Rubber Seed Oil Modified with Maleic Anhydride and Fumaric Acid and Their Alkyd Resins as Binders in Water-Reducible Coatings

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ABSTRACT: Rubber seed oil (RSO) was modified with different amounts of maleic anhydride, and RSO alkyds (50% oil length) were modified to various extents by the incorporation of different amounts of maleic anhydride and fumaric acid. All the resins were evaluated as water-reducible binders. Modification with maleic anhydride increased the acid and saponification values of RSO but reduced the iodine value. RSO modified with maleic anhydride exhibited lower amounts of volatile organic compounds (<20 g/L) than the corresponding RSO alkyds (34–87 g/L). The alkyd samples were superior to the modified RSO in chemical resistance. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3256–3259, 2003

Key words: resins; coatings; copolymerization; modification; monomers

INTRODUCTION

Oils used in surface coatings belonging to the linolenic and conjugated acid groups, such as linseed, oiticica, safflower, tall, perilla, and tung oils, possess pronounced drying abilities.[1–3] These oils owe their industrial value to their ability to dry into hard, solid films after being applied as thin layers. In many applications, the natural forms of the oils do not fulfill the technical requirements of the film properties, such as resistance to weathering, chemicals, acids, water, alkalis, and abrasion.[4] However, because of developments in the surface coating industry, stringent end-use requirements, such as faster drying and improved color, have necessitated special treatments of oils. Following the development of the functionality concept,[5] various forms of modifications (e.g., the incorporation of a drying oil into a polyester system to give alkyd resins, thermal polymerization, and the modification of an oil with monomers possessing double bonds) have been introduced to fulfill these stringent requirements.[6–8] Castor oil and lesquerella oil, which are naturally nondrying, are now transformed into drying oils through modification by dehydration.[9–12] This development in coating technology has given rise to modern-day hard, oil-soluble synthetic resins with performance characteristics far superior to those of natural resins.

Copolymer vegetable oils, synthesized via vinyl monomer modification of vegetable oils, are interesting both chemically and from the viewpoint of practical applications. They are widely used in certain specialty gloss coatings for paper and in surface conditioning primers for masonry; they also have potential in interior gloss and semigloss enamels.[8]

In this study, rubber seed oil (RSO) was modified by treatments with maleic anhydride and fumaric acid and then used in the preparation of phthalate alkyds. The use of RSO in the production of alkyd resins suitable as binders in solvent-borne and water-reducible coatings has been studied extensively in our laboratory.[13–15] It was hoped that the successful vinyl monomer modification of RSO and its alkyds would improve the quality of their films and expand the frontiers of applications of RSO as a technical oil.

EXPERIMENTAL

Materials

RSO, extracted by solvent extraction, was obtained from the Rubber Research Institute of Nigeria (Benin City, Nigeria). The fatty acid composition of the oil is given in Table I.[13] Laboratory-grade phthalic anhydride, maleic anhydride, fumaric acid, glycerol, triethylamine, and xylene were obtained from British Drug House (Poole, England).

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TABLE I
Major Fatty Acid Composition of RSO

Fatty acid	Composition (%)
Saturated	
$C_{16:0}$ palmitic acid	10.2
$C_{18:0}$ stearic acid	8.7
Total	18.9
Unsaturated	
$C_{18:1}$ oleic acid	24.6
$C_{18:2}$ linoleic acid	39.6
$C_{18:3}$ linolenic acid	16.3
Total	80.5
Others	0.6

Methods

Monomer modification of RSO

Five samples of RSO modified with maleic anhydride were prepared by the heating of RSO (at 230°C under reflux) with (A) 2, (B) 5, (C) 10, (D) 15, and (E) 20% maleic anhydride (w/w) for about 1.5 h. The properties of the modified RSO samples were evaluated according to IUPAC methods.[16] Each sample of the modified RSO was heated with triethylamine (10% w/w) at 80°C and then evaluated as a binder for water-reducible coatings.[14]

Preparation of the monomer-modified RSO alkyds

An alkyd resin with a 50% oil length was formulated with RSO, glycerol, and phthalic anhydride and modified to various degrees with maleic anhydride (samples M1–M5 in Table II) and fumaric acid (samples F1–F5 in Table III). All the alkyds were formulated to an alkyd constant of about 1.0. The reactions were carried out in a 2-L, three-necked, round-bottom flask fitted with a motorized stirrer and a Dean–Stark apparatus carrying a water-cooled condenser. An inert atmosphere was created in the flask by nitrogen gas bubbling, and the temperature of the reaction ranged between 230 and 250°C. Xylene (10% w/w) was employed as the cooking solvent.

In a typical reaction, RSO and a catalyst (lead II oxide) were heated to 200°C, and glycerol was added. The temperature was quickly raised to 230–250°C, and heating was continued until the reaction mixture was soluble in anhydrous methanol (1:3 w/w). It was allowed to cool to about 120°C, phthalic anhydride was added, and the temperature was quickly raised to 250°C for the polycondensation reaction. The efflux was drained into the Dean–Stark apparatus, in which xylene was separated from the water of condensation and returned to the reaction flask through an overflow point. The progress of the reaction was monitored by the determination of the acid values of aliquots of the reaction mixture until an acid value of 60–80 mg of KOH/g was reached. The setup was allowed to cool down to about 120°C, and the calculated amount of maleic anhydride or fumaric acid was added and processed to an acid value of about 40 mg of KOH/g at 200°C. The required quantity of triethyl amine was added at about 100°C.

TABLE II
Formulation of Maleic-Anhydride-Modified RSO Alkyd Resins

Ingredient	M1	M2	M3	M4	M5
RSO (g)	115.13	115.13	115.13	115.13	115.13
Glycerol (g)	68.99	66.75	63.72	60.05	56.16
Phthalic anhydride (g)	89.45	86.72	82.15	77.59	73.02
Maleic anhydride	1.83	4.56	9.13	13.69	31.69
Triethylamine (%)	10	10	10	10	10

TABLE III
Recipe for Fumaric-Acid-Modified RSO Alkyd Resins

Ingredient	F1	F2	F3	F4	F5
RSO (g)	115.13	115.13	115.13	115.13	115.13
Phthalic anhydride (g)	89.45	86.72	82.15	77.59	73.02
Glycerol (g)	68.99	66.75	63.72	60.05	56.16
Fumaric acid (g)	1.83	4.56	9.13	13.69	31.69
Triethylamine (g)	30.00	30.37	30.80	31.24	31.69

Preparation of the coatings

Samples A–E (RSO modified with maleic anhydride), M1–M5 (RSO alkyds modified with maleic anhydride), and F1–F5 (RSO alkyds modified with fumaric acid) were used to prepare 60% (w/w) solution with propan-2-ol. The solution was made slightly alkaline by neutralization with a 25% ammonia solution. Cobalt and manganese dryers were added first and were followed by water (70% w/w) and a surfactant. The resultant solution was stirred vigorously and then applied as thin layers on glass plates, which were baked in an oven at 100°C for 1 h. The physicochemical properties and chemical resistance of the films were determined according to ASTM standard methods.

RESULTS AND DISCUSSION

Physical and chemical properties of the copolymer RSO

Some physicochemical properties of RSO modified with maleic anhydride (samples A–E) are compared with those of unmodified RSO in Table IV. The results show that the color of RSO is unaffected by modification. Acid and saponification values increase as the percentage of maleic anhydride modification increases. However, the reverse is the case for the iodine value. The iodine value, a measure of unsaturation, ranges from 143.21 for sample A to 123.27 for sample E. These values are lower than

TABLE IV
Some Physicochemical Properties of Monomer-Modified RSO

Property	Crude RSO	Monomer-modified RSO				
		A	B	C	D	E
Color	Brown-yellow	Brown-yellow	Brown-yellow	Brown-yellow	Brown-yellow	Brown-yellow
Acid value (mg of KOH/g)	22.80	24.50	31.19	49.01	61.85	75.81
Saponification value (mg of KOH/g)	139.01	139.14	144.05	161.04	170.84	178.48
Iodine value (g of I_2/100 g)	146.55	143.21	139.35	135.72	130.60	123.27
Nonvolatile matter (%)		99.53	99.06	99.40	98.74	98.32
VOC (g/L)		8.6	8.5	8.6	17.4	17.3

TABLE V
Physicochemical Properties of Maleic-Anhydride-Modified RSO Alkyds

Property	M1	M2	M3	M4	M5
Color	Brown-yellow	Brown-yellow	Brown-yellow	Brown-yellow	Brown-yellow
Acid value (mg of KOH/g)	5.58	7.74	10.36	12.50	14.34
Saponification value (mg of KOH/g)	295.9	292.03	291.93	269.26	246.53
Iodine value (g of I_2/100 g)	79.96	79.21	78.56	77.43	78.13
Nonvolatile matter (%)	94.64	96.09	95.08	90.08	93.23
VOC (g/L)	51.6	34.0	43.0	87.7	60.6

the iodine value of 146.55 of the unmodified RSO. Although the chemistry of the reaction between maleic anhydride and vegetable oil is not yet clearly understood, it is believed that during the modification of unconjugated oils such as RSO with monomers containing double bonds, a hydrogen atom could be abstracted from a methylene group in the α position to a double bond as the fatty acid.[17] The resultant methylene radical may initiate a branching reaction or resonate with the existing unsaturation to introduce conjugation that can take part in a Diels–Alder reaction with maleic anhydride or fumaric acid. This is likely responsible for the decrease in the iodine values of samples A–E. Nonvolatile matter content ranges from 98.32% for sample E to 99.53% for sample A. This shows a marginal decrease with an increase in the percentage of maleic anhydride modification. The amount of volatile organic compounds (VOCs) is lower at a lower level of maleic anhydride modification than at higher levels. Therefore, on the premise of VOCs being the most desirable property, samples A–E can be regarded as suitable binders for the production of low-VOC, nonpolluting, and environmentally friendly coatings.

Physical and chemical properties of the alkyds

The performance properties of RSO alkyds modified by maleic anhydride are given in Table V. The alkyds are slightly darker in color than samples A–E. Their acid values increase with an increase in the percentage of maleic anhydride modification. Their saponification values range from 246.53 mg of KOH/g for sample M5 to 295.98 mg of KOH/g for sample M1; there is a decrease as the percentage of maleic anhydride content increases. The iodine values of the alkyds decrease marginally with an increase in the percentage of maleic anhydride content. The nonvolatile matter ranges from 90.08% for sample M4 to 96.09% for sample M2. The amount of VOCs ranges from 34 g/L for sample M2 to 87.7 g/L for sample M4. The percentages of nonvolatile matter obtained in this study are higher than the average of 70% obtained for solvent-borne RSO alkyds[18] but are lower than those of RSO modified with maleic anhydride. They are useful binder in low-VOC coatings. However, modified RSO seems to be superior to the alkyds in this respect.

Table VI shows the properties of RSO alkyds modified with fumaric acid. The color of the binder is unaffected by the modification. The acid value increases with the percentage of fumaric acid modifica-

TABLE VI
Properties of Fumaric-Acid-Modified RSO Alkyds (50% Oil Length)

Property	F1	F2	F3	F4	F5
Color	Brown	Brown	Brown	Brown	Brown
Acid value (mg of KOH/g)	5.84	11.65	12.77	28.51	30.43
Saponification value (mg of KOH/g)	299.63	329.09	287.63	275.57	264.72
Iodine value (Wijs; g of I_2/100 g)	69.08	50.39	70.21	56.26	62.56
Nonvolatile matter (%)	93.02	94.64	96.07	91.00	92.22
VOC (g/L)	60.2	51.0	34.4	78.3	69.2

TABLE VII
Chemical Resistance Test of Monomer-Modified RSO Films

Type of coating	Medium			
	Distilled water	NaCl (5% solution)	0.1 *M* H_2SO_4	0.1 *M* KOH
A	2	2	2	4
B	1	1	2	4
C	3	1	3	4
D	3	3	3	4
E	1	1	1	4

1 = no effect; 2 = wrinkle; 3 = blistering; 4 = removed film.

TABLE IX
Chemical Resistance of Fumaric-Acid-Modified RSO Alkyds

Alkyd types	Medium			
	Distilled water	NaCl (5% solution)	0.1 *M* H_2SO_4	0.1 *M* KOH
F1	1	1	1	5
F2	1	1	1	5
F3	1	1	1	5
F4	1	1	1	5
F5	1	1	1	5

1 = no effect; 2 = wrinkle; 3 = blistering; 5 = film removed.

tion. The saponification value decreases with an increase in the percentage of fumaric acid modification. This trend is similar to that found for M1–M5. The iodine value ranges from 50.59 for sample F2 to 70.21 for sample F3. The nonvolatile matter ranges from 91% for sample F4 to 96.07% for sample F3. The VOC values are 60.2, 51, 34.4, 78.3, and 69.2 g/L for samples F1–F5, respectively. These values are comparable to the VOC values found for RSO phthalate alkyds modified with maleic anhydride.

Chemical resistance of the coatings

Table VII shows the results for the chemical resistance of samples A–E. All the samples are highly susceptible to alkalis. Sample M5, containing 20% maleic anhydride, is highly resistant to acids, brine, and water. At lower percentages of maleic anhydride modification, the resistance of the films decreases, except for B and C, which exhibit excellent resistance to brine and water (only sample B)

The results listed in Table VIII show improvements in the chemical resistance of RSO alkyd films upon modification with maleic anhydride. Samples M1–M5 show excellent resistance to acids, brine, and water but poor resistance to alkalis.

Similarly, the results listed in Table IX show improvements in the chemical resistance of RSO alkyds to acids, brine, and water upon modification with fumaric acid. It can be deduced that these resins have potential for applications for which resistance to alkalis is not the main requirement.

TABLE VIII
Chemical Resistance of Maleic-Anhydride-Modified RSO Alkyds

Alkyd type	Medium			
	Distilled water	NaCl (5% solution)	0.1 *M* H_2SO_4	0.1 *M* KOH
M1	1	1	1	3
M2	1	1	1	4
M3	1	1	1	4
M4	1	1	1	4
M5	1	1	1	4

1 = no effect; 2 = wrinkle; 3 = blistering; 4 = film removed.

CONCLUSIONS

The results of this study show that the modification of RSO with monomers such as maleic anhydride and the modification of RSO alkyds with the same monomers greatly enhance the quality of RSO and its alkyds as binders in low-VOC, nonpolluting, and environmentally friendly coatings.

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References

1. Encyclopedia of Polymer Science and Technology; Mark, H. F.; Graylord, N. G.; Bikales, N. M., Eds.; Interscience: New York, 1966; Vol. 5, p 216.
2. The Lipid Handbook, 2nd ed.; Gunstone, F. D.; Harwood, J. L.; Padley, F. B., Eds.; Chapman & Hall: London, 1994; p 313.
3. Gardener, C. J Am Oil Chem Soc 1959, 36, 568.
4. Oil and Colour Chemists' Association of Australia Surface Coatings; Chapman & Hall: London, 1981; Vol. 1, p 1.
5. Carothers, W. H. Chem Rev 1931, 8, 353.
6. Kraft, W. M. J Am Oil Chem Soc 1959, 36, 583.
7. Killeffer, D. H. Ind Eng Chem 1938, 29, 1365.
8. Helmreich, R. F. J Am Oil Chem Soc 1959, 36, 523.
9. Thames, S. F.; Yu, H.; Wang, W. D. Ind Crops Prod 1997, 6, 169.
10. Thames, S. F.; Yu, H.; Wang, M. D.; Schuman, T. P. J Appl Polym Sci 1995, 58, 943.
11. Bolley, D. S. J Am Oil Chem Soc 1959, 36, 513.
12. Thames, S. F.; Yu, H, Wang, M. D.; Schuman, T. P. J Appl Polym Sci 1995, 58, 943.
13. Aigbodion, A. I.; Pillai, C. K. S. Prog Org Coat 2000, 38, 187.
14. Aigbodion, A. I.; Pillai, C. K. S. J Appl Polym Sci 2001, 79, 2431.
15. Aigbodion, A. I.; Okieimen, F. E. Eur Polym J 1996, 32, 1105.
16. Standard Methods for the Analysis of Oils, Fats and Derivatives; Paqout, C.; Haunfenne, A., Eds.; Blackwell Scientific: Oxford, 1987.
17. Hewitt, D. H.; Armitage, F. J. Oil Colour Chem Assoc 1946, 29(312), 109.
18. Aigbodion, A. I.; Okieimen, F. E. J Rubber Res Inst Sri Lanka 1995, 74, 31.