



Synthesis and characteristics of *Zanthoxylum bungeanum* seed oil-based alkyd resin modified by epoxy resin and their blends with HMMM

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Abstract

Waterborne alkyd resins based on *Zanthoxylum bungeanum* seed oil modified with epoxy resin were prepared by polyesterification reaction. The different base catalysts were examined on the alcoholysis reaction. Further, epoxy-modified waterborne alkyd resins were blended with hexamethoxy methyl melamine to improve the properties like curing time, chemical resistance and thermal stability. The properties of the prepared resins (acid value, drying time, pencil hardness, adhesion, flexibility, chemical resistance and thermal stability) were studied. The prepared polymers were characterized by FT-IR spectroscopy, particle size analysis and thermogravimetric analysis. ZSO-based alkyd resins modified epoxy resin and their blends with HMMM (EWA:HMMM = 3:1) showed enhanced chemical resistance, physical properties and thermal stability.

Graphic abstract



Keywords Waterborne coating · Alkyd resin · Epoxy resin · *Zanthoxylum bungeanum* seed oil

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Introduction

Alkyd resins, first synthesized in the 1920s, have persisted in the endless competition with the growing synthetic polymer resins till nowadays due to their structural versatility, compatibility and facile processing [1, 2]. Alkyds have been proven to be superior to others in many applications with special demands because of their excellent mechanical, wetting and durability characteristics. Alkyd resins account for approximately 50% of all resins consumed in protective paint application [3].

In recent years, growing public concern about environmental pollution caused by accumulation of solid waste and petroleum resources exhaustion has stimulated the development of biodegradable polymers as well as composite materials from renewable resources [4, 5]. Scientific and technological innovation pays more and more attention to the connotation of green chemistry, which is opening the way to the sustainable development of new generation of biodegradable polymers. As one of the most abundant biological resources, vegetable oils are considered the promising renewable raw materials for polymers because of its availability, low-cost, biodegradability and versatile applications [6–8]. It was reported that edible oils such as linseed oil [9], castor oil [10], coconut oil [11] and sunflower oil [12] can be used for designing alkyds. But in the context of high oil prices, as well as the ever growing demand in food sector, the focus on non-edible oil as feedstock has been increased in the past two decades [13]. Nowadays, increasing attention has been paid to non-edible oil as raw materials to prepare alkyds such as rubber seed oil [14], yellow oleander (*Thevetia peruviana*) seed oil [15] and tung oil [16]. The utilization of non-edible oils for coatings can reduce the dependency on edible oils also an alternative way to utilize the waste seeds that will turn into value-added products.

The *Zanthoxylum bungeanum* plant which belongs to the rutaceae family with a long cultivation history in China can withstand heat and cold and readily adapts to various soils and climate conditions [17]. In 2018, there were approximately 20 million tons of *Z. bungeanum* seeds oil (ZSO) produced in Shaanxi Province of China annually of which 60%, 25% and 15% were used in animal feed, chemical industry and food industry, respectively [18]. In the chemical industry, ZSO is used as an ingredient or component in many manufactured products, such as oil corrosion inhibitor [19], coatings [20] and biodiesel [21]. ZSO contains high amounts of unsaturated long-chain fatty acids whose major component is oleic acids, linoleic acid and α -linolenic acid [22] which is applicable for the synthesis of alkyd resins.

To improve the properties of alkyds, it can be modified with other suitable resins by chemical or physical methods including acrylate [23, 24], styrene [25], inorganic nanomaterials [26, 27] or epoxy resins [28]. However, among all alkyds, epoxy resins owe a privileged position as better thermal stability, mechanical properties, low volatile content, curing time, solvent resistance and so on [29, 30]. Assanvo et al. [31] reported the preparation of epoxy-modified alkyd resins based on ricinodendron heudelotii oil. The performance of the synthesized resin was improved by blending with epoxy resin. Gogoi et al. [8] studied the synthesis and characterization of alkyd resins based on jatropha curcas oil and their blends with epoxy resin.

The adverse effects of volatile organic content (VOC) on the environment have directed research in the coating industry toward eco-friendly direction involving low-toxic organic solvent amounts and high solid contents [32]. Waterborne paints are the most practical and effective solution [33–35]. The prepared waterborne alkyd resins based on ZSO have some shortcomings such as low hardness, relatively poor water, acid and alkaline resistances, in our earlier work [36]. In order to overcome the reported drawbacks of alkyds, we used epoxy resin to prepare epoxy-modified water-soluble alkyd resins by polyesterification reaction and blend with hexamethoxy methyl melamine (HMMM). This work reports a low-cost and biodegradability technique for designing ZSO-based alkyd resins with low VOC through neutralization reaction. The fabricated ZSO-based alkyd resins exhibited improved performance characteristics, including drying time, hardness, water resistance, acid resistance, alkali resistance and thermal behavior.

Experimental

Materials

Zanthoxylum bungeanum seed oil (ZSO) was kindly supplied by Hancheng Jintaiyang *Z. bungeanum* seed oil Co., Ltd. (China), and the fatty acid composition of ZSO is given in Table 1. Phthalic anhydride (PA), trimethylolpropane (TMP), 1,2,4-benzenetricarboxylic anhydride (TMA), triethylamine (TEA), ammonia, ethylene glycol monobutyl ether, benzoic acid (BA) and xylene were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Water-based drying catalyst (Octa-Soligen 421 aqua) was obtained from Ruiju Paints Co., Ltd. (Guangdong, China). The bisphenol A epoxy resins (EP20, epoxy value = 0.22 mol/100 g) and hexamethoxy methyl melamine (HMMM) were acquired from Xi'an resin Co., Ltd. (China). All chemical reagents used were analytical grade.

Methods

Purification of *Z. bungeanum* seed oil (ZSO)

The crude ZSO was in three stages comprising degumming, deacidifying and decoloration reaction. The crude ZSO and concentrated phosphoric acid (0.2 wt% of

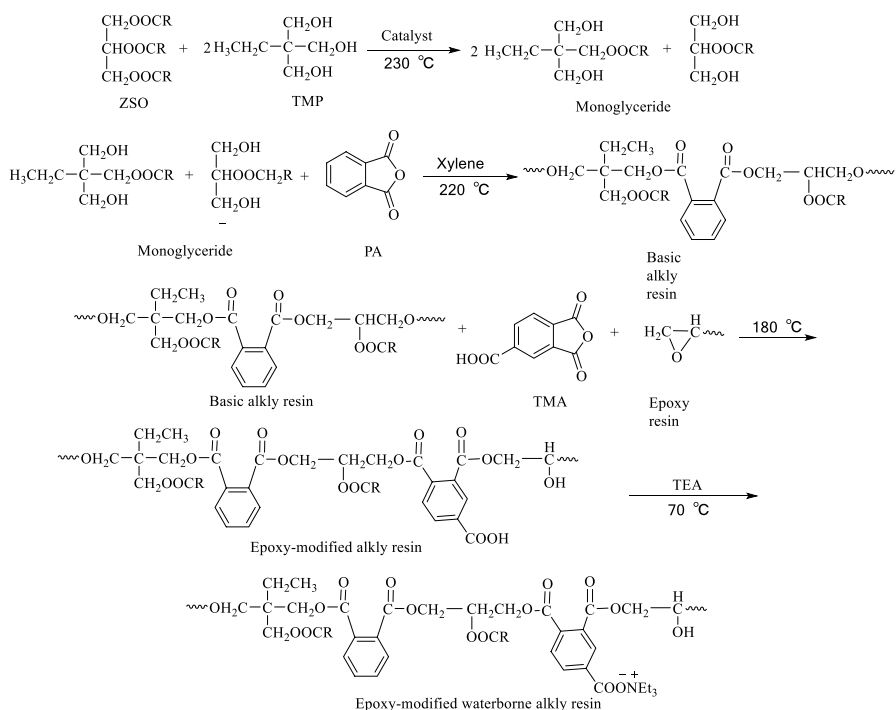
Table 1 Major fatty acid composition of ZSO

Fatty acid composition	(%)
Palmitic acid	28
Oleic acids	30
Linoleic acid	18
α -Linolenic acid	11
8,11-Octadecadienoic acid	13

ZSO) were charged into a 1000-mL three-necked flask equipped with a mechanical stirrer, thermometer and reflux condenser. The mixture was heated to 70 °C and mixed with 2 wt% aqueous solution of NaOH (10 wt% of the ZSO) to remove excess phosphoric acid. The aqueous phase was separated by centrifugation, and the oil phase was dried with anhydrous sodium sulfate. In the second stage, the degummed oil, absolute methanol (weight of oil/methanol=1.3:1) and concentrated sulfuric acid (2 wt% of the ZSO oil) as catalyst were added into the system and heated to 60 °C for 2 h. The oil and water phases are separated through a separating funnel, and the oil phase was washed two times with 100 mL of water to remove excess methanol and dried with anhydrous sodium sulfate [21]. In the third stage, the purified oil and bleaching earth (1 wt% of the ZSO) were added to the flask, and the mixture was heated to 100 °C for 30 min. Afterward, the mixture was filtered with a sintered glass filter.

Synthesis of epoxy-modified waterborne alkyd resins based on ZSO

In this study, epoxy-modified waterborne alkyd resin was prepared in three stages including alcoholysis, polyesterification and neutralization reaction (Scheme 1). The purified ZSO (24.51 g, 0.03 mol) and TMP (8.04 g, 0.06 mol) were charged into the flask. The reaction mixture was slowly heated up to 120 °C, and the catalyst (NaOH or LiOH) was added into the system. The reaction temperature was raised to 230 °C



Scheme 1 Synthetic pathway of epoxy-modified waterborne alkyd resin based on ZSO

until monoglyceride was formed. The mixture in 95% ethanol (reaction mixture/ethanol = 1:3 v/v) is a clear solution indicating that the reaction is completed, and then, the reaction mixture was cooled down to 180 °C.

In the second stage, PA (10.00 g) and xylene as the azeotropic solvent (5% of the alkyd resin) were added to the monoglyceride and the mixture was heated to 220 °C. The acid value of reaction mixture was measured at different time intervals accordingly by ASTM D 1639 to monitor proceeding of the reaction. The reaction was quenched by allowing it to cool when the acid value was about 10 mg KOH/g. TMA (6.2 g) and EP20 were added into the system at 180 °C to evaluate the effect of epoxy resin ratio on properties of waterborne alkyd resin. The reaction temperature was kept constant until the acid value was 50–60 mg KOH/g.

In the third stage, the reaction mixture was cooled to 120 °C, the epoxy-modified alkyd resins were diluted to 85% of solid content by adding ethylene glycol monobutyl ether, and the alkyd resins were neutralized with TEA. Alkyd resins were diluted to 50% of solid content by water. All resins were obtained as stable dark red transparent solutions.

Blending of epoxy-modified waterborne alkyd resin with HMMM and curing

The epoxy-modified waterborne alkyd resin and HMMM were blended at the different ratio of 1 ~ 5:1(w/w) to obtain blend resins. Then, the blend resin films were cured at 80 °C and 100 °C for 1 h in oven.

Characterization and measurement of ZSO and the alkyd resin

Analytical methods of ZSO

Standard methods were used to find the specific gravity (ASTM D 287), viscosity (ASTM D 445), the viscosity of the ZSO by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. Acid value (ASTM D 664): Briefly, 1 g of the ZSO sample was diluted in 20 mL of the neutralized solvent mixture (xylene/isopropanol 1:1) and titrated with a standard solution of 0.5 mol/L potassium hydroxide (KOH) with phenolphthalein as indicator. Saponification value (ASTM D 464): Typically, 1 g of ZSO was taken with 25 mL alcoholic KOH solution, heated for 1 h in a steam bath with occasional shaking and titrated the excess KOH with the 0.5 mol/L hydrochloric acid solution. Iodine value (ASTM D 1959) of the ZSO: The iodine value was determined by titrating with 0.05 mol/L sodium thiosulfate solution to the mixture reagents until the disappearance of the blue color.

Characterization and measurement of dry films

The structure of cured films was characterized by Fourier-transform infrared spectroscopy (FT-IR) [Perkin Elmer spectrum 1730 (USA)] using KBr pellet in the range of 4000–500 cm^{-1} . The particle studies were performed on particle

size analyzer [Malvern particle size analyzer ZS Nano S (UK)] to measure the diameters and distributions of the alkyds. The morphologies and particle diameters of the resins were determined by transmission electron microscope (TEM) [FEI Tecnai G2 F20 S-TWIN (USA)], the sample was dispersed in ethyl alcohol by ultrasound for 15 min, and two drops of the solution were placed onto TEM grids prior to image capture. The thermal behavior of samples was studied by thermogravimetric (TG) analysis [Perkin Elmer TGA-4000, (USA)] at the heating rate of 10 °C/min under N₂ atmosphere in the range of 20~600 °C.

A copper sheet (5.0 cm×8.0 cm×0.2 mm) was used as a substrate after it was polished with 800-grit emery paper and scrubbed with absolute ethanol for evaluating flexibility, gloss, adhesion, hardness, water, alkali and acid resistances. The ZSO oil-based alkyd resin modified by epoxy resin on the copper sheet was prepared by coating method and cured at room temperature prior to measurements. The thickness of films was 0.3 mm. The pencil hardness of films was measured with the help of pencil hardness tester. Film hardness was performed with lead pencils graded from 6B to 6H as per ASTM D 3363. The adhesion of the film was characterized using the crosscut adhesion method (ASTM D 3359), which was related to the removal of the coating from the test area. The flexibility was tested with a mandrel tester. The films were bent over a 6.25-mm-diameter mandrel through 180° and examined for any damage, detachment or cracking of the film according to the standard procedure as per ASTM D 1737. Gloss was measured at an angle of 60° (ASTM D 523) with a gloss meter. The coating resistance to distilled water, NaCl, NaOH and HCl was investigated at 20±2 °C for 24 h. The films were visually observed. (1—completely unaffected, 2—unaffected, slightly color changed, 3—film faintly swelled, 4—film slightly cracked and blistered, 5—film cracked and removed).

Results and discussion

Physical and chemical properties of ZSO

Crude *Z. bungeanum* seed oil has darker color, higher acid value and higher gum content, which has adverse effects on the synthesis of alkyd resin. The physical and chemical properties of purified ZSO are presented in Table 2. Compared with crude ZSO, the acid value of purified ZSO was reduced from 74 mg KOH/g to 3 mg KOH/g. The iodine value (iodine value = 142 g I₂/100 g oil) is an indication of the degree of unsaturation which is the most crucial to its application in surface coating. This shows that a thin layer of ZSO is not capable of drying into a hard film by the process of auto-oxidation on exposure. However, due to the higher degree of unsaturation compared to palm oil and soybean oil, the bio-resin from ZSO can be cured more effectively.

Table 2 Physical and chemical properties of *Zanthoxylum bungeanum* seed oil (ZSO)

Properties	Crude ZSO	Purified ZSO
Physical state	Light brown liquid	Pale yellow liquid
Specific gravity at 30 °C	0.953	0.967
Viscosity, mm ² /s at 40 °C	31	40
Saponification value, mg KOH/g oil	200	200
Acid value, mg KOH/g oil	74	3
Iodine value, g I ₂ /100 g oil	142	142

Effect of different catalytic systems on alcoholysis

In alcoholysis stage, the end point of reaction was determined by a 95% ethanol tolerance test. In this study, NaOH and LiOH were selected as catalyst, respectively. The time required for ‘end point’ of each catalyzed reaction is shown in Fig. 1a, b. The determination of end point is useful in preventing prolonged alcoholysis reaction time that can lead to aggravation of side reactions, such as formation of polyglycerols. As shown in Fig. 1, the LiOH and NaOH as catalyst significantly reduced the reaction time. The lower catalyst content and a relatively short reaction time are conducive to improve the conversion and prevent the aggravation of side reactions. It is obvious that 0.04% LiOH exhibited a relatively shorter ‘end point’ time (20 min), while 0.10% NaOH can be required at the same ‘end point’ time.

Effect of epoxy resin ratio on properties of waterborne alkyd resin

Physical properties of epoxy-modified waterborne alkyd resin coating

In this work, the physical properties of epoxy-modified waterborne alkyd resin are shown in Table 3. The flexibility of the films via the bending of panel at 180° but no cracking, damage or peeling was observed. This indicated the excellent flexibility of

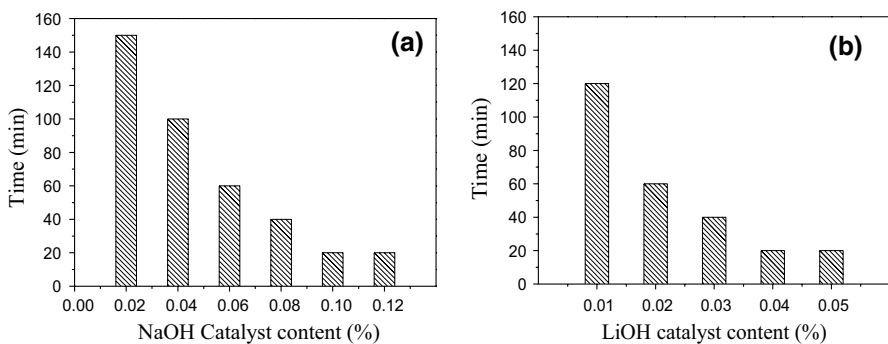


Fig. 1 Effect of different catalysts on alcoholysis

Table 3 Physical properties of epoxy-modified waterborne alkyd resin

Epoxy resin ratio (% by weight)	WA	EWA1	EWA2	EWA3	EWA4	EWA5
	0	4.6	8.8	12.7	16.4	19.7
^a Resin appearance	T	T	T	T	T	T
Solid content/wt%	45	45	45	45	45	45
^b Set-to-touch time/h	1.5	1.5	1.2	1.2	1	1
^b Solid drying time/h	10	6	5.5	5	5	6
^c Pencil hardness	B	HB	H	H	2H	2H
Flexibility	Pass	Pass	Pass	Pass	Pass	Pass
^d Adhesion/grade	4	4	4	5	5	5
Gloss(60°)	143.7	129.3	129.4	124.6	125.0	120.8

^aT=transparent, NT=non-transparent

^b2%wt waterborne drier was added

^cPencil hardness: 4B < 3B < 2B < B < HB < H < 2H

^dAdhesion grade: 0 < 1 < 2 < 3 < 4 < 5, only 4 or 5 grade is eligible

the films. This is mainly due to the oil acted as a permanent plasticizer. The gloss property which caused good film forming and leveling is important in esthetic or decorative appearance. As presented in Table 3, since the glosses are influenced by the roughness and the texture of the film, the excellent gloss obtained for all synthesized resins at 60° confirmed homogeneous drying and good compatibility of the reactants. The adhesion of the films to the substrate was characterized by using the crosshatch adhesion method. A rating of 5 indicated no coating removal from the test area, while a rating of 0 indicated the removal of more than 65% of the coating. The test results showed that all synthesized alkyd resins have good adhesion properties from Table 3, most likely due to polar terminal hydroxyl and ether bonds which could bring strong cohesion between resin and substrate. The hardness of the films improved significantly by modifying epoxy resin. This can be attributed to high cross-linking of alkyd resin with epoxy resin and rigid six-membered ring structure from epoxy resin.

Chemical resistance of epoxy-modified waterborne alkyd resin coating

As shown in Table 4, the water and acid resistance of a coating are very important to ensure high durability during use. Generally, the synthesized alkyds were unaffected by the distilled water and acidic solution, except for a slight color change. When testing the NaOH resistance, it was observed that the coated films of all alkyds were strongly affected by alkaline environment, causing some color change, swelling and blistering. The poor alkaline resistance of these films was attributed to the presence of alkali hydrolysable ester group in alkyd resin backbones. It was observed that epoxy-modified waterborne alkyd resin has a better resistance in the medium compared with unmodified alkyd resin. The better water, alkaline and acidic resistance of epoxy-modified waterborne alkyd resin could be explained by the high cross-link density of their networks, which decreased the chance for chemical medium

Table 4 Chemical resistance of epoxy-modified waterborne alkyd resin

Chemical medium	WA	EWA1	EWA2	EWA3	EWA4	EWA5
Distilled water	2	2	2	1	1	1
2 wt% HCl	3	2	2	2	2	2
2 wt% NaOH	5	4	4	3	3	3
2 wt% NaCl	2	2	2	1	1	1
Xylene	4	4	4	4	3	3
Acetone	3	3	3	3	2	2

1—completely unaffected, 2—unaffected, slightly color changed, 3—film faintly swelled, 4—film slightly cracked and blistered, 5—film cracked and removed

penetrating the inner parts of the film. Xylene was used to evaluate the nonpolar solvent resistance, and polar solvents, such as acetone, are regularly used to estimate the prepared resin. If the films are less affected by chemical medium, it means that the solvent molecules find it harder to penetrate the cross-linked network indicating less free volume.

The properties of their (epoxy-modified waterborne alkyd resin) blends with HMMM

Hexamethoxy methyl melamine (HMMM) is usually used as a cross-linking agent blended with other resins, such as oil-modified alkyd resin, acrylic resin and epoxy resin. The cross-linking reaction between the film-forming resin and melamine resin is very complex. The principal function is to cross-link the molecule of the primary film-forming vehicle in a coating, in order to build a three-dimensional polymer network with high performance properties. The cross-linking reaction is the condensation of HMMM (such as methoxymethyl and hydroxymethyl groups on HMMM) with the functional group (hydroxyl, carboxy groups) of the resin/polymer to form the polymer–melamine cross-link [37]. In order to improve the performance of modified alkyds (EWA), EWA4 was used to blend with HMMM at different ratios by weight. The physico-chemical properties of cured film are presented in Table 5. EWA4-H3 and EWA4-H4 exhibited shorter curing time compared to EWA4-H1 and EWA4-H2. The pencil hardness tended to increase as curing agent HMMM increased. This could be explained by the fact that the resins synthesized with a high number of HMMM had a higher degree of branching and molar mass. The results of chemical resistance of blend resins are too shown in Table 5. Generally, the synthesized alkyds were unaffected by the distilled water and acidic solution, except for a slight color change. The performance of EWA4-H3 (EWA4:HMMM (3/1)) is the best than others.

FT-IR analysis

The FT-IR spectra of ZSO, ZSO monoglyceride and alkyd resin are shown in Fig. 2, respectively. The broad single absorption peak at 3472 cm^{-1} confirmed the

Table 5 Physical properties of EWA and their blending with HMMM coating

Sample	EWA4-H1	EWA4-H2	EWA4-H3	EWA4-H4	EWA4-H5
EWA4:HMMM (w/w)	1:1	2:1	3:1	4:1	5:1
Solid drying time/min (80 °C)	40	30	20	20	20
Solid drying time/min(100 °C)	20	20	15	15	15
^a Pencil hardness	2H	2H	3H	4H	4H
Flexibility	Pass	Pass	Pass	Pass	Pass
Adhesion/grade ^b	5	5	5	5	5
Distilled water ^c	1	1	1	2	2
2 wt% HCl ^c	1	1	1	1	1
2 wt% NaOH ^c	2	2	2	3	3
2 wt% NaCl ^c	1	1	1	2	2

^aPencil hardness: 4B < 3B < 2B < B < HB < H < 2H < 3H

^bAdhesion grade: 0 < 1 < 2 < 3 < 4 < 5, only 4 or 5 grade is eligible

^c1—completely unaffected, 2—unaffected, slightly color changed, 3—film faintly swelled, 4—film slightly cracked and blistered, 5—film cracked and removed

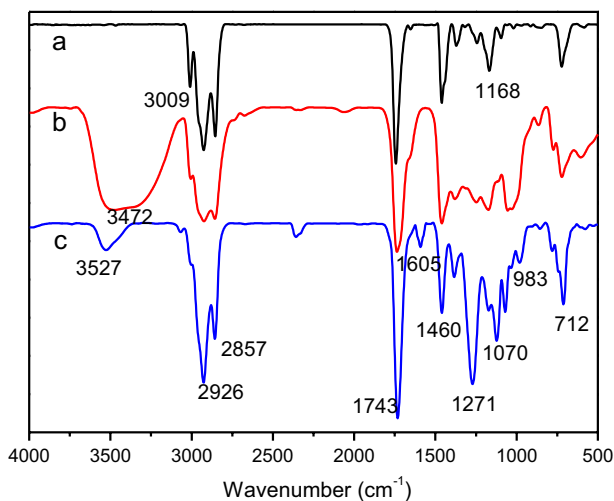


Fig. 2 FT-IR spectra of ZSO (a), ZSO monoglyceride (b) and alkyd resin (c)

presence of hydroxyl group in the monoglyceride of ZSO. The FT-IR spectra of the ZSO-based alkyd resin reflect an intensity reduction in the absorption band of the hydroxyl terminals, indicating the occurrence of esterification with ZSO. The peak at 3009 cm^{-1} corresponded to olefinic C–H stretching due to the unsaturated fatty acids of ZSO. The peak observed at 2926 and 2857 cm^{-1} is attributed asymmetric and symmetric stretching vibrations of CH_2 group, respectively. The bands at 1467 and 1377 cm^{-1} are assigned to CH_3 bending. The stretching vibration of the ester carbonyl group is observed at 1743 cm^{-1} . In the FT-IR spectrum of the

alkyd resins, the aromatic C=C stretching of phthalic anhydride was observed at 1650–1450 cm^{-1} . The band at 712 cm^{-1} is assigned to the C–H bending vibration of the benzene ring.

The FT-IR spectra of epoxy resin and epoxy-modified alkyd resins are shown in Fig. 3, respectively. The broad bands observed between 3461 and 3515 cm^{-1} are attributed to the hydroxyl group stretching vibration. The peaks at 1608 cm^{-1} , 1500 cm^{-1} and 1456 cm^{-1} are skeleton vibration of the benzene ring. The peak observed at 1728 cm^{-1} is attributed to the stretching vibration of the ester carbonyl group. It was found in Fig. 3e that the absorption peaks of epoxy groups at 910 cm^{-1} disappeared compared with Fig. 3d, indicating some modification with ZSO-based alkyd resin through the ring opening of epoxy resin. Therefore, it has also been confirmed that the epoxy-modified alkyd resins have been successfully synthesized.

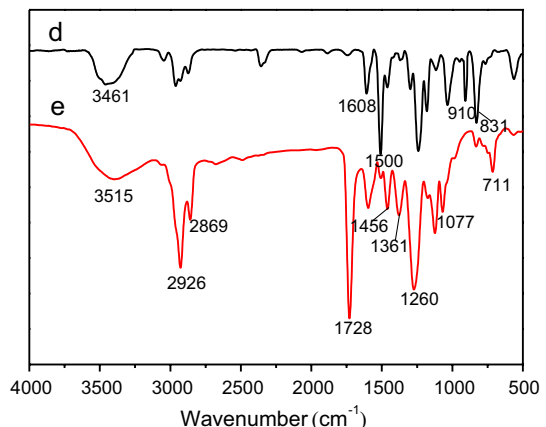
Particle size analysis

The particle distribution profile of the waterborne alkyd resin (WA) and epoxy-modified waterborne alkyd resins (EWA) is presented in Fig. 4. The average diameter of WA (a) and EWA (b) is approximately 30.94 and 92.04 nm, and the polydispersity index is 0.294 and 0.520, respectively. It indicated that the emulsion average particle size of EWA is larger than WA since the epoxy resin was incorporated into the alkyd resin by polyesterification. TEM images of the WA and EWA are presented in Fig. 5. The TEM micrographs of the WA (a) and EWA (b) showed spherical shapes and good dispersion of the particles without agglomeration.

Thermal properties

Thermal stability is a very significant property of the films, and the TGA curves of WA, EWA and EWA-H3 are shown in Fig. 6. The films of WA, EWA and EWA-H3 were investigated using the thermogravimetric analysis in nitrogen atmosphere, at a

Fig. 3 FT-IR spectra of epoxy resin (d) and epoxy-modified alkyd resin (e)



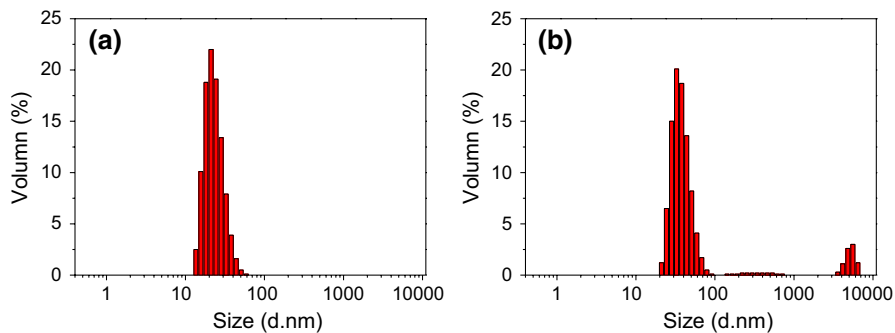


Fig. 4 Particle size distribution of WA (a) and EWA (b)

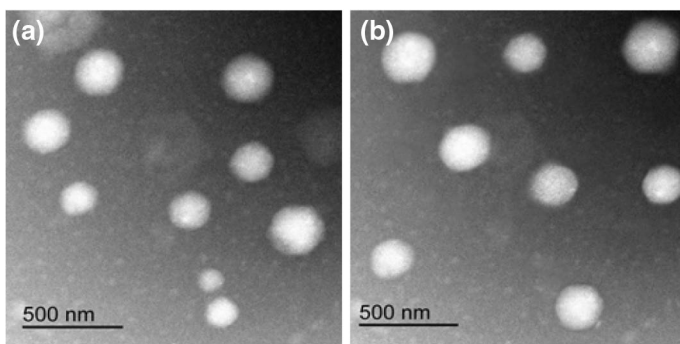
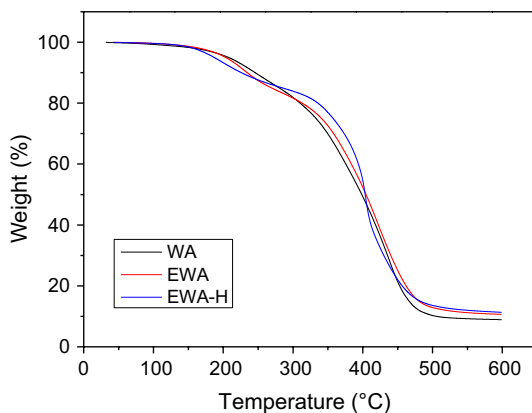


Fig. 5 TEM images of WA (a) and EWA (b)

Fig. 6 TG curves of WA, EWA and EWA-H



heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. It is worth mentioning that the thermal behavior of the different alkyd resins was similar. This indicates that different alkyd resin samples have the same mechanism of degradation and molecular structure. Each curve shows three stages of degradation. The first stage of weight loss mainly resulted from

Table 6 Thermal behavior data of the alkyd resins

Alkyd resin	T ₁₀ (°C)	T ₄₀ (°C)	Residue at 550 °C (%)
WA	246	376	9.23
EWA	234	383	11.21
EWA-H	226	394	11.99

evaporation of the high boiling solvent. The prominent second stage was decomposition of the C–O and C–C linkages, which was the main weight loss stage. It is observed that EWA-H has good thermal stability at 300~400 °C compared with WA and EWA. The third stage was due to degradation of the char residue. From Table 6, we can see that the temperature corresponding to a 40% weight loss of WA, EWA and EWA-H was 376, 383 and 394 °C, respectively. This could be explained by the fact that the high cross-linking of alkyd resin with epoxy resin and HMMM.

Conclusion

In present work, we have developed the epoxy-modified waterborne alkyd resins (EWA) from *Z. bungeanum* seed oil by three-step approaches including alcoholysis, polyesterification and neutralization reaction. The epoxy resin and HMMM in the prepared resin play an important role in altering the properties of these resins. The blends exhibited superior performances in terms of drying time, hardness, chemical resistance, adhesion, flexibility and thermal stability. The TEM micrographs of the resins showed spherical shapes and good dispersion of the particles without agglomeration. The research revealed that ZSO can be utilized as a potential source of raw material for the alkyd coating industry.

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References

1. Soucek M, Johansson MKG (2012) Alkyds for the 21st century. *Prog Org Coat* 73(4):273. <https://doi.org/10.1016/j.porgcoat.2012.01.004>
2. Hofland A (2012) Alkyd resins: from down and out to alive and kicking. *Prog Org Coat* 73(4):274–282. <https://doi.org/10.1016/j.porgcoat.2011.01.014>
3. Murillo EA, Lopez BL, Brostow W (2012) Thermal, hydrolytic, anticorrosive, and tribological properties of alkyd–silicone hyperbranched resins with high solid content. *J Appl Polym Sci* 124(5):3591–3599. <https://doi.org/10.1002/app.34611>
4. Dubrulle L, Lebeuf R, Fressancourt-Collinet M, Nardello-Rataj V (2017) Optimization of the vegetable oil composition in alkyd resins: a kinetic approach based on FAMES autoxidation. *Prog Org Coat* 112:288–294. <https://doi.org/10.1016/j.porgcoat.2017.06.021>

5. Gandini A, Lacerda TM, Carvalho AJF, Trovatti E (2016) Progress of polymers from renewable resources: furans, vegetable oils, and polysaccharides. *Chem Rev* 116(3):1637–1669. <https://doi.org/10.1021/acs.chemrev.5b00264>
6. Chiplunkar PP, Pratap AP (2016) Utilization of sunflower acid oil for synthesis of alkyd resin. *Prog Org Coat* 93:61–67. <https://doi.org/10.1016/j.porgcoat.2016.01.002>
7. Essien EE, Umoren SA, Effiong EE (2016) Synthesis and characterization of *Luffa cylindrica* fatty acids-based alkyd resins. *Res Chem Intermed* 42(3):2177–2189. <https://doi.org/10.1007/s11164-015-2141-z>
8. Gogoi P, Das D, Sharma S, Dolui SK (2015) Synthesis and characterization of *Jatropha curcas* oil-based alkyd resins and their blends with epoxy resin. *J Renew Mater* 3(2):151–159. <https://doi.org/10.7569/JRM.2014.634129>
9. Iseri-Caglar D, Basturk E, Oktay B, Kahraman MV (2014) Preparation and evaluation of linseed oil based alkyd paints. *Prog Org Coat* 77(1):81–86. <https://doi.org/10.1016/j.porgcoat.2013.08.005>
10. Bhat SI, Ahmad S (2018) Castor oil-TiO₂ hyperbranched poly (ester amide) nanocomposite: a sustainable, green precursor-based anticorrosive nanocomposite coatings. *Prog Org Coat* 123:326–336. <https://doi.org/10.1016/j.porgcoat.2018.06.010>
11. Ataei S, Khorasani SN, Torkaman R, Neisiany RE, Koochaki MS (2018) Self-healing performance of an epoxy coating containing microencapsulated alkyd resin based on coconut oil. *Prog Org Coat* 120:160–166. <https://doi.org/10.1016/j.porgcoat.2018.03.024>
12. Selim MS, Shenashen MA, Elmarakbi A, El-Saeed AM, Selim MM, El-Safty SA (2017) Sunflower oil-based hyperbranched alkyd/spherical ZnO nanocomposite modeling for mechanical and anticorrosive applications. *RSC Adv* 7(35):21796–21808. <https://doi.org/10.1039/C7RA01343D>
13. Naylor RL, Higgins MM (2018) The rise in global biodiesel production: implications for food security. *Glob Food Secur* 16:75–84. <https://doi.org/10.1016/j.gfs.2017.10.004>
14. Ong HR, Ramli R, Khan MMR, Yunus RM (2016) The influence of CuO nanoparticle on non-edible rubber seed oil based alkyd resin preparation and its antimicrobial activity. *Prog Org Coat* 101:245–252. <https://doi.org/10.1016/j.porgcoat.2016.08.017>
15. Bora MM, Gogoi P, Deka DC, Kakati DK (2014) Synthesis and characterization of yellow oleander (*Thevetia peruviana*) seed oil-based alkyd resin. *Ind Crops Prod* 52:721–728. <https://doi.org/10.1016/j.indcrop.2013.11.012>
16. Xu X, Chen L, Guo J, Cao X, Wang S (2017) Synthesis and characteristics of tung oil-based acrylated-alkyd resin modified by isobornyl acrylate. *RSC Adv* 7(48):30439–30445. <https://doi.org/10.1039/C7RA02189E>
17. Yin X, Xu X, Zhang Q, Xu J (2018) Rapid determination of the geographical origin of Chinese red peppers (*Zanthoxylum Bungeanum* Maxim) based on sensory characteristics and chemometric techniques. *Molecules* 23(5):1001/1–1001/11. <https://doi.org/10.3390/molecules23051001>
18. Yatigala NS, Bajwa DS, Bajwa SG (2018) Compatibilization improves performance of biodegradable biopolymer composites without affecting UV weathering characteristics. *J Polym Environ* 26(11):4188–4200. <https://doi.org/10.1007/s10924-018-1291-7>
19. Yang XF, Tang MM, Liu YY, Ma YM (2018) Compound of mannich base corrosion inhibitor. *Surf Technol* 47(5):77–82. <https://doi.org/10.16490/j.cnki.issn.1001-3660.2018.05.012>
20. Lei R, Ma YM, Yang XF (2019) Preparation of *Zanthoxylum bungeanum* seed oil-based waterborne alkyd resin based on postconsumer PET bottles. *Paint Coat Ind* 49(4):34–40. <https://doi.org/10.12020/j.issn.0253-4312.2019.4.34>
21. Wang W, Lu P, Tang H, Ma Y, Yang X (2017) A *Zanthoxylum bungeanum* seed oil-based carbon solid acid catalyst for the production of biodiesel. *New J Chem* 41(17):9256–9261. <https://doi.org/10.1039/C7NJ01271C>
22. Ahmad F, Ahmad I, Osman SM (1980) The C16 monoenoic acid of *Zanthoxylum alatum* seed oil. *J Am Oil Chem Soc* 57(7):224–225. <https://doi.org/10.1007/BF02673945>
23. Buyukyonga ON, Akgun N, Acar I, Guclu G (2017) Synthesis of four-component acrylic-modified water-reducible alkyd resin: investigation of dilution ratio effect on film properties and thermal behaviors. *J Coat Technol Res* 14(1):117–128. <https://doi.org/10.1007/s11998-016-9835-z>
24. Elrebii M, Kamoun A, Boufi S (2015) Waterborne hybrid alkyd-acrylic dispersion: optimization of the composition using mixture experimental designs. *Prog Org Coat* 87:222–231. <https://doi.org/10.1016/j.porgcoat.2015.06.006>
25. Bat E, Guenduez G, Kisakuerek D, Akhmedov IM (2006) Synthesis and characterization of hyperbranched and air drying fatty acid based resins. *Prog Org Coat* 55(4):330–336. <https://doi.org/10.1016/j.porgcoat.2006.01.005>

26. Radoman TS et al (2015) Effect of surface modified TiO₂ nanoparticles on thermal, barrier and mechanical properties of long oil alkyd resin-based coatings. *Express Polym Lett* 9(10):916–931. <https://doi.org/10.3144/expresspolymlett.2015.83>
27. Gumfekar SP, Kunte KJ, Ramjee L, Kate KH, Sonawane SH (2011) Synthesis of CaCO₃-P(MMA-BA) nanocomposite and its application in water based alkyd emulsion coating. *Prog Org Coat* 72(4):632–637. <https://doi.org/10.1016/j.porgcoat.2011.07.005>
28. Gao J, Wu X, Tian C (2013) Waterborne epoxy/alkyd resin insulation coatings modified by siloxane. *Appl Mech Mater* 380–384:4340–4343. <https://doi.org/10.4028/www.scientific.net/AMM.380-384.4340>
29. Gogoi P, Boruah M, Bora C, Dolui SK (2014) Jatropha curcas oil based alkyd/epoxy resin/expanded graphite (EG) reinforced bio-composite: evaluation of the thermal, mechanical and flame retardancy properties. *Prog Org Coat* 77(1):87–93. <https://doi.org/10.1016/j.porgcoat.2013.08.006>
30. Patil DM, Phalak GA, Mhaske ST (2017) Synthesis of bio-based epoxy resin from gallic acid with various epoxy equivalent weights and its effects on coating properties. *J Coat Technol Res* 14(2):355–365. <https://doi.org/10.1007/s11998-016-9853-x>
31. Assanvo EF, Gogoi P, Dolui SK, Baruah SD (2015) Synthesis, characterization, and performance characteristics of alkyd resins based on Ricinodendron heudelotii oil and their blending with epoxy resins. *Ind Crops Prod* 65:293–302. <https://doi.org/10.1016/j.indcrop.2014.11.049>
32. Charamzova I, Vinklerek J, Honzicek J (2018) Effect of primary driers on oxidative drying of high-solid alkyd binder: investigation of thickness effects by mechanical tests and infrared spectroscopy. *Prog Org Coat* 125:177–185. <https://doi.org/10.1016/j.porgcoat.2018.09.001>
33. Ma S, Qian J, Zhuang Q, Li X, Kou W, Peng S (2018) Synthesis and application of water-soluble hyperbranched polyester modified by trimellitic anhydride. *J Macromol Sci Part A Pure Appl Chem* 55(5):414–421. <https://doi.org/10.1080/10601325.2018.1453261>
34. Guclu G (2010) Alkyd resins based on waste PET for water-reducible coating applications. *Polym Bull* 64(8):739–748. <https://doi.org/10.1007/s00289-009-0166-4>
35. Acar I, Bal A, Guclu G (2013) The use of intermediates obtained from aminoglycolysis of waste poly(ethylene terephthalate) (PET) for the synthesis of water-reducible alkyd resin. *Can J Chem* 91(5):357–363. <https://doi.org/10.1139/cjc-2012-0370>
36. Jang YJ, Ma YM, Yang XF (2017) Synthesis and properties of water-soluble alkyd resin based on *Zanthoxylum bungeanum* seed oil. *Paint Coat Ind* 47(9):6–11. <https://doi.org/10.12020/j.issn.0253-4312.2017.9.11>
37. Dhoke SK, Sinha TJM, Dutta P, Khanna AS (2008) Formulation and performance study of low molecular weight, alkyd-based waterborne anticorrosive coating on mild steel. *Prog Org Coat* 62(2):183–192. <https://doi.org/10.1016/j.porgcoat.2007.10.008>

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