

Novel Binder System for Ultraviolet-Curable Coatings Based on Tobacco Seed (*Nicotiana rustica*) Oil Derivatives as a Renewable Resource

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ABSTRACT: Several coatings have been developed to reduce volatile organic component emissions, such as water-borne coatings, high-solid coatings, powder coatings, and radiation-curable coatings. Ultraviolet-curable coatings are one such boon to paint industries, not only reducing volatile organic components but also increasing productivity. Most polymers industrially produced nowadays are based on petroleum, which is a limited resource. Developing new procedures for making polymers based on natural renewable resources is a resounding theme for this decade and the future also. In response to both these needs, we have investigated the use of tobacco seed (*Nicotiana rustica*) oil in the synthesis of radiation-curable coatings. In this work, the alcoholysis of oil in various ratios with polyhydroxyl compounds was performed to prepare novel poly-

ols, and these different polyols were reacted further with excess polyisocyanate to produce isocyanate-terminated prepolymers. The prepolymer were further reacted with hydroxyethyl methacrylate to produce urethane acrylate oligomers. The radiation-curable coating compositions were than prepared by the mixing of these oligomers with different reactive diluents, photoinitiators, and activators. These coating compositions were studied for their various physical and film characteristics, and certain coating compositions from tobacco seed oil were found to show very excellent overall coating properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 71–81, 2008

Key words: coatings; oligomers; photopolymerization; radiation; renewable resources

INTRODUCTION

Agricultural raw materials precede petrochemicals by millennia in nonfood applications. Vegetable oils,¹ for instance, were used for illumination and lubricating purposes and for coatings and paints for many centuries before an abundant and cheap supply of mineral oil became available for a wide range of products.² This has resulted in a steady decline in the use of renewable resources in the paint and coating industries and in other nonfood fields. As an illustration, the total volume of fats and oils used in drying oil products is now less than a third of the volume in 1950. When we realize that the total volume of resins in paints has increased substantially since that time, the reduction in the share of vegetable-oil-based products becomes even more striking.³ However, in the past few years, consumer and industrial interest in environmentally friendlier paints and coatings has been growing tremendously. This trend has been spurred not only by the realization that the supply of fossil resources is inherently

finite but also by a growing concern for environmental issues, such as volatile organic compound (VOC) emissions and recycling or waste disposal problems at the end of a resin's economic lifetime. Furthermore, developments in organic chemistry and fundamental knowledge of the physics and chemistry of paints and coatings have enabled some problems encountered previously in vegetable-oil-based products to be solved. This has resulted in the development of coating formulations with much improved performance that are based on renewable resources. These advances have, on the one hand, led to a further reduction in the use of organic solvents in paint systems through the development of, for example, new radiation-curable coatings, water-based paint formulations, and high-solid systems. On the other hand, they have also led to increased interest in the use of renewable resources, that is, resources derived from agriculture, in paint and coating formulations. Tobacco seed oil, a nontraditional oil, has been studied as a renewable raw material for numerous industrial uses. Tobacco seed oil,⁴ like safflower oil, is rich in linoleic acid (content > 70%). It is obtained from the seeds (oil content = 30–43%) of two species of plants, *Nicotiana tabacum* and *Nicotiana rustica*, and has been produced to some small extent in Bulgaria,

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TABLE I
Physical Properties of Tobacco Seed Oil

No.	Characteristic	Specification	Result
1	Refractive index	1.474–1.483	1.458
2	Relative density at 25°C	0.923–0.925	0.924
3	Color (Gardner)	12–15	14
4	Acid value (mg of KOH/g)	2-mg maximum	1.6
5	Iodine value	140–145	141.1
6	Saponification value	189–190	190.7

Turkey, India, and Greece and to a lesser extent in the United States. The oil is free of harmful substances and can be used for edible purposes after refining. It is particularly adapted for the preparation of nonyellowing alkyd resins, but it is not produced in large quantities. The physical properties are reported in Table I, and the fatty acid compositions are reported in Table II. The various important characteristics are very well described in the literature.⁵

The surface coating industry is a huge consumer of petroleum-based materials, such as solvents, polymers, and additives; currently, this industry is passing through a boom of environmental pollution regulations, which are forcing technologists to develop low-VOC, fast-curing, high-performance, easy-to-apply coatings, such as radiation-cured coatings, including ultraviolet (UV)-cured and electron-beam-cured coatings. The very advanced and thrust area of UV-curable coatings were reviewed by Lockwood⁶ and Xu and Shi⁷ in an excellent manner, who described their significance in the field of surface coatings.

In this study, tobacco seed oil was used as a source of a renewable raw material to prepare polyols in combination with various polyhydroxyl compounds. These polyols, in turn, were reacted with stoichiometrically excessive amounts of polyisocyanates to produce isocyanate prepolymers, and a subsequent reaction with a hydroxyl-functional acrylic monomer resulted in urethane acrylate. The urethane acrylate was studied to develop high-performance and environmentally friendly UV-curable coating compositions. The various aspects of their preparation, characterization, curing by UV light, film-per-

formance properties, and so forth are described in great detail.

EXPERIMENTAL

Materials

In this study, crude tobacco seed oil was obtained from Tobacco Research Station of Agriculture University (Anand, India) and was analyzed by gas chromatography; it was found to have the major fatty acid composition of linoleic acid (C_{18:2}), which was about 68.95%, and the physical properties are shown in Tables I and II. Trimethylol propane (TMP; equivalent weight = 44.7, melting point = 60°C, boiling point = 295°C, density = 9.5, specific gravity = 1.14), glycerol (equivalent weight = 30.7, melting point = 18°C, boiling point = 290°C, density = 10.5, specific gravity = 1.26), diethylene glycol (DEG; equivalent weight = 53.1, boiling point = 246°C, density = 9.3, specific gravity = 1.12), and hydroxyethyl methacrylate (HEMA) were obtained from Himalaya Resins (Halol). Toluene diisocyanate (TDI; equivalent weight = 87, melting point = 13.6°C, boiling point = 120°C) and isophorone diisocyanate (IPDI; equivalent weight = 111, boiling point = 153°C) were obtained from Marigold Coating Pvt., Ltd. (V.U. Nagar). Dibutyl tin dilaurate was obtained from Sun Chemicals Industry (Bombay, India); the photoinitiator and reactive diluents were obtained from M/s. Chitichem (Baroda, India). The physical properties of the reactive diluents are shown in Table III.

Methods

Step 1: Synthesis of novel polyols based on tobacco seed oil

Alcoholysis of tobacco seed oil with DEG, glycerin, and TMP was carried out separately in the presence of powdered LiOH with molar ratios of 1 : 0.75, 1 : 1, and 1:2 (oil/polyol) with the following process. The reaction was carried out under a nitrogen atmosphere in a 500-mL, four-necked flask equipped with a thermometer, mechanical stirrer, heating arrangement,

TABLE II
Fatty Acid Composition of Tobacco Seed Oil

No.	Name	C group	Tobacco seed oil	
			Theoretical (%)	Gas chromatography (%)
1	Palmitic acid	C ₁₆	8–11	9.74
2	Stearic acid	C ₁₈	3.2–3.9	3.79
3	Oleic acid	C _{18:1}	10–12	10.54
4	Linoleic acid	C _{18:2}	65–69	68.95
5	Linolenic acid	C _{18:3}	3–5	4.08
6	Arachidic acid	C ₂₀	0.1–0.3	0.23

TABLE III
Physical Properties of the Reactive Diluents and Crosslinkers

No.	Test	2-Ethyl hexyl acrylate	Ethylene glycol dimethacrylate	Trimethylol propane trimethacrylate
1	Physical appearance	Clear, water-white, liquid	Clear, water-white liquid	Clear, water-white liquid
2	Refractive index at 28°C	1.433	1.4522	1.4701
3	Density at 25°C	0.880	1.049	1.061
4	Brookfield viscosity (cPs) at 25°C	5	6	44
5	Flow time (s) at 25°C (FC no. 4)	18	22	45

FC, Ford cup.

Dean–Stark assembly, and condenser. The oil and polyol in a stoichiometric ratio along with the catalyst (LiOH) were charged into the flask and heated to a temperature of 250–260°C. The progress of alcoholysis was checked at regular time intervals, and practically the endpoint was taken as the point at which solubility in alcohol was reached. At this stage, heating was stopped, and the reaction mixture was allowed to cool to room temperature. The reaction scheme explaining this reaction is depicted as Scheme 1. The compositions tried in preparing the series of polyols are described in Table IV. The resulting polyols were characterized with the standard methods.

Step 2: Preparation of the prepolymer isocyanate

A dry four-necked flask (as used in step 1) was placed in a water bath, polyisocyanates (IPDI/TDI) were added, and the temperature of the bath was raised to 40°C with constant stirring; novel polyols (from step 1) were added dropwise through a dropping funnel (within 2 h), and the temperature of the bath was raised to 50–55°C. The reaction was further continued until the desired NCO percentage was obtained (the NCO percentage was determined by the dibutylamine back-titration method⁸). The flask was cooled to room temperature, and the product was made ready for the next step.

Step 3: Preparation of the urethane acrylate oligomer

To a 500-mL, four-necked flask containing the cooled isocyanate-terminated prepolymer prepared previously, a hydroxyl-functional acrylic monomer (HEMA) was added dropwise, and the contents

were stirred for about 1 h at 55°C until the NCO percentage became zero. This yielded the urethane acrylate oligomer. Thus, series of urethane acrylate oligomers were prepared with the compositions listed in Table V. The reaction scheme is shown in Schemes 2 and 3.

Synthesis of the UV-curable coating compositions

A urethane acrylate oligomer was placed in a beaker, and a stoichiometric amount of a reactive diluent and photoinitiator was stirred at room temperature. The amounts of the ingredients used in the aforementioned syntheses were fixed (Table VI), and their physical properties are listed in Table VII.

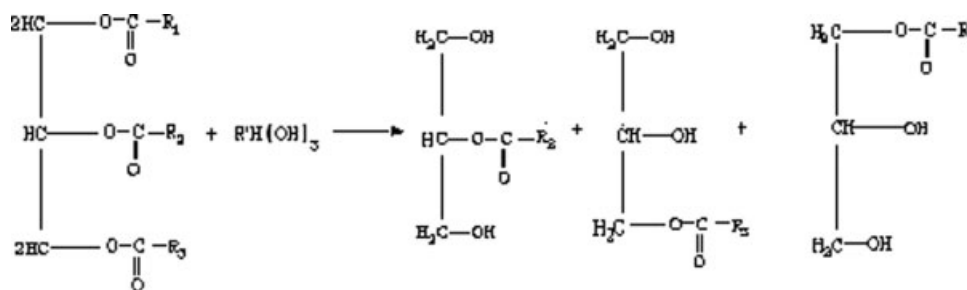
Application and curing of the coating composition

A sample to be irradiated was coated onto MS steel test panels. An excess of the sample was placed at one end of the substrate and, with a rod applicator, was drawn across the substrate, with even pressure pushing excess material off the edge. This method produced coatings with a thickness of 23–26 μm.

For UV curing, an instrument at Shrirama Multi-tech, Ltd. (Ahmedabad, India), was used. The assembly was equipped with two 12-in. medium-pressure mercury arc lamps and a variable-speed conveyer (50–500 ft/min). Only one lamp was used at a time in the testing (operated at 200 W/in.).

Coating evaluation

The coatings were evaluated within 1 h after irradiation. The coatings were examined for various mechani-



Scheme 1 Alcoholysis of a triglyceride.

TABLE IV
Compositions and Characterization of Novel Polyols Based on Tobacco Seed Oil

No.	Description code ^a	Polyol type	Oil : polyol ratio	OH value	Color	Viscosity at 30°C	OH value	Specific gravity	Iodine value
1	DT-1	DEG	1 : 0.75	77.20	10	200	76.3	0.94	126
2	DT-2		1 : 1	102.64	10	225	102.0	0.95	125
3	DT-3		1 : 2	192.47	10	225	189.1	0.97	128
4	GT-1	Glycerin	1 : 0.75	121.22	11	250	112.7	0.94	121
5	GT-2		1 : 1	159.22	11	250	147.3	0.95	125
6	GT-3		1 : 2	299.02	11	275	279.8	0.96	128
7	TT-1	TMP	1 : 0.75	119.2	12	200	113.3	0.98	127
8	TT-2		1 : 1	155.97	12	200	154.1	0.98	128
9	TT-3		1 : 2	282.39	12	225	279.5	0.99	125

^a Initial D = DEG; initial G = glycerin; initial T = TMP; final T = tobacco seed oil.

cal properties such as adhesion, flexibility, impact resistance, and scratch hardness according to ASTM D 3359-97a, ASTM D 0522-93, and ASTM 2197. The impact resistance of the dried films was checked with a tubular impact tester. The results are reported in Table VIII. The films were also evaluated for their chemical, corrosion, and solvent resistance with the methods of characterization described in the literature.⁹ The results of the film characterization are reported in Table IX.

RESULTS AND DISCUSSION

Physical characteristics of the novel polyols

Color and clarity

The liquid novel polyols derived from tobacco seed oil are a little darker than their parent oils. This may be due to partial oxidation of fatty acid components during the hydrolysis reaction.¹⁰

Viscosity

The viscosity of the liquid novel polyols derived from tobacco seed oil can be compared and visualized on the basis of hydrogen bonding and the number of free hydroxyl groups. The hydroxyl values of DT-3, GT-3, and TT-3 (Table IV) are higher than those of other description codes, and this is mainly due to their tendency to form intermolecular hydrogen bonding in comparison with the corresponding ones. At the same time, because TMP is slightly bulkier than glycerin and DEG, it also affects the tendency of hydrogen bonding of these compounds.

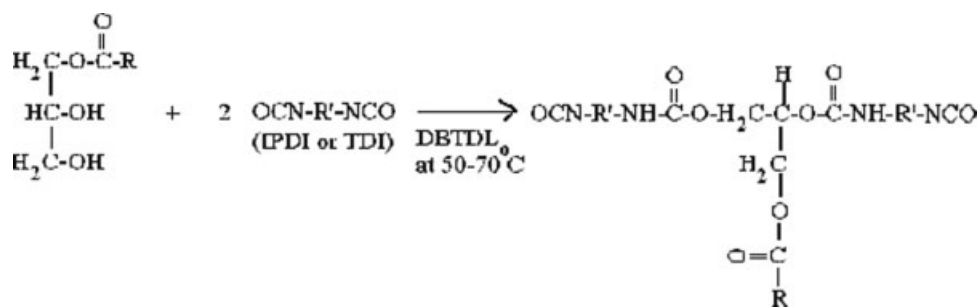
Hydroxyl values

The hydroxyl values of the entire range of novel polyols prepared have been experimentally determined, and the results are reported in Table IV. The tobacco

TABLE V
Compositions of Urethane Acrylates

No.	Description code ^a	Polyol type	Oil : polyol ratio	OH value	OH equivalent	NCO (%)	NCO (equiv)	Composition (wt %)			
								Oil	Polyol	Diisocyanate	HEMA
1	DT-1 ar	DEG	1 : 0.75	77.20	726.64	4.66	900.64	64.87	5.63	16.88	12.62
2	DT-1 al			77.20	726.64	4.22	948.64	68.98	5.37	20.58	12.07
3	DT-2 ar		1 : 1	102.64	546.57	5.82	720.57	57.60	6.66	20.46	15.28
4	DT-2 al			102.64	546.57	5.46	768.57	54.54	6.30	24.70	14.46
5	DT-3 ar		1 : 2	192.47	291.47	9.02	465.47	39.74	9.20	29.22	21.84
6	DT-3 al			192.47	291.47	8.17	513.47	36.78	8.51	34.50	20.20
7	GT-1 ar	Glycerin	1 : 0.75	121.22	462.79	6.59	636.79	56.08	4.27	22.70	16.95
8	GT-1 al			121.22	462.79	6.13	684.79	52.78	4.02	27.25	15.95
9	GT-2 ar		1 : 1	159.78	351.11	8.00	525.11	48.65	4.95	26.55	19.85
10	GT-2 al			159.78	351.11	7.33	513.11	45.34	4.60	31.58	18.48
11	GT-3 ar		1 : 2	299.02	187.62	11.61	361.62	31.72	6.44	35.40	26.44
12	GT-3 al			299.02	187.62	10.25	409.62	28.90	5.88	41.14	24.08
13	TT-1 ar	TMP	1 : 0.75	119.2	470.6	6.51	644.60	54.74	6.02	22.46	16.78
14	TT-1 al			119.2	470.6	6.06	692.60	51.55	5.65	26.98	15.82
15	TT-2 ar		1 : 1	155.97	359.69	7.87	533.69	47.28	6.92	26.22	19.58
16	TT-2 al			155.97	359.69	7.22	581.69	44.10	6.44	31.20	18.26
17	TT-3 ar		1 : 2	282.39	198.65	11.27	372.65	30.58	8.94	34.62	25.86
18	TT-3 al			282.39	198.65	9.98	420.65	27.90	8.16	40.34	23.60

^a Initial D = DEG; initial G = glycerin; initial T = TMP; final T = tobacco seed oil; ar = TDI; al = IPDI.



Scheme 2 Preparation of a prepolymer isocyanate.

seed oil based novel polyols, with an increase in the hydroxyl group content, show an increase in their hydroxyl values. At the same time, in almost all the polyols synthesized, the experimental hydroxyl values are slightly lower than the theoretically calculated values. This can be attributed to the following factors:

1. There may be a possibility of a side reaction such as etherification of the polyols under the conditions of processing.¹¹
2. The polyols may have undergone an addition reaction with carbon-carbon double bonds to produce a hydroxyl acid.¹²

These side reactions would consume hydroxyl groups without a loss of carboxyl groups. This might result in the reduction in experimental hydroxyl values.

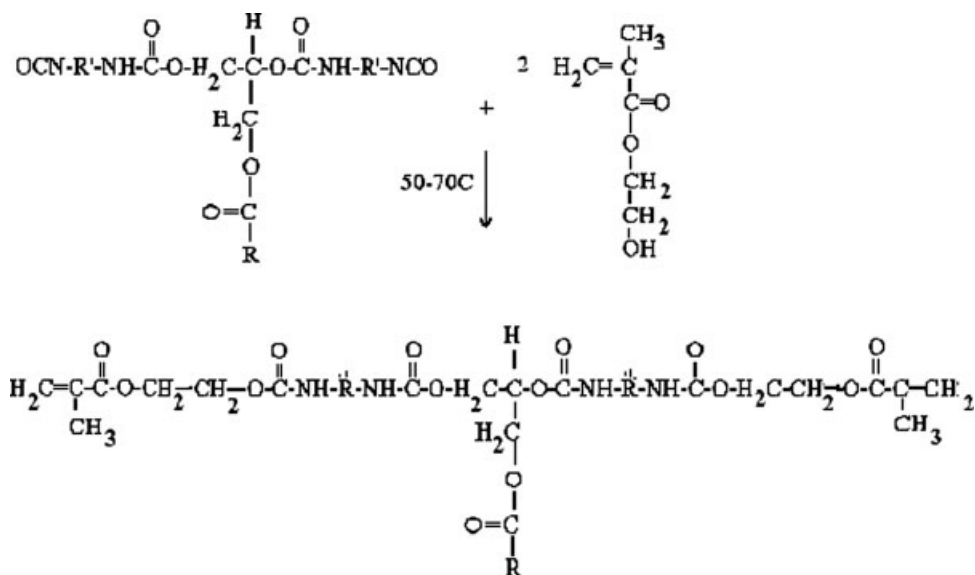
Iodine value

From the results for the iodine values of all the liquid polyols, it appears that the degree of unsatura-

tion of fatty acid chains is not significantly altered. On the basis of the iodine values of the corresponding oil, it has been found to be very close to the experimentally determined value (Table IV). These results are consistent with the proposed mechanism for the polymerization of alkyds,¹³ in which the unsaturation of fatty acids is not believed to be taking part in the reactions. The unsaturated fatty acid system might have undergone polymerization to form a dimer by a mechanism suggested by Harrison et al.¹⁴ However, such a reaction would not occur at the lower processing temperature, in the absence of any catalyst, or in the inert atmosphere.

Gas chromatography

The oils used for this work were characterized for their fatty acid composition with gas chromatography. The chromatograms of tobacco seed oil are shown in Figure 1. The fatty acid composition of the oil used in this work is shown in Table II, which reveals that tobacco seed oil has the highest linoleic



Scheme 3 Preparation of a urethane acrylate oligomer.

TABLE VI
Composition of the UV-Curable Coatings

No.	Ingredient	wt %	Function
1	Urethane acrylate	65.00	Oligomer
2	2-Ethyl hexyl acrylate	20.00	Reactive diluent
3	Ethylene glycol dimethacrylate/trimethylol propane trimethacrylate	10.00	Crosslinking monomer
4	Benzophenone	3.50	Photoinitiator
5	DMEA	1.50	Activator/catalyst
	Total	100.00	

DMEA, dimethyl ethanol amine.

acid (C_{18:2}) content (68.95%) and oleic acid (C_{18:1}) content (10.54%).

Infrared (IR) spectral study

Figure 2 presents the IR spectra of nontraditional vegetable oil (tobacco seed oil) and a polyol derived from it. The peak at 3400 cm⁻¹ is sharper and longer in the polyol than in the parent oil, and this confirms the presence of free hydroxyl groups upon the alcoholysis of the oil with the polyhydroxyl compound. The peak at 1750 cm⁻¹ also becomes sharper and longer in the polyol than in the oil, and this also confirms the alcoholysis (transesterification) reaction of the oil with the polyhydroxyl compound. The strong and sharp band at 1150 cm⁻¹ can well be assigned to C—O stretching of a secondary —C—OH group along with the band at 1350 cm⁻¹ due to bending of the C—OH group in the polyol. Similarly strong bands at 1050 and 1350 cm⁻¹ can be assigned to O—H bending vibrations and C—O stretching vibrations of primary alcohol groups (—CH₂OH present) in the polyols.

The absorption bands at 1580–1600 cm⁻¹ can be attributed to diene-type unsaturation present in the oil and polyols, and the strong bands at 1700 cm⁻¹ can, of course, be attributed to the carbonyl group of esters. The unsaturation is also confirmed by the presence of —C—H bending vibrations due to the —CH=CH— group at 1420 cm⁻¹ in both the oil and polyols.

Physical characteristics of the urethane acrylate oligomers

The urethane acrylate oligomers prepared as previously discussed are free-flowing liquids similar to a conventional oligomer. Various characteristics of these oligomers have been determined with the standard methods.^{15,16} Thus, properties such as the nonvolatile contents (%), appearance, color and clarity, viscosity [cPs; RV-II viscometer, Brookfield],

and density (wt/ltr) have been determined. The results are reported in Table X.

These urethane acrylates have also been characterized with instrumental methods such as IR spectroscopy (Fourier transform infrared spectrophotometer, Nicolet; Fig. 2) and gel permeation chromatography (GPC) for molecular weight determination (Figs. 3–5).

Color and clarity

All the reported urethane acrylate oligomers based on nontraditional oil are clear and transparent liquids. However, the urethane acrylate oligomers based on nontraditional oil in this study are somewhat darker in color. This could be due to the pres-

TABLE VII
Physical Properties of the UV-Curable Coatings

No.	Description code ^a	Color (Gardner scale)	Viscosity (cPs)	Wt/ltr
1	DTD-1 ar	2	440	1.06
2	DTD-1 al	2	470	1.07
3	DTT-1 ar	2	490	1.07
4	DTT-1 al	3	495	1.07
5	DTD-2 ar	3	630	1.09
6	DTD-2 al	3	500	1.09
7	DTT-2 ar	2	585	1.09
8	DTT-2 al	2	570	1.09
9	DTD-3 ar	2	605	1.11
10	DTD-3 al	3	595	1.11
11	DTT-3 ar	2	635	1.11
12	DTT-3 al	2	655	1.11
13	GTD-1 ar	2	555	1.07
14	GTD-1 al	3	585	1.07
15	GTT-1 ar	3	670	1.07
16	GTT-1 al	3	645	1.07
17	GTD-2 ar	3	611	1.08
18	GTD-2 al	3	600	1.08
19	GTT-2 ar	3	680	1.09
20	GTT-2 al	3	700	1.10
21	GTD-3 ar	2	700	1.10
22	GTD-3 al	2	650	1.10
23	GTT-3 ar	2	740	1.11
24	GTT-3 al	2	685	1.11
25	TTD-1 ar	3	550	1.08
26	TTD-1 al	3	489	1.08
27	TTT-1 ar	2	586	1.08
28	TTT-1 al	2	565	1.08
29	TTD-2 ar	2	650	1.09
30	TTD-2 al	2	600	1.09
31	TTT-2 ar	2	700	1.10
32	TTT-2 al	2	620	1.10
33	TTD-3 ar	2	650	1.11
34	TTD-3 al	2	600	1.11
35	TTT-3 ar	2	950	1.11
36	TTT-3 al	2	820	1.11

^a Initial D = DEG; initial G = glycerin; initial T = TMP; middle T = tobacco seed oil; final D = ethylene glycol dimethacrylate as the crosslinker monomer; final T = trimethylol propane trimethacrylate as the crosslinker monomer; ar = TDI; al = IPDI.

TABLE VIII
Mechanical Properties of the UV-Curable Coatings

No.	Description code ^a	DFT (μm)	Adhesion (crosshatch) ^b	Flexibility (1/8" mandrel) ^b	Scratch hardness	Impact resistance ^b
1	DTD-1 ar	24	P	P	1200	F
2	DTD-1 al	23	F	P	1200	F
3	DTT-1 ar	24	P	P	1300	P
4	DTT-1 al	26	P	P	1200	F
5	DTD-2 ar	26	P	P	1500	P
6	DTD-2 al	25	P	P	1200	P
7	DTT-2 ar	24	P	P	2100	P
8	DTT-2 al	23	P	P	2000	P
9	DTD-3 ar	24	P	P	2000	P
10	DTD-3 al	25	P	P	1800	P
11	DTT-3 ar	27	P	P	2500	P
12	DTT-3 al	26	P	P	2200	P
13	GTD-1 ar	26	P	P	1500	P
14	GTD-1 al	24	P	P	1400	P
15	GTT-1 ar	22	P	P	2200	P
16	GTT-1 al	23	P	P	1600	P
17	GTD-2 ar	24	P	P	2100	P
18	GTD-2 al	26	P	P	1800	P
19	GTT-2 ar	26	P	P	2700	F
20	GTT-2 al	26	P	P	2500	P
21	GTD-3 ar	25	P	P	2600	P
22	GTD-3 al	24	P	P	2400	P
23	GTT-3 ar	27	F	F	3200	F
24	GTT-3 al	26	P	P	2800	F
25	TTD-1 ar	23	P	P	2100	P
26	TTD-1 al	25	F	P	1700	F
27	TTT-1 ar	25	P	P	2800	P
28	TTT-1 al	24	P	P	2500	P
29	TTD-2 ar	26	P	P	3600	P
30	TTD-2 al	24	P	P	3400	P
31	TTT-2 ar	23	P	P	4000	P
32	TTT-2 al	24	P	P	3600	P
33	TTD-3 ar	22	P	P	3900	F
34	TTD-3 al	26	P	P	3500	P
35	TTT-3 ar	25	F	F	4500	F
36	TTT-3 al	27	P	F	4000	F

DFT, dry film thickness.

^a Initial D = DEG; initial G = glycerin; initial T = TMP; middle T = tobacco seed oil; final D = ethylene glycol dimethacrylate as the crosslinker monomer; final T = trimethylol propane trimethacrylate as the crosslinker monomer; ar = TDI; al = IPDI.

^b P = pass; F = fail.

ence of unsaturated fatty acid in the tobacco seed oil, as depicted in the compositions.

Nonvolatile contents

The nonvolatile percentages of all the experimental sets of urethane acrylate oligomers derived from nontraditional oil are in the vicinity of the theoretical values, and the results are reported in Table X. This clearly indicates the absence of any unreacted monomeric compounds as well as the presence of low-molecular-weight degradation products.

Viscosity

The viscosity of the urethane acrylate oligomers derived from nontraditional oil increases as the molar content of the polyol increases from 0.75 to 2

in the case of DEG, glycerin, and TMP. This may be due to the higher molecular weight¹⁷ of the oligomers present in the prepared sets. This is also supported by GPC chromatogram (Figs. 3–5), in which, as we go from lower (1 : 0.75) to higher (1 : 2) oil/polyol ratios, the weight-average molecular weight increases from 2000 to 3650. This could be due to increased interaction between the oil and polyol.

IR spectroscopy

Representative IR spectra of the urethane acrylate oligomer series based on nontraditional oil are shown in Figure 2. In all the spectra, the —N—H stretching and bending vibration of the urethane linkage can be observed at 3380–3300 and 1550–1500 cm⁻¹, respectively. In the spectrum, bands at 2950–

TABLE IX
Chemical Resistance, Corrosion Resistance, and Solvent Resistance

No.	Description code ^a	5% H ₂ SO ₄ for 7 days ^b	5% NaOH for 7 days ^b	5% NaCl for 7 days ^b	MEK double rub
1	DTD-1 ar	3	3	3	40
2	DTD-1 al	4	4	3	45
3	DTT-1 ar	4	4	4	45
4	DTT-1 al	4	4	4	55
5	DTD-2 ar	4	4	4	55
6	DTD-2 al	4	4	5	60
7	DTT-2 ar	4	5	5	70
8	DTT-2 al	5	5	5	85
9	DTD-3 ar	4	5	4	95
10	DTD-3 al	4	5	5	95
11	DTT-3 ar	5	5	4	95
12	DTT-3 al	5	5	5	95
13	GTD-1 ar	3	3	4	50
14	GTD-1 al	3	4	4	55
15	GTT-1 ar	3	4	4	65
16	GTT-1 al	4	5	4	70
17	GTD-2 ar	4	5	4	75
18	GTD-2 al	5	5	5	75
19	GTT-2 ar	5	5	4	85
20	GTT-2 al	5	5	5	85
21	GTD-3 ar	5	5	5	95
22	GTD-3 al	5	5	5	100
23	GTT-3 ar	5	5	5	100
24	GTT-3 al	5	5	5	100
25	TTD-1 ar	3	3	3	60
26	TTD-1 al	3	3	4	60
27	TTT-1 ar	4	5	5	80
28	TTT-1 al	5	4	4	80
29	TTD-2 ar	4	4	5	90
30	TTD-2 al	5	5	5	100
31	TTT-2 ar	4	5	5	100
32	TTT-2 al	5	5	5	90
33	TTD-3 ar	4	5	5	95
34	TTD-3 al	5	5	5	95
35	TTT-3 ar	5	5	5	120
36	TTT-3 al	5	5	5	120

MEK, methyl ethyl ketone.

^a Initial D = DEG; initial G = glycerin; initial T = TMP; middle T = tobacco seed oil; final D = ethylene glycol dimethacrylate as the crosslinker monomer; final T = trimethylol propane trimethacrylate as the crosslinker monomer; ar = TDI; al = IPDI.

^b 1 = complete lifting of film; 2 = film softening and rust spot observed; 3 = severe blistering; 4 = very slight blistering; 5 = not affected.

2850 and 1470–1430 cm⁻¹ can be observed that are due to the —C—H stretching vibration of the alkane chain in the oil. The sharp bands at 1710–1730 cm⁻¹ reveal the presence of an ester group. The unsaturation present in each can be clearly seen by the sharp —C=C— stretching absorption at 1640 cm⁻¹ and by the out-of-plane =C—H bending vibration at 900 and 1010 cm⁻¹. The additional band at 770–815 cm⁻¹ confirms the presence of double bonds (—C=CH—). The disappearance of the band in this frequency region is evidence for the extent of curing.

Number-average and weight-average molecular weights

The GPC scans of urethane acrylate oligomers of different molar ratios are shown in Figures 3–5. Two

peaks can be observed in the chromatographs, indicating two polymeric moieties in the system. This may be due to the formation of urethane acrylate and the thermal polymerization of the oil during its synthesis. The weight-average molecular weight of the oligomers was found to be in the range of 2000–3650 g/mol, as expected in a typical system having an oil, polyol, isocyanate, and hydroxyl-functional monomers.

Performance properties of the UV-curable coating compositions

Thermal properties [thermogravimetric analysis (TGA)]

Figure 6 shows the TGA thermograms of cured films of the tobacco seed oil derivatives. The TGA thermo-

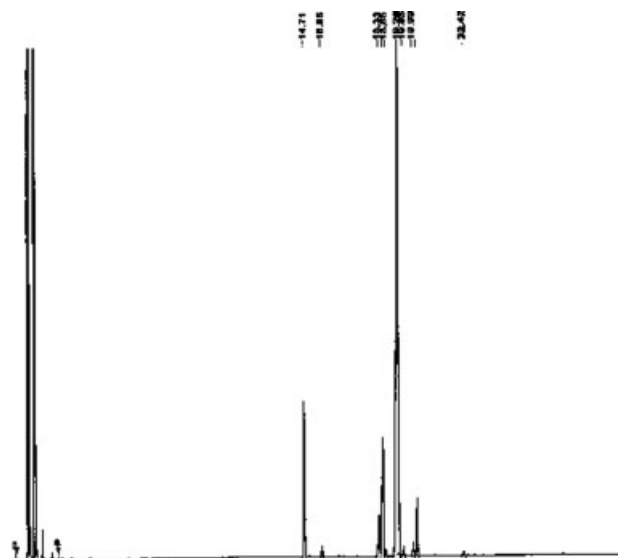


Figure 1 Gas chromatography of tobacco seed oil.

grams clearly indicate good thermal stability for the cured films up to 100°C with only minimum weight loss, which may be due to some unreacted components. The TGA thermograms also indicate that degradation occurs in three steps. In the first step, degradation through a urethane linkage may be occurring, leaving partially crosslinked products, and finally this cured product degrades completely at a slow rate in the third stage. The entire thermograms show a trend similar to that typically reported for such compositions.¹⁸

Adhesion and flexibility

Adhesion and flexibility are the most important characteristics of all coatings. To function effectively and satisfactorily, the surface coatings must adhere well and should not be affected by any mechanical abuse. The results of flexibility and adhesion shown in Table VIII reveal the excellent performance of most of the experimental batches based on tobacco seed oil. The compositions DTD-1 ar, DTD-1 al, GTT-3 ar, TTD-1 al, and TTT-3 ar, based on tobacco seed oils, showed poor performance. This can be attributed to the lower oil ratio, higher functionality of polyol, and aromatic type of isocyanate.¹⁹ The higher extent of adhesion and flexibility reveals that most of the experimental sets showed satisfactory performance.

Impact resistance

The results for impact resistance showed similar trends in all the aforementioned experimental sets. The reason for satisfactory impact resistance can be assigned to the inclusion of oil in the dry film.

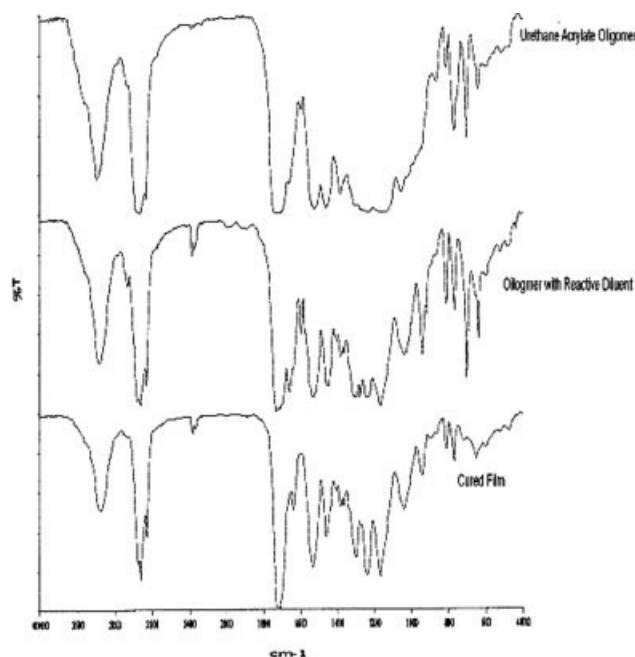


Figure 2 IR spectra of the oligomer, coating composition with a reactive diluent, and cured film.

The long fatty chain, having a greater number of carbon atoms, contributes to the good flexibility and impact resistance of the cured films.

Scratch hardness

The results for scratch resistance are shown in Table VIII for tobacco seed oil. In the case of dry film formation by UV-light curing, the unsaturation present

TABLE X
Physical Properties of Urethane Acrylate

No.	Description code ^a	Color	Specific gravity	Solids (%)	Viscosity
1	DT-1 ar	16	1.02	99.50	1275
2	DT-1 al	14	1.02	98.70	1450
3	DT-2 ar	14	1.03	98.85	2540
4	DT-2 al	13	1.03	99.35	2165
5	DT-3 ar	12	1.05	99.60	3574
6	DT-3 al	10	1.05	99.87	3289
7	GT-1 ar	15	1.03	98.95	3175
8	GT-1 al	15	1.03	98.25	3086
9	GT-2 ar	13	1.04	99.24	4125
10	GT-2 al	13	1.04	98.15	4015
11	GT-3 ar	12	1.05	99.57	4700
12	GT-3 al	10	1.06	98.64	4250
13	TT-1 ar	14	1.03	98.69	2960
14	TT-1 al	14	1.05	99.98	2575
15	TT-2 ar	13	1.05	99.75	3975
16	TT-2 al	13	1.06	99.60	3800
17	TT-3 ar	10	1.06	99.45	5270
18	TT-3 al	10	1.06	98.74	4965

^a Initial D = DEG; initial G = glycerin; initial T = TMP; final T = tobacco seed oil; ar = TDI; al = IPDI.

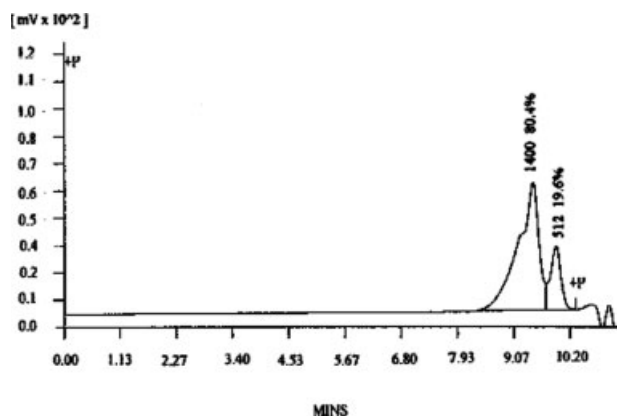


Figure 3 GPC of an oligomer (1 : 0.75).

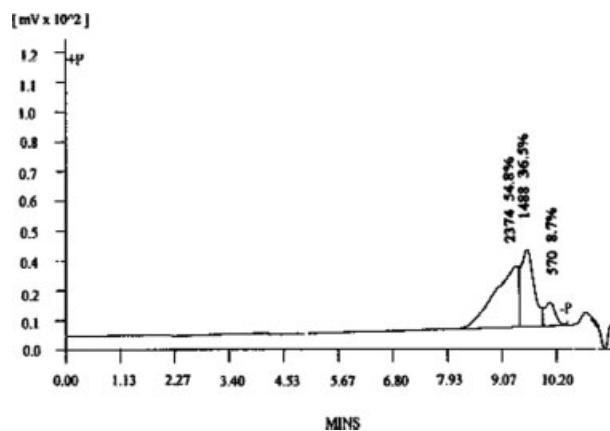


Figure 5 GPC of an oligomer (1 : 2).

in the oil also participates in improved crosslinking via the double bond of fatty acid. This leads to better homogeneity, better film integrity, and better packing of the polymer chains. Also, the aromatic nature of the isocyanate moiety further enhances the film hardness and toughness. Thus, the experimental sets based on a higher functionality polyol (TMP), a higher functionality acrylate reactive diluent, and a lower proportion of oil gave better scratch hardness. This can be seen in the results for TTT-3 ar and TTT-3 al. This can be attributed to their differences in terms of the iodine value.

Chemical resistance and solvent resistance

The results for chemical and solvent resistance, as shown in Table IX, are quite encouraging in terms of cured coating performance. The higher crosslinking density in the respective experimental sets showed improved solvent and chemical resistance of the cured films. Also, the acid and alkali resistance of the films based on a lower proportion of oil showed

better results. This could be due to lower ester linkages that are vulnerable to acid and alkali attack. Thus, a greater number of polyurethanes imparts better chemical resistance.²⁰

IR spectroscopy

The IR spectra were scanned for monitoring the presence of unsaturations in the resin (due to acrylate groups) and for their utilization during UV radiation to produce cured coating films. The disappearance of the band in the $815\text{--}770\text{-cm}^{-1}$ frequency region was monitored for the extent of curing. The band intensity increased as the urethane acrylate resin was mixed with reactive diluents (Fig. 2), and

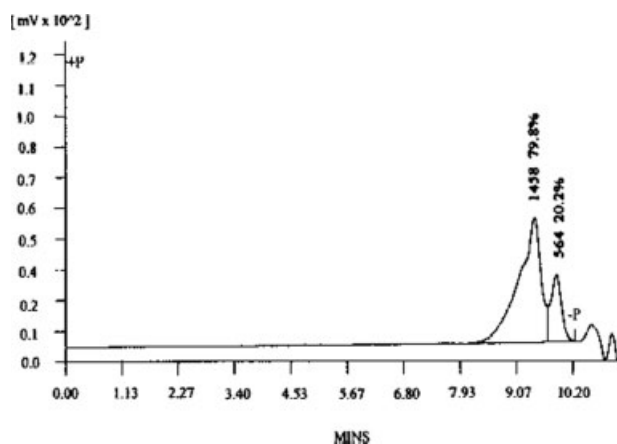


Figure 4 GPC of an oligomer (1 : 1).

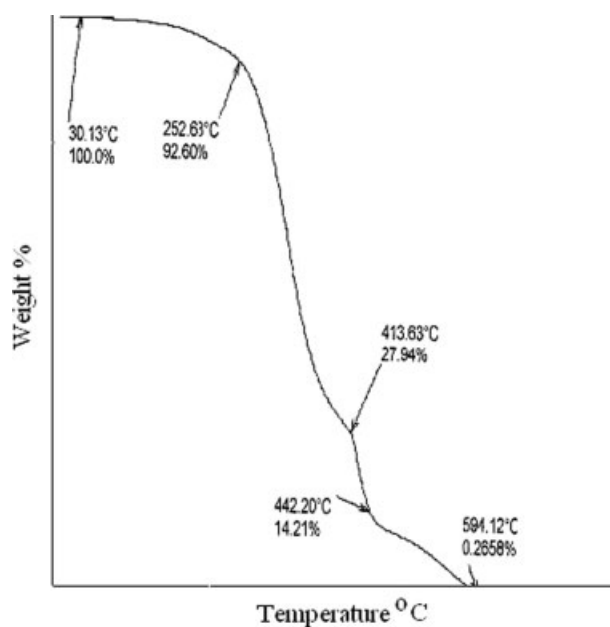


Figure 6 TGA scan of a cured film based on tobacco seed oil (TTT-3 ar).

after the irradiation of the coating compositions with UV light, the intensity decreased significantly, as shown in the IR spectrum of the cured film (Fig. 2). This observation clearly confirms the participation of reactive diluents in the curing of the film.

CONCLUSIONS

UV-curable coatings based on novel polyols from renewable resources such as tobacco seed oil have been prepared satisfactorily and show good curing characteristics. The physicochemical properties of the urethane acrylate oligomers as well as the final coating compositions containing a reactive diluent and photoinitiator are in good agreement with the currently used equivalent polyester and epoxy as well as urethane acrylates. The instrumental analysis has confirmed the satisfactory synthesis of urethane acrylates and coating compositions. As these compositions do not contain volatile organic solvents, which contribute to VOCs, the resulting coatings are ecofriendly and meet the legislative requirements of the various regulatory authorities in the field of surface coatings. The performance of the cured films confirms their successful curability in the presence of a photoinitiator (benzophenone) and UV-light source. Also, the results of the cured films lead us to conclude that these UV-curable urethane acrylate coatings have potential for high-performance, ecofriendly industrial coating applications.

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