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ORIGINAL PAPER

Synthesis and Characterization of Canola Oil Alkyd Resins Based on Novel Acrylic Monomer (ATBS)

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Abstract A water-reducible alkyd resin was synthesized using the renewable resource canola oil and then chemically modified with styrene and the novel monomer acrylamido tertiary butane sulfonic acid (ATBS). Infrared spectroscopy and nuclear magnetic resonance techniques were used for structural elucidation of newly synthesized resins. Analyses of their physico-chemical and thermal properties revealed that styrene and ATBS-grafted water-reducible polymers have better thermal, chemical and coating properties than canola oil alkyd resins.

Keywords Polymers · Coatings · Biobased products

Introduction

During the past decade, there has been an increasing demand by the Environmental Protection Agency (EPA) to reduce the emission of volatile organic components (VOC). This has prompted researchers to develop environmentally friendly coatings with low VOC or to use water as a solvent [1]. Aliphatic and aromatic solvents are used in the synthesis and dilution of alkyd resins. Several attempts have been made to modify alkyd resins to make them VOC compliant. However, the gloss performance of conventional alkyd resins could not be achieved with modified alkyd resins. High solid alkyd resins have economic and technical benefits, such as improved hiding power with significant reductions in cost. However, their use in the coating industry has been constrained because of their high viscosities [2, 3]. One attractive approach to overcome this problem was to produce resins with high acidic values (>40 mg of KOH/g). However, this resulted in low molecular weight resins with unsatisfactory properties such as slow drying (caused by amines, which are used to neutralize the carboxylic acid groups to produce a water-reducible binder [4]. Modification of alkyd resins by acrylic monomers confers durability and general resistance properties and also enhances the application and film forming properties of conventional alkyd resins. Solomon [5] suggested that acrylation should proceed either by condensation or by grafting monomers onto the alkyd resin. Most of the industrial demand for polymeric resins depends upon petroleum feedstock. However, the price of oil has significantly increased over the years, and this non-renewable source of energy is rapidly moving toward complete exhaustion. Consequently, for more than a decade, the use of renewable resources with plant origins has gained importance in the surface coating industry.

Traditional seeds like soybean, rice bran, sunflower and castor oils have already been commercially explored for the synthesis of alkyd resins [6]. However, few attempts have been made with canola oil in the field of polymers [7]. Canola oil is extracted from *Brassica campestris* (*Brassica napus* L. and *B. campestris* L.). Because it has lower erucic acid content than traditional rapeseed oil and low glucosinolate (toxin) percentages, canola oil is suitable for human consumption and for livestock feed production. Another product, known as LEAR (low erucic acid rapeseed), was derived from the cross-breeding of *Brassica juncea* and is also referred to as canola oil (CO) [8]. In the present work, canola oil was used for the synthesis of alkyd resin (COA). To combine the technical benefits of alkyd and acrylic resins, canola oil alkyd was grafted with styrene monomer. The newly synthesized styrenated COA

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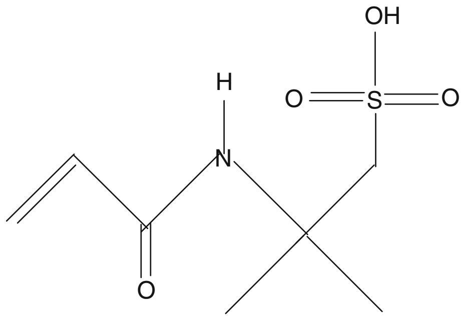

Fig. 1 Chemical structure of acrylamido tertiary butane sulfonic acid (ATBS)

was further modified by partial and complete replacement of styrene with different weight ratios of the novel anionic acrylic monomer acrylamido tertiary butane sulfonic acid (ATBS). The acrylic monomers, [9, 10] introduced onto the backbone of the alkyd resin, improved coating properties such as weatherability, chemical resistance and hardness. Therefore, they are the most attractive polymers to be incorporated onto the backbone of alkyd resins. ATBS is a novel monomer with a wide spectrum of properties, including its hydrogen-bonding capability and polyelectrolyte behavior in aqueous solutions. It is a relatively strong acid that has broad applications, which include packaging films, foam stabilizers, photographic materials and water absorbents. The shielding effect produced from the unique geminal dimethyl structure of ATBS offers excellent hydrolytic stability to newly synthesized polymer resins [9–13]. Figure 1 illustrates the structure of ATBS, and Table 1 lists its technical parameters. The primary objective of this paper was to synthesize water-reducible canola oil alkyd (COA) using the novel versatile anionic crosslinkable monomer, ATBS. The sulfonic group of ATBS was neutralized with an amine to impart water solubility. Considering the current importance of renewable resources, it is highly desirable to achieve a much better understanding of the role of canola oil and ATBS in water-reducible alkyd resins.

Experimental

Materials

Canola oil was supplied by V.V. Anand & Co, Erode, Tamil Nadu, India.

Glycerol, phthalic anhydride, maleic anhydride, triethylamine (TEA), and azobisisobutyronitrile (AIBN) were procured from S. D. Fine Chemicals, Mumbai. All the chemicals used in the present work were of AR grade. Styrene was supplied by Fluka. Acrylamido tertiary butane sulfonic acid (ATBS) was provided by Vinati Organics Ltd., Mumbai. The physico-chemical properties and fatty acid composition of canola oil are displayed in Tables 2 and 3, respectively.

Table 1 Technical parameters of acrylamido tertiary butane sulfonic acid (ATBS)

Parameters	Specifications
Appearance	White powder
Nonvolatile matter	99.0% Min.
Moisture	0.30% Max.
Color apha (25% Aq. Solution)	100 Max

Table 2 The physico-chemical properties of canola oil

	Refined Canola oil
Odor	–
Color	Pale yellow
Iodine value	115.0
% Free fatty acid	0.1
Saponification no	192.0
% Unsaponified matter	0.9
Specific gravity	0.99

Synthesis of Canola Oil Alkyd Resin (COA)

A resin reactor equipped with thermometer, mechanical stirrer, Dean-Stark apparatus and nitrogen gas inlet was charged with canola oil and glycerol (as per the formulation given in Table 4). Calcium octoate was used as a catalyst (0.01% w/w based on oil). The temperature was slowly raised to 240 °C and maintained until the monoglycerides were formed, which was confirmed with a methanol test [14].The reaction temperature was brought down to 120 °C, and the required amount of phthalic anhydride and maleic anhydride were added to the reactor. The batch was further processed at 220 °C for 8–10 h. The reaction was continued until the acid value decreased below 10 mg of KOH/g.

Grafting of Alkyd Resin

A three-necked round-bottom flask equipped with a thermometer, condenser, and mechanical stirrer was charged with COA, styrene and ATBS (Table 5). AIBN was used as an initiator (0.1% of the weight of COA), and the reaction mixture was heated at 60 °C for 1 h [15]. The reaction temperature was maintained at 60 °C for an additional 0.5 h to ensure reaction completion between novel monomer and styrene. The ATBS grafted COA was neutralized

Table 3 Fatty acid composition of canola oil

	Refined canola oil[a] (%)
C16 Palmitic acid	4.5
C18 Stearic acid	1.5
C20:0 Arachidic acid	0.5
C22:0 Behenic acid	0.5
C16:1 Palmitoleic acid	0.5
C18:1 Oleic acid	57.0
C18:2 Linoleic acid	21.5
C18:3 Linolenic acid	10.0
C20:1 Gadoleic acid	2.0
Others	1.5
Total	100.0

[a] Ref. 7

Table 4 Composition and properties of canola oil alkyd resin

Ingredients	Weight (g)
Canola oil	110
Glycerol	38.2
Phthalic anhydride	59
Maleic anhydride	1.23
Xylene	80
Resin properties	
Solid content (%)	69.2
Acid value (mg of KOH/g)	8.34

Table 5 Composition of ATBS/styrenated COA

Ingredients	Weight (g)				
	S1	S2	S3	S4	S5
COA (70%)	100	100	100	100	100
Styrene	40	20	10	5	–
ATBS	–	20	30	35	40
TEA	–	1.0	1.1	1.2	1.4

S1 = 100% styrenated canola oil alkyd resin
S2 = 50:50 (Styrene:ATBS) canola oil alkyd resin
S3 = 25:75 (Styrene:ATBS) canola oil alkyd resin
S4 = 12.5:87.5 (Styrene:ATBS) canola oil alkyd resin
S5 = 100% ATBS canola oil alkyd resin

using a stoichiometric amount of triethylamine. This was followed by the addition of distilled water (50% w/w).

Film Preparation

The newly synthesized water-reducible polymers were coated onto mild steel and glass panels, using a bar coater ("sheen" make) of 50 microns. The coated panels were allowed to dry at room temperature for a week before testing.

Characterization

^{1}H NMR

^{1}H-NMR spectra of styrenated COA and ATBS-styrenated COA were recorded using a Bruker 300 MHz NMR spectrophotometer at ambient temperature. Deuterated chloroform was used as the solvent.

FTIR

IR spectra of ATBS, styrenated COA and ATBS-styrenated COA were recorded using a Perkin Elmer instrument (spectrum one) in the range of 400–4,000 cm^{-1}. Samples were dissolved in carbon tetrachloride and placed on sodium chloride pellets to record IR spectra.

Pencil Hardness

A relative measurement of hardness was performed by rating the hardness of lead pencils as per ASTM D3363-92a.

Scratch Hardness Test

Scratch hardness was determined using a scratch hardness tester with a hardened steel hemispherical needle point 1 mm in diameter, according to ASTM D 5178.

Adhesion

A cross-cut adhesion test was performed as per ASTM D-3359-95a. The samples were coated on mild steel panels and cut into squares of 1 mm × 1 mm using a crosshatch tester ("sheen make"). Adhesive tape was applied on the cross-cut section and firmly rubbed with finger tips and stripped off after 1 min. The number of squares intact gives a measure of adhesion of the sample.

$$\text{Adhesion (\%)} = \frac{\text{Numberofsquaresintactinthetapeappliedarea}}{\text{Total Number of squares in the tape applied area}} \times 100$$

Flexibility

Flexibility is related to elongation and can be measured using a conical mandrel (1/4″), as per ASTM D 522-399. In order to check flexibility, samples coated on tin plates were tested using the conical mandrel and examined visually for cracks in the films.

Impact Resistance

Impact resistance was measured using a falling weight type impact tester (Komal Scientific, Mumbai, India), as per ASTM D2794A.

Water Resistance

Glass panels coated with samples were allowed to dry for a week. Wax was applied on the edges in order to prevent the penetration of water under the film from the open ends. The panels were immersed in water and examined for changes in appearance after 24 h.

Chemical Resistance

Glass panels coated with samples were immersed in 2% w/w sulfuric acid, 2% w/w sodium hydroxide and 5% w/w sodium chloride solutions. Changes in the appearance of the films were noted after 24 h.

Solvent Resistance

The solvent resistance test was carried out as per the "Double Rubs" method, using a piece of white cotton cloth (ASTM D1308). The solvents used were methyl ethyl ketone and toluene. The results reported were the maximum number of double rubs at which the film detached from the surface.

Thermogravimetric Analysis

The decomposition profiles of COA, styrenated COA and ATBS-styrenated COA were thermogravimetrically analyzed using a 'Diamond' Perkin Elmer analyzer. Film samples ranging from 4 to 5 mg were placed in a platinum sample pan and heated 30–900 °C under a N_2 atmosphere, at a heating rate of 10 °C/min.

Results and Discussion

The specific gravity of canola oil is same as that of other vegetable oils, indicating that there are no heavy elements present in the oil. The iodine value of canola oil (115.0) indicates that it is a nondrying oil.

^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectrum of ATBS showed the following signals: 1.422 ppm (s, 6H,–2CH_3), 2.996 ppm (s, 2H, –CH_2), 6.10 ppm (m, 2H, –CH_2) and 8.2 ppm (s, 1H, NH). The APUD revealed peaks in the range of 1.83–1.88 ppm, which can be attributed to the hydrogens in the main chain. The CH_2 group bonded to the sulfonic acid showed a signal at 3.8 ppm. Figures 2 and 3 show the ^{1}H-NMR spectra of styrenated COA and ATBS-styrenated COA (S2 50:50), respectively. The signal assignments are listed in Table 6. The peak at δ 0.9–0.998 ppm corresponds to the terminal methyl groups of the fatty acids. The huge peak at δ 1.2–1.29 ppm originates from the methylene groups [16, 17] surrounded by single-bonded carbon atoms (–CH_2–). The acylglycerol with one proton appeared to overlap with the olefinic signal at about δ 5.25 ppm. On the other hand, the signals of the four protons from the two acylglycerol (–CH_2OCOR) units appear at δ 4.1 and 4.3., respectively [18, 19].The middle range of the proton spectra (δ 3.3–6.6) contains peaks from the vinyl protons of the fatty acids

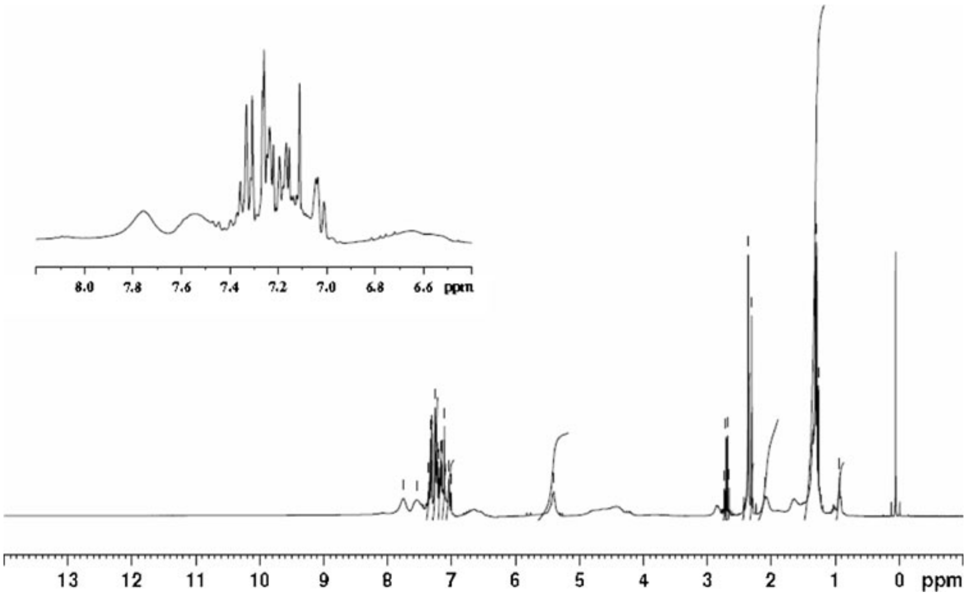

Fig. 2 ^{1}H-NMR spectrum of styrenated canola oil alkyd

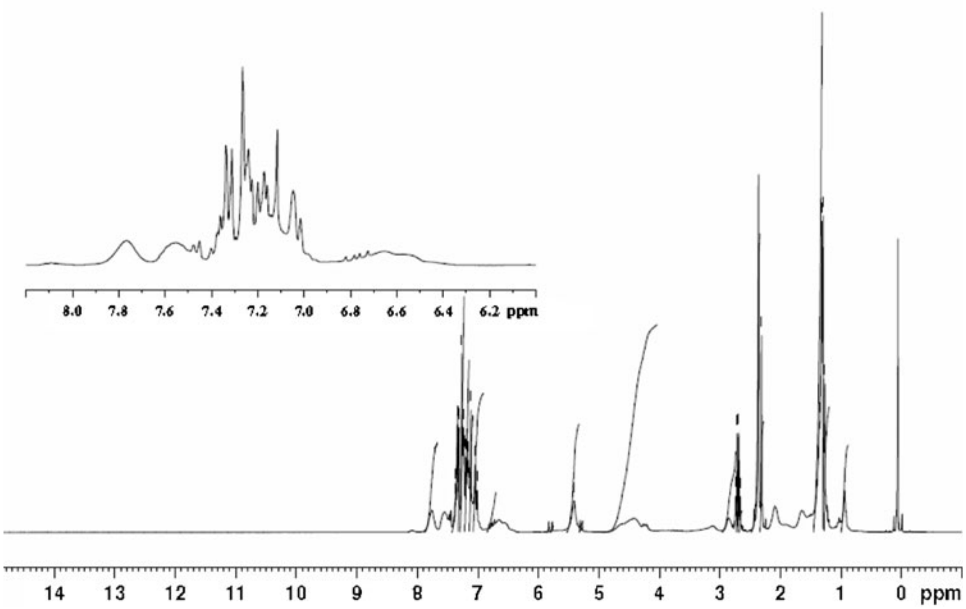

Fig. 3 ^{1}H-NMR spectrum of ATBS-styrenated canola oil alkyd

(FA) incorporated onto the alkyd resins (δ 5.3) and from the protons of neighboring hydroxyl or ester groups. The absence of peaks in the range of 5.3–6.1 ppm confirms the grafting of the vinyl group of ATBS onto COA. The peaks in the range of δ 7.2–7.7 ppm correspond to aromatic protons originating from styrene, phthalic and maleic ester fragments of the polyester [18, 19].

FTIR

Figure 4 represents the FTIR spectra of ATBS, COA and ATBS-styrenated COA (S2 50:50). In the IR spectrum of ATBS, the band corresponding to the OH group in sulfonic acid appears at 2,946 cm^{-1}. The band at 1,614 cm^{-1} is due to the C=C stretching vibration of the vinyl group. Doublets are observed at 1,373 cm^{-1} for geminal dimethyl groups. The band at 924 cm^{-1} is due to methyl rocking vibration. In addition to these typical bands for sulfonic acid (SO_2), asymmetric and symmetric bands were observed at 1,248 and 1,077 cm^{-1}, respectively. The sharp bands arising from 1,000 to 900 cm^{-1} are due to =C–H wagging in the vinyl group of ATBS. The bands at 2,932 and 2,859 cm^{-1} can be attributed to asymmetric and symmetric stretching modes of CH_3 and CH_2 groups, respectively. In the case of ATBS-styrenated COA, the band in the range of 1,600–1,400 cm^{-1} became weak, which confirms the grafting of ATBS on alkyd resin. The weak absorption band at 1,180 cm^{-1} can be attributed to SO_2 stretching vibrations, which also confirms the grafting of ATBS onto the alkyd resin. It is worth noting that the effectiveness of the reaction between the monomers can be confirmed by the absence of the characteristic band of vinyl monomers, due to C=C at 978 cm^{-1} [10, 11].

Coating Properties

As canola oil is nondrying, its coating properties cannot be analyzed.

Pencil Hardness

Table 7 reveals that the hardness of water-reducible alkyd resins increased with an increase in ATBS content. The presence of acrylic monomer contributes to the toughness of the resin. Maximum pencil hardness value is achieved in the case of 100% ATBS-modified canola oil alkyd resin, which may be due to a higher degree of compatibility between alkyd and acrylic components.

Scratch Hardness

As seen in Table 7, scratch hardness increased with an increase in ATBS content in water-reducible alkyd resins. The 100% ATBS-modified canola oil alkyd resin provided the maximum scratch hardness due to a higher amount of ATBS content.

Adhesion and Flexibility

The results of the adhesion and flexibility tests are encouraging. As Table 7 reveals, the COA resin grafted with styrene and ATBS passed the adhesion and flexibility test.

Impact Resistance

The impact resistance (both reverse and forward) of grafted resins remains the same with up to 75% of ATBS content (replaced with styrene in COA). It then shows a downward trend. This may be attributed to the brittleness of the films due to a higher percentage of ATBS.

Table 6 Signals present in ^{1}H-NMR spectra of canola oil and alkyd resins and their assignment

δ (ppm)	Assignment
0.9–0.998	$-CH_3$ terminal methyl
1.2–1.29	$-CH_2$ saturated aliphatic chain
1.61	$-CH_2-C$ methylene α to terminal methyl
2.07	$-CH_2-C{=}C$ allylic methylene
2.28–2.35	$-CH_2-O-C{=}O$ acyl methylene
2.81–2.84	$-C{=}C-CH_2-C{=}C$ diallylic methylene
4.00–4.17	$-CH_2-O-CO-$ in α position in glyceryl
4.27–4.32	$-CH{=}CH-$ olefinic (FA chain)
5.26–5.37	$-CH-O-CO-$ in β position in glyceryl
7.2–7.7	Aromatic protons of phthalic and maleic anhydride esters

Chemical Resistance

Based on the data displayed in Table 7, all the styrenated and ATBS grafted COA films exhibited excellent resistance to water, acid, alkali and salt solutions. However, in the case of COA, the film was completely removed in alkali solution, and blistering was observed in salt solution, indicating its poor alkali and salt resistance.

Solvent Resistance

In general, alkyd films show poor solvent resistance. The solvent resistance would be expected to increase as acrylic content increases. It can be seen from Table 7 that grafted resin and COA are able to withstand acetone up to hundred double rubs. However, there was a marginal increase in methyl ethyl ketone resistance of grafted COA resin with an increase in acrylic content.

Thermogravimetric Analysis

Thermal degradation of styrenated COA, ATBS-styrenated COA and COA samples (Fig. 5) was studied by the

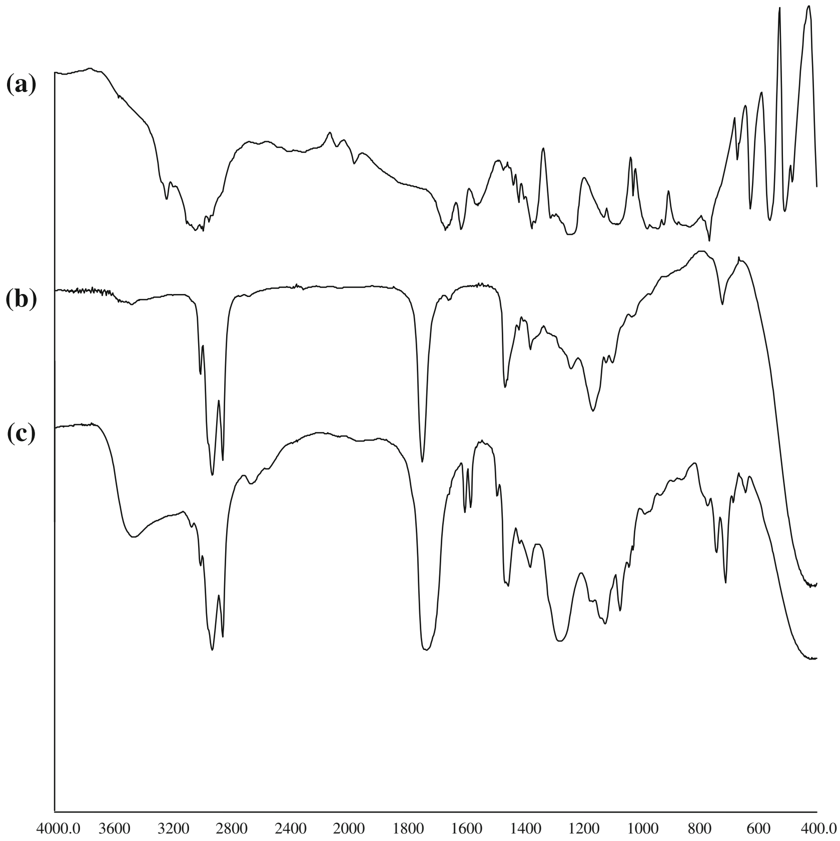

Fig. 4 FTIR spectra of **a** ATBS **b** Canola oil alkyd and **c** ATBS-styrenated canola oil alkyd

Table 7 Coating properties of water reducible canola oil alkyd resins

	COA	S1	S2	S3	S4	S5
Coating characteristics						
Pencil hardness	–	H	2H	3H	4H	5H
Scratch hardness (g)	–	1,000	1,100	1,200	1,300	1,400
Adhesion	–	100%	100%	100%	100%	100%
Flexibility	–	Passes	Passes	Passes	Passes	Passes
Impact[a] resistance						
Direct	–	50	50	50	37.5	37.5
Reverse	–	50	50	50	37.5	37.5
Chemical resistance						
Water	NE	NE	NE	NE	NE	NE
Alkali	FR	NE	NE	NE	NE	NE
Acid	NE	NE	NE	NE	NE	NE
Salt	SB	NE	NE	NE	NE	NE
Solvent resistance						
Acetone Rub	–	100	100	100	100	100
MEK Rub	–	50	55	57	60	65

NE no effect, *SB* slight blush, *FR* film removed

[a] The values are arrived at by multiplying the weight of indenter in lbs (6.25 lbs) with the maximum height in inches, from where indenter falls without any visible damage of film

S1 = 100% styrenated canola oil alkyd resin

S2 = 50:50 (Styrene:ATBS) canola oil alkyd resin

S3 = 25:75 (Styrene:ATBS) canola oil alkyd resin

S4 = 12.5:87.5 (Styrene:ATBS) canola oil alkyd resin

S5 = 100% ATBS canola oil alkyd resin

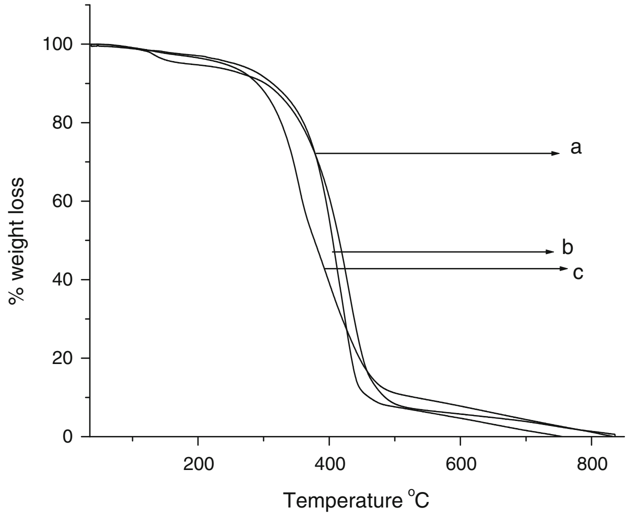

Fig. 5 TGA curves of COA and COA grafted resins. **a** ATBS-styrenated COA **b** 100% styrenated COA **c** COA

Table 8 TGA data of COA, styrenated COA and ATBS-styrenated COA

Polymer type	IDT	$T_{10\%}$	$T_{30\%}$
COA	100	300	350
Styrenated COA	110	316	400
ATBS-styrenated COA	120	330	400

COA: 100% canola oil alkyd resin

Styrenated COA: 100% styrenated canola oil alkyd resin

ATBS-styrenated COA: ATBS- styrenated canola oil alkyd resin

IDT: Initial decomposition temperature

$T_{10\%}$: Temperature at which 10% weight loss occurred

$T_{30\%}$: Temperature at which 30% weight loss occurred

thermogravimetric method. The thermal stability was evaluated by using the IDT (initial decomposition temperature) and the thermal indexes T_{10} (10%) and T_{30} (30%) of weight loss (Table 8). There was hardly any weight loss before 100 °C for all these compounds. The weight loss of COA was more pronounced when heated above 300 °C. It is interesting to note that the thermal indexes for the grafted polymer are higher than for the COA resin [10, 11].Thus, it can be inferred that the thermal stability of COA resin can be enhanced by grafting acrylic monomer (ATBS) and styrene

Conclusion

The renewable resource canola oil can be used successfully for the synthesis of water-reducible alkyd resins**.** The results of the study show that the modification of COA with monomers such as styrene and ATBS can greatly enhance the quality of water-reducible canola oil alkyd resin.

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