

Synthesis and characterization of hyperbranched silane-modified alkyd as a polymer for environmentally friendly low VOC polyurethane coatings

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Abstract

Purpose – The purpose of this paper is to introduce a new method for modification of alkyd resin by using 3-triethoxysilylpropyl succinic acid anhydride (TESP-SA) as the core material for low volatile organic components (VOCs) polyurethane coating applications.

Design/methodology/approach – The structural, physical, thermal and film properties of the silane-modified (SM) alkyd were evaluated and compared with those of a silane-free alkyd resin that was prepared by a single-step method. The synthesis reaction was described in a detailed scheme and evidenced by ATR-FTIR measurements and ^{13}C -NMR spectroscopy.

Findings – SM alkyd has synthesized with high solid content (85%) and low viscosity (5700 cP). As a result, environmentally friendly coatings with lower (VOC) emission are possible by using this type of alkyd polymer. The results showed that the presence of the Si atom in the final structure improved the thermal stability against the higher levels of aromatic rings in the silane-free alkyd. It was found that coatings based on SM alkyd have lower values of yellowing factor (Δa) and an increase of gloss retention percentage at different intervals of exposure to the quick ultraviolet weathering conditions.

Practical implications – The synthesized SM alkyd resin provided a practical solution to obtain environmentally friendly coatings with low VOC content, in addition to its improvement in alkyds' overall characteristics, while still using natural resources – fatty acids – instead of totally petroleum resources.

Originality/value – TESP-SA has not been used before in alkyd polymer modifications, and this study can help countries that are interested in using environmentally-friendly coatings.

Keywords Spectroscopy, Coating, Silane, Polyurethane

Paper type Research paper

Introduction

Polyurethanes are formed by a simple polyaddition reaction between hydroxyl-containing materials (polyol) with isocyanate-containing materials (hardeners). Coatings, in general, contain four types of raw material, namely, resins or binders, pigments or pigment-like substances, solvents or dispersing media, and additives. Not all paints have every ingredient, major differences occur between the polymers and resins that are used in paints formulated for different purposes. Resins are the most important component, as they provide the basis of the film forming a layer. They are also called binders because they have to wet and disperse the pigments and bind them in paint or film layer. Physically, polymers are very high viscous liquids that give the impression of being solid. But, unlike true solids in the physical sense that have crystalline structures, polymers do

not consist of a structured arrangement of molecules; like liquids, the distances between the molecules have only average values.

There is a wide range of coating polymers, but only polyol types – hydroxyl-containing polymers – are recommended for polyurethane applications, some of them are acrylic polyols, polyester polyols and alkyd polyols. Conventional alkyds are polyester compounds of glycerol and phthalic anhydride acid modified by the addition of some vegetable oils or fatty acids (Rämänen and Maunu, 2014; Dullius *et al.*, 2006; Boruah *et al.*, 2012; Odetoye *et al.*, 2012; Azimi, *et al.*, 2013). They are derived from polyols and a dicarboxylic acid or carboxylic acid anhydride. The term alkyd is a modification of the original name “alcid”, reflecting the fact that they are derived from alcohol and organic acids. Approximately 200,000 tons of alkyd resins are produced each year (Jones, 2003).

Coatings based on non-modified conventional alkyds are not expensive, but these failed to obtain high-performance or environmentally friendly coatings. The biggest two defects are chalking and loss of gloss within a period of 6-

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12 months in tropical climates because of the weathering conditions (intense UV radiation, thermal fluctuations and high humidity). For these reasons, coating formulators need high performance alkyd resin to be flawless, accepted hardness, higher thermal stability, chemical and corrosion resistance and also have high protection against harsh weather conditions. Attempts have been made to solve this issue; alkyd has been hybridized with other compounds such as acrylics (Elrebii *et al.*, 2015; Shui *et al.*, 2014), silicones acrylics (Murillo *et al.*, 2011, 2012), CuO nanoparticle (Ong *et al.*, 2015), phenytoin (Teo *et al.*, 2017) and carbon nanotubes (Rukhov *et al.*, 2018). Vallejo *et al.*, 2015 studied and evaluated the effect of the phenol contents on the structural, thermal, rheological and film properties of the hyperbranched alkyd resins (HPAR); the resulted HPARs exhibited low viscosities, which increased with the phenol content. Glass transition temperature (T_g) was directly proportional to phenol content, also, the hybridization with phenol improves the thermal stability, hardness and chemical resistance against NaOH solution 0.1 M.

Jana *et al.* (2018) used fatty acids, polyols and different amount of chain extender, dimethylol propionic acid (DMPA) in the synthesis of modified hyperbranched alkyd. Jana *et al.* found that increase in the DMPA percentage raises the polymer branching, which is confirmed by $^1\text{H-NMR}$ spectroscopic analysis. Branching in the alkyd polyurethane increases chain entanglement as well as compactness in the structure, in addition; the branching leads to increase in glass transition temperature (T_g) of the alkyd urethane coating film. Owing to the compact structure, such type of high solid highly branched polymers performs better gloss retention under UV radiation as well as natural outdoor exposure. The final properties of the applied coating, such as film hardness, adhesion, abrasion resistance and corrosion resistance, are improved also by increasing the branching in the alkyd structure.

Kanai *et al.* (2007) hybridized the alkyd resin with silicone and acrylic moieties in the structure to obtain high-performance resin for long-life exterior coatings, they reacted 2-hydroxyethyl methacrylate with silicone soya alkyd resin through a chemical reaction, and the reaction has been confirmed from ^{13}C NMR analysis and FTIR measurements. They concluded that incorporation of 30 per cent silicon acrylic monomer into soya alkyd resin has resulted in superior weathering properties with good gloss retention in addition to higher tensile strength compared to the non-hybridized silicone soya alkyd resin.

Trialkoxy silanes are an organosilicon compound having the generic formula RSiX_3 , in which R is an alkyl, alkenyl or aryl group and X is an alkoxy group, in addition, R may contain an active organic functional group. A wide range of silanes were used in coating polymer synthesis to improve the mechanical properties, such as scratching resistance, hardness, adhesion to different substrates, and weathering and chemical resistance such as acids and alkalis. Different methods are developed to introduce the silanes into the coatings network, some of them by direct addition to the final coatings formulation (El-Bindary *et al.*, 2017; Gupta *et al.*, 2012; Seeber *et al.*, 2017) and others by reacting the

silane with many types of polymers at different steps (Mannle *et al.*, 2014; Ooij *et al.*, 2011); all these methods proved excellent results for enhancing coatings performance and also proved that silanes can react with wide range of polymers. Many reactions can be obtained by variation of the functional group of the R arm (epoxy, anhydride, acids, isocyanato, alkyl, mercapto or vinyl) (Alibakhshi *et al.*, 2018; Yuan *et al.*, 2017; Pourhashem *et al.*, 2017).

In the present study, we used TESP-SA in the hybridization and synthesis of hyperbranched alkyd using commercially available acids (coconut fatty acids, stearic acid, 2-Ethylhexanoic acid, phthalic anhydride acid and benzoic acid), Trimethylol propane. The effect of alkyd branched structure on the properties of alkyd urethane coating particularly gloss, gloss retention under accelerated quick ultraviolet (QUV) radiation and thermal stability have been reported and compared with a silane-free alkyd polymer.

Experimental

Materials

TESP-SA was supplied by (Wacker Co., Germany), commercially available phthalic anhydride was purchased from (Thirumalai Chemicals Ltd., India), stearic acid from (Colorquimica SA), 2-Ethylhexanoic acid from (KH Neochem Co, Japan), coconut oil fatty acid and glycerin were purchased from (M/s. Jitu Enterprises, India), benzoic acid 99 per cent from (IG Petrochemicals Ltd., India). Trimethylolpropane 99 per cent and pentaerythritol were supplied by (Perstorp Ltd.), Toluene Diisocyanate (TDI 75 per cent) with commercial name *Polurene AD* was supplied by (Sapici Co., Italy). All solvents (Xylene 99.9 per cent, N butyl acetate 99.9 per cent and methoxy propyl acetate 99.9 per cent) were supplied by (El-Mohandes for coatings and solvents Co., Egypt). Surface additive Byk 310 was purchased from (BYK Chemie, Germany). All materials were used directly without any further purification.

Alkyd polymer synthesis

To a four-necked round-bottom flask (1 L), fitted with a reflux condenser, thermometer and mechanical stirrer, 79.14 g of TESP-SA (0.26 mol) and 104.65 g of trimethylol propane (0.78 mol) were added. This system was kept under nitrogen flow, and the reaction mixture was heated from 140°C to 160°C gradually for approximately 3 h under stirring till a calculated amount of ethanol was collected (theoretically 35.93 g). Then, a respective amount of xylene (approximately 50 g) as azeotropic solvent – to facilitate water elimination – and 120 g of Phthalic anhydride acid (0.81 mol.) were added to the flask and temperature was raised to 180°C during a reaction time of 1 hour to esterify only the first carboxylic group of the phthalic acid. Finally, adding 155 g of trimethylol propane (1.16 mol.), 66 g of coconut fatty acid (0.32 mol.), 58 g of benzoic acid (0.47 mol.), 57.76 g of 2-Ethylhexanoic acid (0.39 mol.) and 92.46 g of stearic acid (0.32 mol.) to the reaction system. Under continuous stirring, the reaction temperature was kept at 200°C for 3 h and then increased to 220–235°C for additionally 5 h. Then the reaction continued until an acid value of 10 mg KOH/g was obtained in the sample. After reaching the required acid value, the reaction was allowed to cool and

n-Butyl acetate was diluted to obtain solid content 85 Wt.%. **Scheme 1** shows the proposed chemical reaction, where all mole values were divided by 0.26 to obtain integer numbers to facilitate scheme understanding.

Unmodified alkyd polymer (silane-free) was synthesized for comparison with our new silane-based alkyd polymer by use of a one-step process using conventional raw materials: phthalic anhydride, stearic acid, coconut fatty acid, pentaerythritol and glycerin. The final alkyd formulations are listed in **Table I**.

Both reaction mixtures of silane-modified (SM) and unmodified alkyd were washed with distilled water to remove unreacted materials and dried with anhydrous Na_2SO_4 . Then alkyds have been thinned to 70 per cent solid content by N butyl acetate 99.9 per cent and filtered to remove foreign matter, skins or gel particles.

Apparatus and characterization methods

Acid value

Acid value was determined according to ASTM D1639-90 by titrating the resin sample against standard alcoholic KOH solution (0.1 N) every 30 min till approach value of 10.

FTIR measurements

FTIR measurements for SM polymer, monomer and coating film were conducted with alpha equipment, Bruker Co. All measurements were carried out by using a MIRacle Single Reflection Horizontal ATR (PIKE Technologies), applying for investigating liquid and powder samples. A diamond crystal was used throughout the study, usually 80 scans were recorded, and OPUS NT software version 7.5 was used for data evaluation and manipulation.

Scheme 1 Synthesis of SM alkyd resin

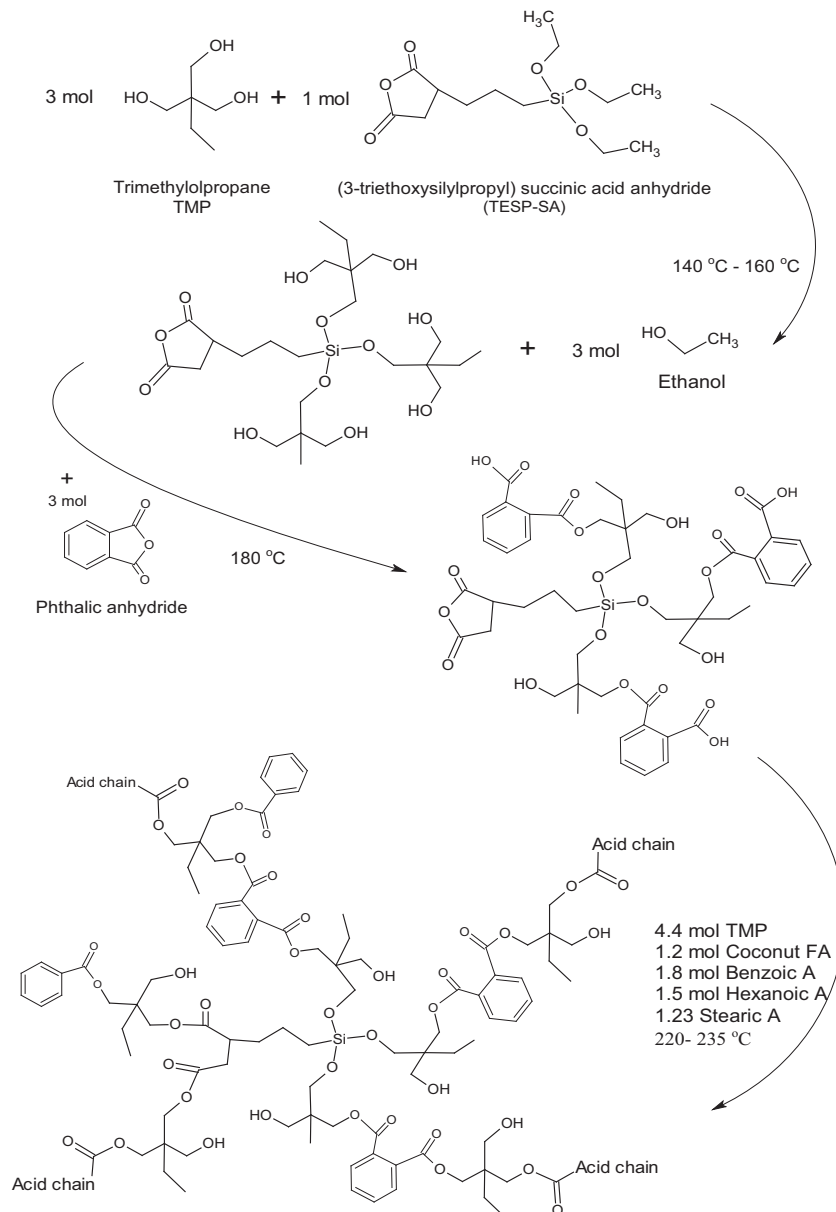


Table I Unmodified and SM alkyd resins formulations

Material	Unmodified- alkyd	SM-alkyd
TESP-SA	–	10.8
Trimethylol propane	–	35.4
Pentaerythritol	6.5	–
Glycine	21.1	–
Phthalic anhydride	39.8	16.4
Coconut FA	22.1	9.0
Benzoic acid	–	7.9
2-Ethylhexanoic acid	–	7.9
Stearic acid	10.5	12.6
Total	100 (%)	100 (%)

Thermal stability analysis

Thermal stability of SM and unmodified alkyd samples were done using STA PT1000 TG-DSC (STA Thermogravimetric Analyzer) from Linseis Company. Both samples were mixed with isocyanate TDI by using mixing ratio 2:1 and then kept in a desiccator for complete reaction for about 3 days. Samples were tested under a nitrogen atmosphere at a heating rate of 10 k/min.

¹³C NMR spectroscopy

¹³C NMR spectra were recorded on Bruker NMR spectrometer (100 MHz). Deuterated chloroform was used as a reference solvent. ¹³C NMR of TESP-SA as a monomer, and SM alkyd samples were recorded for confirmation of the chemical structure of reaction products.

Accelerated weathering test

It was done by using QUV-accelerated weather tester model QUV/se, weathering resistance of SM and unmodified alkyd samples were evaluated as per method ASTM D4587 Cycle 2 by exposing the coated panels (150 mm 375 mm 3 1 mm) to QUV radiation (340 nm irradiance) and high humidity condition. A weathering cycle comprising 4 h dark period of condensation exposure (at 50°C) and 4 h of UV exposure (at 60°C) was maintained during the study. To simulate outdoor weathering, the panels were prepared by applying a coating layer of polyurethane varnish over a single white coat of base surface. Gloss measurements (before, during and after exposure) at 60° angle were carried out at periodic intervals as per method ASTM D523.

Film properties analysis

To compare the film properties, final wood coating formulations were done by using both alkyd polymers (unmodified and SM) according to Table II, Component (A). Then, both coatings were mixed with isocyanate solution [component (B)] by mixing ratio 2:1. By using film applicator, the two coatings were applied on a steel surface which was pre-coated with white primer; samples then were kept in a desiccator for complete reaction for about 3 days before the final examinations.

Physical properties

The physical properties of both polymers were compared, and gloss was measured at 60° according to the ASTM D523

Table II Polyurethane coating formulation

Quantity/gm.	Material
Component (A)	
Polymer	80
N-Butyl acetate	5
Methoxy propyl acetate	9.8
Xylene	5
Byk 310	0.2
Total (A)	100 (gm.)
Component (B)	
Polurene AD	64
N Butyl Acetate	36
Total (B)	100 (gm.)

method using gloss meter PCE-PGM 100 (PCE Instruments Company). The yellowing of the coatings during the UV exposure was measured by using a data color instrument in order to measure the Δa values by time, according to the ASTM D 2244 method. Viscosity measurements were carried out according to method ASTM D2196 by using Brookfield viscometer from Ametek CO., model DVEEHBT J0, at 25°C, spindle number 5 and speed of 5 rpm.

Results and discussion

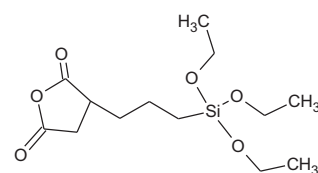
Reaction key of 3-triethoxysilylpropyl succinic acid anhydride

One of the more important preparation routes of alkyd resins is the direct esterification synthesis. Direct esterification is a step-growth polymerization technique, where the polymer is prepared by using the condensation reaction of polyols, such as glycols, and glycerol with diacids or multifunctional anhydrides. It is the first time for using the TESP-SA in alkyd synthesis, regarding its structure (Scheme 2), the organic arm has terminated by succinic anhydride acid group, which can undergo esterification reaction such as phthalic anhydride acid. The other three silicon bonds have been terminated by ethoxy groups that can be hydrolyzed or replaced by higher glycols by the same way such as other silanes to be terminated with a hydroxyl group. By this way, TESP-SA will be able to undergo esterification reaction through its four arms.

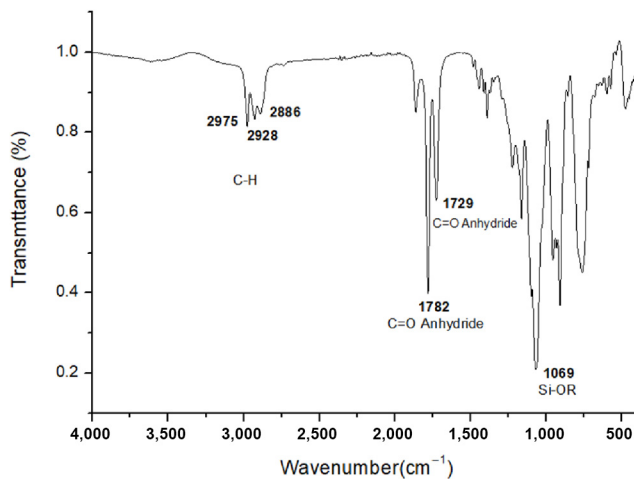
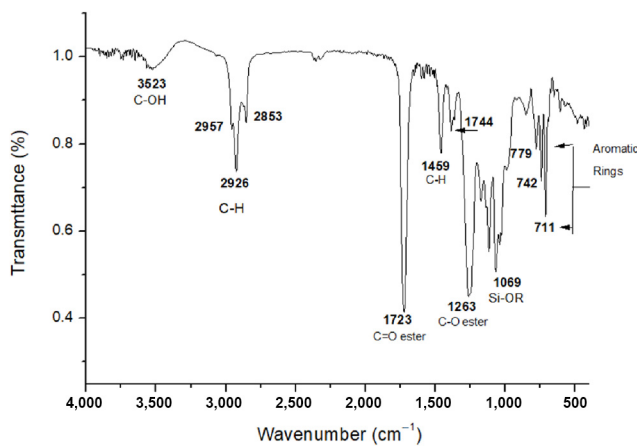
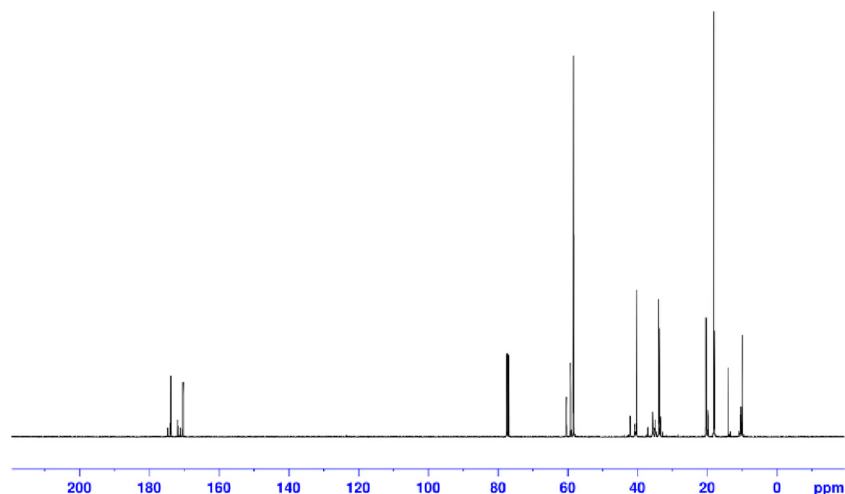
FTIR measurements

The final polymer and TESP-SA as monomer were conducted to demonstrate the participation of the TESP-SA in the final polymer structure. Figure 1 represents the FTIR spectrum of TESP-SA monomer, the most important peaks were at

Scheme 2 TESP-SA structure



(3-triethoxysilylpropyl) succinic acid anhydride (TESP-SA)

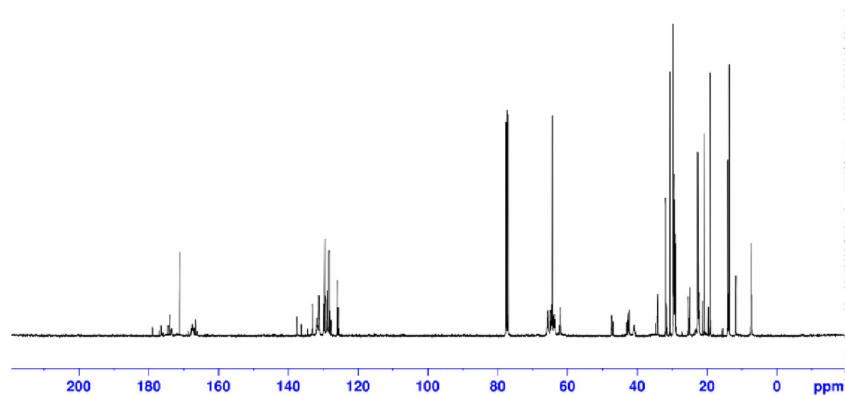
Figure 1 FTIR spectrum of TESP-SA**Figure 2** FTIR spectrum of the SM alkyd resin**Figure 3** ¹³C NMR spectrum of TESP-SA

1,782 cm⁻¹ and 1,729 cm⁻¹ for C=O indicated the presence of the anhydride group, besides another characteristic peak at 1,069 cm⁻¹ indicated the presence of Si-O-C group. Figure 2 represents the FTIR spectrum of the SM polymer, presence of the same peak at 1,069 cm⁻¹ for Si-O-C was the first proof of positive participation in the final polymer structure, secondly, replacement of peaks at 1,782, 1,729 cm⁻¹ of monomer anhydride group by peaks of ester group at 1,723 cm⁻¹ for C=O and 1,263 cm⁻¹ for C-O indicated the successful condensation reaction between the anhydride group of TESP-SA monomer and trimethylolpropane.

The peak at 3,523 cm⁻¹ of the polymer spectrum indicated the presence of -OH groups, the two sharp peaks at 711, 779 cm⁻¹ for the mono-substituted aromatic ring, indicated successful participation of the benzoic acid, also the sharp peak at 742 cm⁻¹ for ortho-substituted aromatic ring, indicated the presence of phthalic aromatic ring.

¹³C NMR spectroscopy

The first step in SM alkyd polymer preparation was a reaction of one mole of TESP-SA with three moles of trimethylolpropane to replace the three ethanol molecules from TESP-SA. The most important peaks at 58.2 and 18.3 ppm in Figure 3 that represent the ¹³C NMR analysis for TESP-SA are because of the carbons of methylene and methyl groups, respectively, of the 3 ethoxy groups (Si-O-CH₂-CH₃). These two peaks at (58.2 and 18.3 ppm) disappeared in Figure 4 that represent the ¹³C NMR analysis of SM alkyd polymer; this shows the completion of the reaction between TESP-SA and trimethylolpropane and liberation of three ethanol groups. It is observed in Figure 3 that there are only two signals at 170.3 and 173.7 ppm which associated with the two carbonyl carbons of the succinic fragment of TESP-SA, while in Figure 4, many signals for ester carbonyl groups appeared in region 171-179 ppm which indicated anhydride ring opening and formation of new ester groups. Other characteristic signals in Figure 4 in range 125-133 ppm are because of the presence of aromatic rings in the final polymer structure.

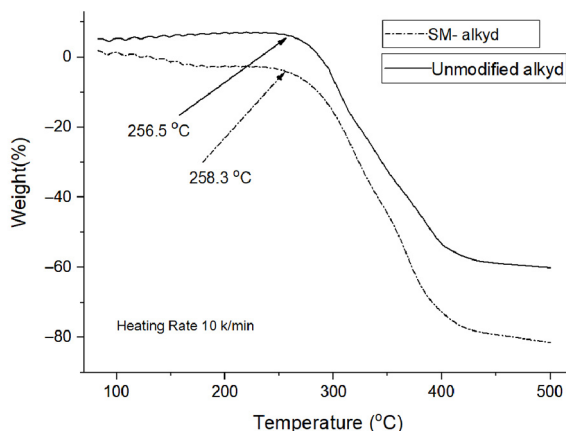
Figure 4 ^{13}C NMR spectrum of the SM alkyd resin

Thermal gravimetric analysis

Figure 5 presents the TGA thermograms of the unmodified and SM alkyd polymers. The decomposition temperature (T_d) values were 256.5 and 258.3°C for unmodified and SM alkyd polymers, respectively. The thermal behavior demonstrated by the unmodified alkyd was because of the formation of CO–Ar bonds, and the presence of the aromatic ring in its composition had a high thermal stability (38.8 per cent of phthalic anhydride in the formula, Table I). Aromatic ethers have a resonating system that includes the two electron pairs of oxygen; the structure is thus stabilized by resonance, which contributes to high thermal stability (Patel *et al.*, 2010). In case of SM alkyd, the aromatic percentage in the final formula was 24.3 per cent (phthalic and benzoic acids) which is much lower than the unmodified alkyd, but the presence of Si atom in the final structure (Scheme 1) maintained thermal stability in addition to a slight increase in decomposition temperature (T_d) value from 256.5 to 258.3°C. Therefore modification of alkyds using silane compounds improved the thermal stability.

Physical properties

The physical properties comparison between unmodified and SM alkyds are shown in Table III; the viscosity of SM alkyd (5700 cP) is lower than that of unmodified alkyd (41300 cP),

Figure 5 Thermal gravimetric analysis of unmodified and SM alkyd resins

indicating that the structures of SM alkyd are more branched than those of unmodified alkyd. The extent of branching also increases the solubility of the polymer in different solvents.

Environmental implications

The main factors required to build a low VOC coating system are high solid content besides lower viscosity, as shown in Table III, the solid content increased by ratio 21 per cent after the modification (70 and 85 per cent for unmodified alkyd and SM alkyd, respectively), in addition, the viscosity decreased by ratio 86 per cent after the modification (41,300 and 57,00 cP for unmodified alkyd and SM alkyd, respectively). The final coatings based on the SM alkyd resin was applied directly after addition of the isocyanate hardener without addition of extra diluents, while coating based on unmodified alkyd was diluted by 20 per cent thinners (diluents); hence, we build a successful environmentally friendly coating system with high solid content and low volatile organic component.

Accelerated weathering test

Factors that are mainly responsible for destructive weathering action on paints are water, light, oxygen and temperature. They may act at different levels independently or together in various combinations and in different sequences. The UV radiation accelerates the surface deterioration of coatings that contain oil or aromatic rings in its structure. The shorter UV radiation was the most effective in decreasing the coating strength, it attacks the surface of the film causing erosion and production of volatile carbon compounds, while the longer UV radiation penetrates deeper into the bulk of the film causing evolution of hydrogen as water and formation of carbonyl groups led to further shrinkage, loss of elongation of the film (Yousif and Haddad, 2013) and embrittlement of the coating.

Table III Physical properties of unmodified and SM alkyd polymers

Test	Method	Unmodified-alkyd	SM-alkyd
Solid content	ASTM D 1353	70 %	85%
Viscosity	ASTM D 2196	41,300 cP	5,700 cP
Color	ASTM D 1544	1	1
Acid value	ASTM D 1639	8.9	9.2

Water in conjunction with the UV also accelerates deterioration by stimulating the production of volatile and water-soluble decomposition products. The higher temperature, in general, is expected to accelerate the degradation reaction depending on the energy of activation of the reaction. Higher temperature also contributes to a decrease in elongation (Yousif and Haddad, 2013) and stiffening of the film. As a result of all the above weathering factors, irreversible chemical degradation reactions occur resulting in the formation of peroxides, polyketones and free radicals.

The free radicals then attack and destroy the aromatic ring structure and decompose all double bonds resulting in the cracking, yellowing and deformation of the polymer film. So, decreasing the percentage of oils, double bonds and aromatic rings in the final polymer structure were the most important targets of this study to improve the weathering resistance. In Table I, the aromatic percentage of the unmodified alkyd was 38.8 per cent (phthalic anhydride) and 24.3 per cent (phthalic and benzoic acids), in case of SM alkyd. Figure 6 represents the large increases in the yellowing factor (Δa) of unmodified alkyd over the SM alkyd at different intervals of exposure to the weathering test. In addition, higher elongation value for SM polymer is attributed to significant freedom of rotation of Si-O-C bond.

Gloss retention is of great significance for maintaining the esthetic appearance of the coating surface for a long time. The gradual reduction in the gloss in both alkyds (Figure 7) at different intervals of exposure was because of the effect of UV radiation that causes scission of ester groups (Singor et al., 2003), in addition to the loss of binder as volatile products, volatilization is caused chiefly by the shorter duration of UV radiation. But the higher gloss retention characteristic of SM alkyd resin is because of the higher bond energy of the Si-O bond (Weinhold and West, 2011) present in silicone that resists the UV degradation on exposure to weather meter and inherent gloss retention property of the silane compounds (Hang et al., 2015).

Conclusions

This study has presented a new solution for the manufacture of alkyd-modified coatings to comply with the global trend of using

Figure 6 QUV Yellowing factor (Δa) of unmodified and SM alkyd resins at different time intervals

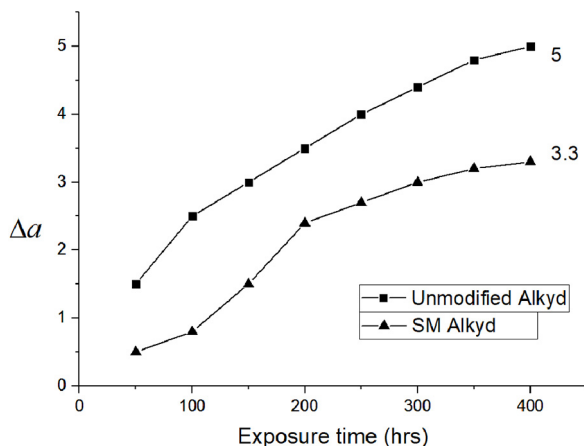
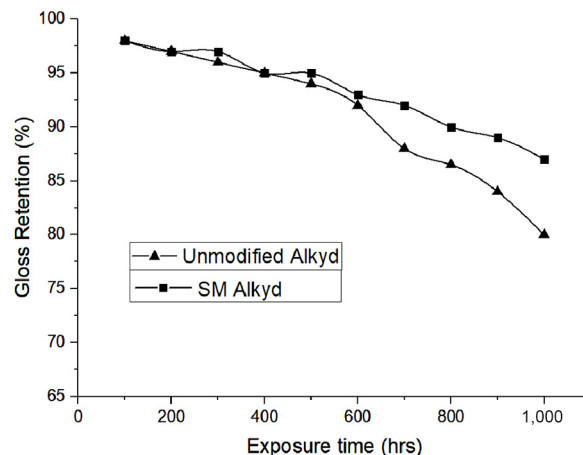


Figure 7 QUV, gloss retention of unmodified and SM alkyd resins at different time intervals



oils and their derivatives as natural resources rather than petroleum resources. These coatings are also more environmentally friendly than non-modified alkyd paints because of their low VOCs ratios. Using succinic acid anhydride silane as the core material into an alkyd polymer through a chemical reaction has led to the enhancement of the final coating characteristics like mechanical properties, gloss retention and longtime yellowing resistance. The reaction between TESP-SA, trimethylolpropane and acid mixture has explained in a detailed scheme, followed by acid value measurements and confirmed by ^{13}C NMR analysis and FTIR measurements. Additionally, it was concluded that these type of modifications have improved the final coating's thermal stability.

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