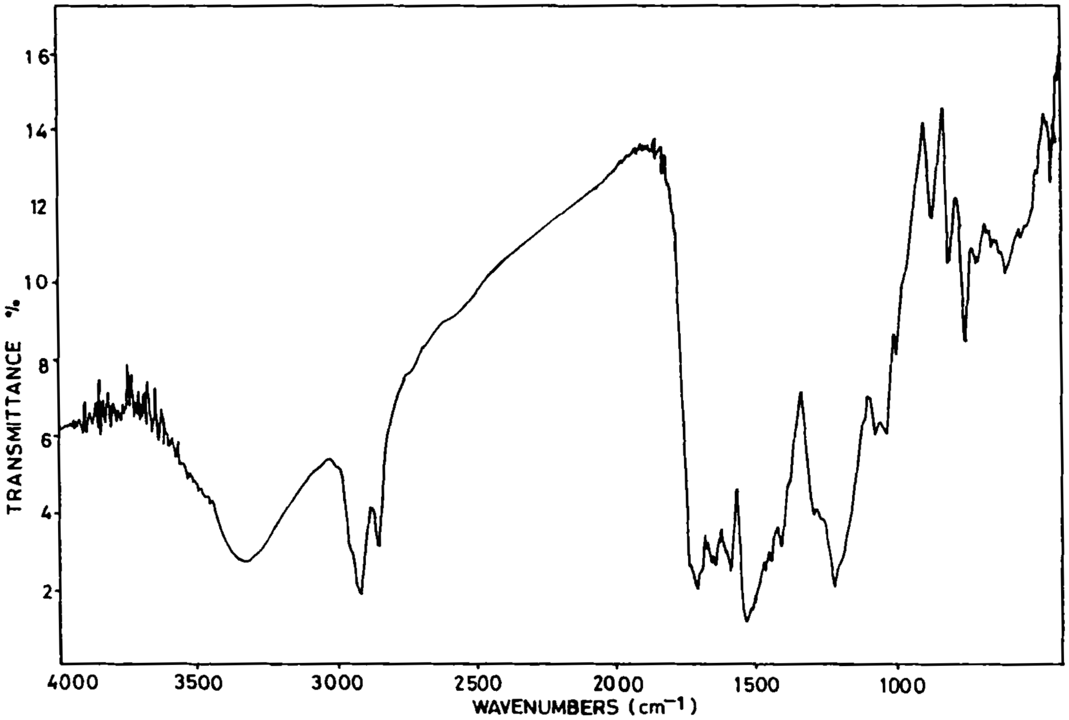

FIGURE 3 IR spectra of styrenated polyurethane.

a mixture of Methyl Ethyl Ketone (MEK) and xylene (1 : 1) on weight basis to an applicable viscosity and was applied on test panels. The coated panels were examined for the various tests suggested by standard bearue.

Styrenated Polyurethane

A broad and stretching band around 3345 cm^{-1} and band around 1600 cm^{-1} indicates the presence of —(NH)— linkage present in the polyurethane. Keyband around 1722 cm^{-1} is attributed to the carbamate group (see Fig. 3).

RESULTS AND DISCUSSION

Tables I and II indicate the various properties of coated panels of different composition.

TABLE II Chemical properties of polyurethane derived from styrenated polyol

% Styrene loaded on polyol	*NCO/OH*	10% *NaOH*	5% *HCl*	*Xylene*	*Benzene*	*Water*
0%	1.0	c, d	e	c	d	e, f
	1.2	c	d, e	c	d	d
	1.4	c	c	b	c	c
10%	1.0	c	d	c	d	c
	1.1	c	c	b, c	d	c
	1.2	c, b	c, d	c	d, c	c, b
	1.3	c, b	b, c	c	c	c, b
	1.4	b	b	c	c	b
20%	1.0	b	c	b, c	c	b
	1.1	b	b	b, c	b, c	b
	1.2	c, b	b	b	b, c	b
	1.3	b	b	b	b	b
	1.4	b	a	b	b	a
50%	1.0	b	b	a	b	b
	1.1	a	a	a	a	b
	1.2	a	a	a	a	a
	1.3	a	a	a	a	a
	1.4	a	a	a	a	a

a = Unaffected; b = Slight loss of gloss; c = Loss of adhesion; d = Slight blistering; e = Swelling; f = Slight affected; g = Ruptured.

Scratch Hardness and Impact Resistance

Test for scratch resistance and impact hardness was performed according to method suggested in IS 1967–1969 method. Scratch resistance increases with the increase in styrene content in the styrenated liquid polyol. This is a result of increase in the styrene moiety within the resin, which is responsible for film forming. Histogram (Fig. 4) indicates that with the increase in amount of styrene in the polyol, scratch resistance increases.

Impact hardness was measured using falling intender weight on the panel. In this method a hemispherical intender of known weight is dropped down to the panel support in which panel is rested. An intender was dropped from certain height until the film cracks. (The maximum height of the instrument is 48 inches and weight of intender is 6.25 lb.).

Impact hardness decreases with the increase in the styrene content in liquid polyol. This may be due to film embrittlement caused by the presence of higher amount of styrene. Over all ratio of styrene to liquid polyol must be enough to show its influence of its effect on the impact properties of the film.

Flexibility Test

Flexibility test was performed according to IS 101-1964, on 1/4" and 1/8 inches conical mandrel. As expected the surface coating composition derived from oil based polyol posses admirable flexibility.

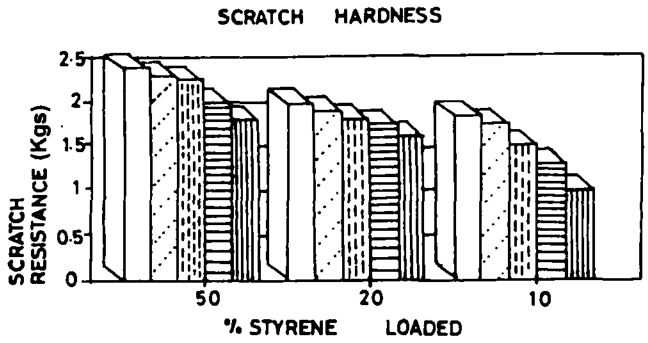

FIGURE 4 Scratch hardness properties of polyol.

All coating prepared in the present case had enough flexibility and they pass through the flexibility test.

Percentage Adhesion

Adhesion of film coated on test panel was examined by stripping test IS 101-1964. It was found to have good adhesion property on metal. It is observed that with the increase in the styrene content within the polyol, percentage adhesion was increased.

Chemical Resistance

Styrene modification of polyester polyol is known to have improved chemical resistance of film with increasing degree of styrenation.

The test of chemical resistance was performed according IS 101-1964 and observed results are tabulated in Table III.

For chemical resistance test the samples panels were dipped in the 5% Alkali solution, 5% Hydrochloric acid solution for 240 hours. It was observed that with increase in the styrene content, the resistivity towards alkali increase.

Resistivity towards water and solvents were also measured and it showed a good resistance towards Xylene, Acetone, and Benzene.

Drying Time (Tack Free Time)

Tack free time of various sets has been reported in Table I, as they give an indication of drying time of the film after its application. Tack free time for all the synthesized composition was reasonably low, as compared to unstyrenated polyurethane. It was observed from the result and histogram displayed in Figure 5, that with the decrease in

TABLE III Drying properties of polyurethane derived from styrenated polyol

NCO/OH	*Styrene loaded*			
ratio	0% (*Min.*)	10% (*Min.*)	20% (*Min.*)	50% (*Min.*)
1.0	33	26	24	20
1.1	32	23	23	18
1.2	27	22	21	17
1.3	20	20	18	17
1.4	18	19	17	14

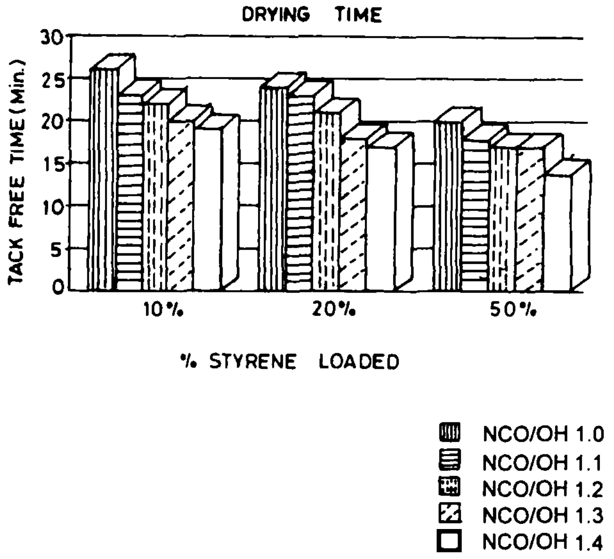

FIGURE 5 Drying properties of styreneated polyol.

the styrene content in the polyol, tack free time decreases. The increase in tack free time is attributed to the increased in thermoplastic character of the resulting coating system with increased amount of styrene [7].

As expected, surface coating derived from oil based polyol must have admirable flexibility. All coating prepared in the present case had good flexibility and they passed through the flexibility test IS 101-1964, on 1/4″ and 1/8″ conical mandrel.

Moisture Content in Polyol

Moisture content determination in the liquid polyol is important. Moisture in polyol, makes it react with di-isocyanate and generation of CO_2 takes place which acts as a blowing agent leading to formation of foam.

$$R{-}N{=}C{=}O + H_2O \rightarrow RNH_2 + CO_2 \uparrow$$

The moisture content within the polyol was found to be within the range of 0.05–3%, which is appropriate of any composition used for surface coating application [9].

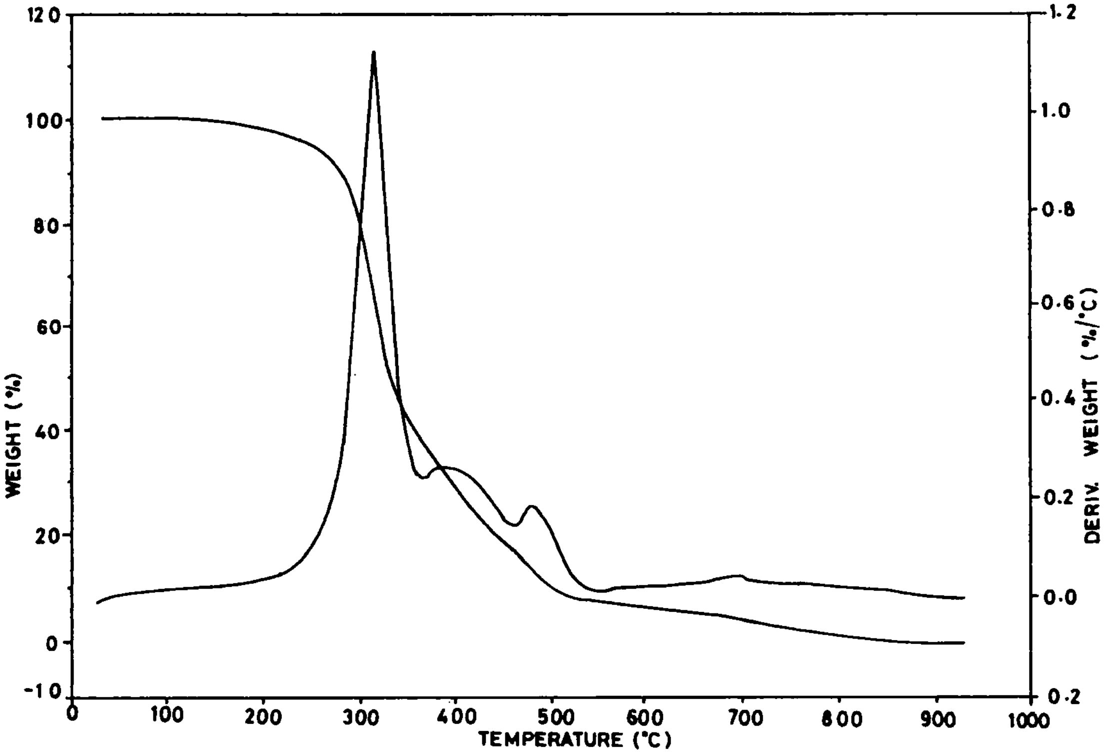

FIGURE 6 Thermogravimetric curves of polyurethane.

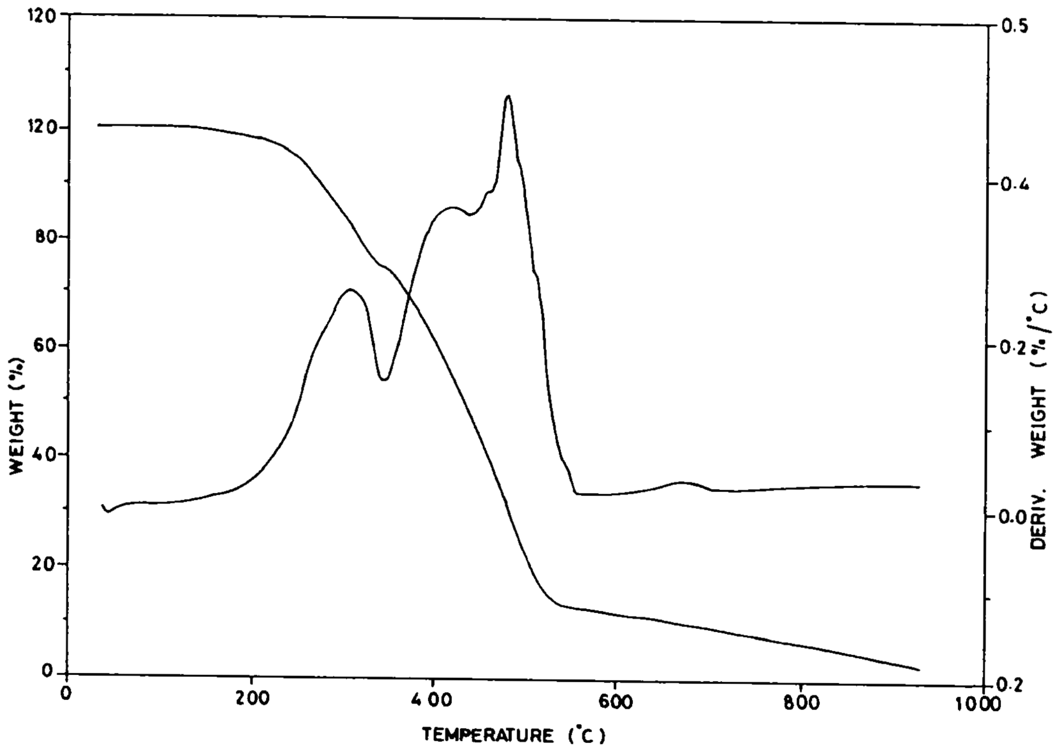

FIGURE 7 Thermogravimetric curves of styrenated polyurethane.

Thermal Analysis

Thermal behavior of polyurethane derived from Glycol Glycoside Polyol and Styrenated polyol was studied using thermogravimetric curves. A perusal of Figures 6 and 7 indicates that polyurethane derived from Glycol Glycoside (USPU) decomposes 10% within the temperature range 25°C-190°C and that of Styrenated polyol based polyurethane (SPU) within the range 0°C-210°C. 60% decomposition of USPU occurs in between 190°C-400°C while in case of SPU temperature range is 220°C-510°C. 90-98% decomposition takes place at 400°C-510°C (USPU) and 510°C-765°C (SPU).

The initial weight loss is attributed to the moisture retained in the sample. The thermal decomposition of SPU is slower compared to USPU. The weight loss accrued at the higher temperature is due to decrosslinking within the polymer. As the styrene, is reacted at the unsaturation present within the polyol, which was providing the flexibility to the polymer [10]. Styrene is incorporated within the polyol; it makes the polyol more rigid in nature and ultimately slower down the rate of decomposition of SPU. Thus the presence of styrene within the polymer attributes the resistivity towards decomposition. The curves indicates that unreinforced polyurethane (USPU) gets decomposed in the single stage, while reinforced polyurethane gets decomposed in multistage providing the resistance towards decomposition. The results obtained on interpreting the thermograms are summarized in Table IV.

TABLE IV Results of thermal analysis

Temperature (°*C*) *Sample* 1(*a*)	*Weight residue* (%)	*Temperature* (°*C*) *Sample* 1(*b*)
165	0	210
237.5	10	255.7
260.5	20	344.5
310.2	30	390.8
352.4	40	440.5
390.5	50	475.3
425.3	60	510.2
450.8	70	535.5
495.7	80	645.7
550.3	90	735.3
585.2	98	765.4

Sample 1(a): Polyurethane derived from Glycol Glycoside based polyol (USPU).
Sample 1(b): Polyurethane derived from Styrenated Polyol (SPU).

CONCLUSION

It can be concluded that styrenated polyurethane can be successfully synthesized by post styrenation technique, using AIBN as initiator to generate the free radical, under experimental condition.

The study of the film properties of the styrenated polyurethane resins reveals that most of mechanical and chemical properties are superior compared to unstyrenated polyurethane. Impact resistance of a given styrenated polyurethane is maximum at 10% and 20% of percentage styrene loaded in liquid polyol and at (NCO:OH) ratio of 1.3, 1.4 and 1.1, 1.3 respectively. Drying time of the styrenated polyurethane is comparatively fast.

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