Studies on the Properties of Polyesters and Polyester Blends of Selected Vegetable Oils

I. O. IGWE,* O. OGBOBE

Department of Polymer and Textile Technology, Federal University of Technology, Owerri, Imo State, Nigeria

Received 25 November 1997; accepted 3 June 1999

ABSTRACT: Melon-seed and rubber-seed oils have been used in the synthesis of polyester resins. Results reveal that rubber-seed oil can completely be substituted for linseed and soyabean oils in the synthesis of both long and medium-oil–length polyester resins. Melon-seed oil was found to be a substitute for 50% of linseed oil and 50% of soyabean oil in the synthesis of long-oil–length polyester resins. It also substituted for 15% of linseed oil and 50% of soyabean oil in the synthesis of medium-oil–length polyester resins. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1441–1446, 2000

Key words: polyester; resin; vegetable oil; surface coatings

INTRODUCTION

There has been an increasing demand for conventional vegetable-drying oils worldwide, resulting in escalating costs of such drying oils as linseed and soyabean oils traditionally used in polyester resin synthesis. This, in turn, has led to increased costs of finished coating products such as paints and varnishes.

In the surface coatings industry, polyester resins have been able to hold their own because of the low cost of ingredients despite stiff competition arising from the use of low-cost vinyl polymers. Phthalic anhydride, the backbone of polyester resins, and polyhydric alcohols(polyols) are produced today in large quantities in industries. However, the production of conventional vegetable-drying oils has not kept pace with demand, leading to increasing costs.

Over the years, efforts have been geared towards arresting the increased costs of polyester ingredients. Fortunately for the drying oils, new vegetable oils are being discovered for polyester resin synthesis, and are documented in the literature. For example, Muralidharan et al.[1] have reported the utilization of rubber-seed and karinotta oils in the synthesis of air-drying, oil-modified polyester resins. Khandelwal and Gogte[2] prepared resins by the reaction of orange-seed oils with glycerol and phthalic anhydride. The gloss, drying time, and alkali resistance of polyester resin film were improved by the replacement of phthalic anhydride with 10% maleic anhydride. Mondo and Rao[3] prepared polyester resins of Jatropha curcas-seed oil by reacting the oil with various anhydrides and determining various parameters of the polyester resin films.

Abd El-Ghaffer[4] used apricot oil extracted from pits in several polyester resin coating formulations by esterification. The comparison tests with coconut oil-based formulations indicate that the Egyptian apricot oil can be used as a substitute in stoving nondrying short polyester resins.

From the literature, no polyester resin based on melon-seed oil has been reported. However, the industrial potential of rubber-seed oil in the coatings industry has been recognized.

Melon- and rubber-seed oils are triglycerides, and are composed of the glycerides of fatty acids. A typical vegetable oil has the general structure:

Correspondence to: I. O. Igwe.
* *Present address:* Department of Chemistry, University of Agriculture, Makurdi, Benue State, Nigeria.

Journal of Applied Polymer Science, Vol. 75, 1441–1446 (2000)

Table I Fatty Acid Composition (%) and Iodine Values of Rubber- and Melon-Seed Oils

Oil Seeds	Oil Content (%)	Oleic	Linoleic	Linolenic	Saturated Fatty Acids	Iodine Values (mgI/g)
Rubber[5,6]	49	21.9	38.2	24.3	15.3	137.7
Melon[7]	51	19	55.1	—	25.9	112.9

$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array}$$

where R_1, R_2, and R_3 stand for the hydrocarbon portions of the fatty acid chains.

Melon-seed oil is light yellow in color, while rubber-seed oil is reddish-brown; both can be obtained from their oil-bearing seeds by solvent extractions.

The chemical compositions of rubber- and melon-seed oils are shown in Table I.

Rubber-seed oil contains mostly linoleic and linolenic acids, with a small proportion of oleic acid and saturated fatty acids. The oil is a drying oil, and is characterized by the property of absorbing oxygen from the atmosphere and drying to an elastic skin (crosslinking) when exposed to air (oxygen) in a thin film. Melon-seed oil, on the other hand, contains largely linoleic and oleic acids, with an appreciable proportion of saturated acids. The oil is classified as a semidrying oil, and the drying process is slower.

The chemical compositions of the oils of rubber and melon seeds show that these oils have comparable levels of unsaturation as the oils (linseed and soyabean) presently used in the coatings industry.

Furthermore, no linolenic acid is found in melon-seed oil, while the amount in rubber-seed oil is small compared to that in linseed oil. Linolenic acid is known to be the cause of yellowing in polyesters prepared from highly unsaturated (oxidizing) oils such as linseed oil. It is, therefore, hoped that polyesters from melon- and rubber-seed oils will be more color retentive.

Both rubber- and melon-seed oils respond to the conventional refining processes of degumming, bleaching, and alkali refining. The optimum bleaching conditions of the oils using various clays, and the solvents that give high extraction yield of the oils, have been established.[8,9]

This article reports the use of rubber-seed oil—a drying oil—and melon-seed oil—a semidrying oil—as possible substitutes for linseed and soyabean oils in the synthesis of oil-modified polyester resins. Sixty percent long and fifty percent medium oil-length polyester resin samples were synthesized with each oil. In addition, polyester resin samples were prepared from blends of rubber-seed, melon-seed, linseed, and soyabean oils to find out the level of substitution of the conventional oils possible by rubber-seed and melon-seed oils. Physical blends of the synthesized polyester samples were made and compared with polyester resins from the oil blends.

Rubber plantations are grown in many tropical regions of the world. In Nigeria, the trees are grown in the Southern States occupying about 200,000 ha of land.[10] The rubber seeds, containing the oil, presently have no domestic/industrial utilization, and rot away at the various plantations each season. Newfield,[11] in his studies, had shown that the quantity of rubber seeds available in Nigeria are more than enough to meet the rubber-seed oil requirements of our oil paint industry and, consequently, has the potential of entering the global surface-coatings industrial market.

Melon seed (*Colocynthis vulgaris*, Shrad) is grown in many states of Nigeria. The total production of melon seeds in the country on the basis of 1992 census was put at 190,000 tons per year, a figure that can meet a paint industry melon-seed requirements for the production of melon-seed oil.

EXPERIMENTAL

The oils of melon (*Colocynthis vulgaris* Shrad) and rubber (*Hevea brasiliensis* (Kunth) Muell) seeds were obtained by solvent extraction. The linseed oil (*Linum usitatissimum* L.) and soyabean oil (*Glycine max* (L) Merr) were obtained in a refined state, and used without further purifi-

Table II Evaluation of Long-Oil Polyester Resins from Individual Oils and Their Blends

			Resistance To			
	Formulation	Drying Performance[a]	Distilled Water	2% H_2SO_4	2% NH_3	2% Na_2CO_3
L1	LSO	S	1	0	4	4
L2	SBO	S	2	0	4	4
L3	RSO	S	2	1	4	4
L4	MSO	NS	—	—	—	—
CB-L5	RSO : LSO (15 : 85)	S	2	1	4	4
CB-L6	RSO : LSO (50 : 50)	S	1	0	4	4
CB-L7	RSO : LSO (85 : 15)	S	2	0	4	4
CB-L8	MSO : LSO (15 : 85)	S	1	0	4	4
CB-L9	MSO : LSO (50 : 50)	S	1	1	4	4
CB-L10	MSO : LSO (85 : 15)	NS	—	—	—	—
CB-L11	RSO : SBO (15 : 85)	S	1	0	4	4
CB-L12	RSO : SBO (50 : 50)	S	1	1	4	4
CB-L13	RSO : SBO (85 : 15)	S	1	0	4	4
CB-L14	MSO : SBO (15 : 85)	S	1	0	4	4
CB-L15	MSO : SBO (50 : 50)	NS	—	—	—	—
						—
CB-L16	MSO : SBO (85 : 15)	NS	—	—	—	

[a] 24-h surface dry, followed by 48 h tack-free dry; S = satisfactory, NS = not satisfactory.
Abbreviations: CB = chemical blend; RSO = rubber-seed oil; MSO = melon-seed oil; LSO = linseed oil; SBO = soyabean oil.

cation. The melon- and rubber-seed oils were alkali refined using Cocks and Rede's method,[12] and bleached. The iodine values of the oils were determined using the ASTM method (D 1959-69, 1973).[13] All the polyester resin samples were prepared by the alcoholysis process in a three-necked reaction kettle equipped with a variable-speed stirrer. PbO(Litharge) was used as the alcoholysis catalyst (0.025% on oil). Glycerol with phthalic anhydride were used for the synthesis. All the resins were synthesized to low acid values, <10 mg KOH/g resin. The long and medium oil-length polyester resin samples were thinned to 64 and 38% solids with xylene, respectively.

Performance Evaluation of the Synthesized Polyester Resin Samples

Drying Tests

A weighed amount of each resin solution was mixed with the required amount of the metal naphthanates to give a drier level of 0.50% Pb and 0.050% Co in the mixture. The resin drier mixtures were applied on glass plates immediately after their preparation, and leveled with a doctor blade. The coated plates were placed on a level surface and allowed to dry at room temperature of 28.0°C. Surface dry after 24 h followed by tack-free dry after 48 h were taken as a satisfactory performance (Muralidharan Nair et al.).[1]

Media Resistance Tests

Four coated glass plates prepared as described above were stoved at 120°C for 3 h and cooled. The plates were immersed one each into four beakers labeled 1–4, and containing distilled water, 2% H_2SO_4, 2% Na_2CO_3, and 2% NH_3 solution, respectively. The immersed coated plates were examined at regular intervals, and the performance of the applied polyester resins on the glass plates into the different media was rated as follows (Muralidharan Nair et al.)[1]: 0—no change, 1—very slight effect, 2—slight effect, 3—definite effect, and 4—bad effect.

RESULTS AND DISCUSSION

The drying and film properties of the synthesized long- and medium-oil–length polyester resin samples are given in Tables II to V. Tables II and IV give the evaluation performance of the long- and medium-length polyester resins of the individual oils (soyabean, melon, rubber seed, and linseed) and their blends, respectively. Tables III and V give the evaluation performance of the physical

Table III Evaluation of Long-Oil Polyester Resin Blends

	Formulation	Drying Performance[a]	Resistance To			
			Distilled Water	2% H_2SO_4	2% NH_3	2% Na_2CO_3
PB-L5	RSOP : LSOP (15 : 85)	S	1	0	4	4
PB-L6	RSOP : LSOP (50 : 50)	S	1	0	4	4
PB-L7	RSOP : LSOP (85 : 15)	S	2	0	4	4
PB-L8	MSOP : LSOP (15 : 85)	S	2	0	4	4
PB-L9	MSOP : LSOP (50 : 50)	S	2	0	4	4
PB-L10	MSOP : LSOP (85 : 15)	NS	—	—	—	—
PB-L11	RSOP : SBOP (15 : 85)	S	2	0	4	4
PB-L12	RSOP : SBOP (50 : 50)	S	1	0	4	4
PB-L13	RSOP : SBOP (85 : 15)	S	1	0	4	4
PB-L14	MSOP : SBOP (15 : 85)	S	2	0	4	4
PB-L15	MSOP : SBOP (50 : 50)	NS	—	—	—	—
PB-L16	MSOP : SBOP (85 : 15)	NS	—	—	—	—

[a] 24-h surface dry, followed by 48 h tack-free dry; S = satisfactory, NS = not satisfactory.
Abbreviations: CB = chemical blend; RSO = rubber-seed oil; MSO = melon-seed oil; LSO = linseed oil; SBO = soyabean oil.

blends of the synthesized polyester resins (both long and medium).

From Table II, the long-oil polyester resins of linseed, soyabean, and rubber oils (L1, L2, and L3) were observed to dry satisfactorily, whereas melon seed oil (L4) did not. All long-oil polyester resins prepared from blends of rubber-seed and linseed oils or soyabean oil show satisfactory air-drying properties. This shows that rubber-seed oil can substitute linseed or soyabean oil up to 85% in the preparation of long-oil polyester resins. This result is in agreement with the work of Muralidharan Nair et al.,[1] who reported that rubber-seed oil could substitute linseed oil up to 80% in the preparation of air-drying long-oil polyester resins.

Table IV Evaluation of Medium-Oil Polyester Resins from Individual Oils and Their Blends

	Formulation	Drying Performance[a]	Resistance To			
			Distilled Water	2% H_2SO_4	2% NH_3	2% Na_2CO_3
M1	LSO	S	1	1	4	3
M2	SBO	S	1	1	4	4
M3	RSO	S	1	0	4	3
M4	MSO	S	1	0	4	4
CB-M5	RSO : LSO (15 : 85)	S	1	1	4	4
CB-M6	RSO : LSO (50 : 50)	S	1	1	4	3
CB-M7	RSO : LSO (85 : 15)	S	1	0	4	3
CB-M8	MSO : LSO (15 : 85)	S	1	2	4	3
CB-M9	MSO : LSO (50 : 50)	S	1	2	4	3
CB-M10	MSO : LSO (85 : 15)	NS	—	—	—	—
CB-M11	RSO : SBO (15 : 85)	S	1	2	4	4
CB-M12	RSO : SBO (50 : 50)	S	1	1	4	4
CB-M13	RSO : SBO (85 : 15)	S	1	2	4	3
CB-M14	MSO : SBO (15 : 85)	S	1	2	4	4
CB-M15	MSO : SBO (50 : 50)	S	1	3	4	3
CB-M16	MSO : SBO (85 : 15)	NS	—	—	—	—

[a] 24-h surface dry, followed by 48 h tack-free dry; S = satisfactory, NS = not satisfactory.
Abbreviations: CB = chemical blend; RSO = rubber-seed oil; MSO = melon-seed oil; LSO = linseed oil; SBO = soyabean oil.

Table V Evaluation of Medium-Oil Polyester Resin Blends

	Formulation	Drying Performance[a]	Resistance To			
			Distilled Water	2% H_2SO_4	2% NH_3	2% Na_2CO_3
PB-M5	RSOP : LSOP (15 : 85)	S	1	1	4	3
PB-M6	RSOP : LSOP (50 : 50)	S	1	0	4	3
PB-M7	RSOP : LSOP (85 : 15)	S	2	1	4	4
PB-M8	MSOP : LSOP (15 : 85)	S	2	1	4	4
PB-M9	MSOP : LSOP (50 : 50)	S	2	2	4	3
PB-M10	MSOP : LSOP (85 : 15)	S	2	2	4	4
PB-M11	RSOP : SBOP (15 : 85)	S	1	2	4	3
PB-M12	RSOP : SBOP (50 : 50)	S	1	2	4	3
PB-M13	RSOP : SBOP (85 : 15)	S	2	1	4	3
PB-M14	MSOP : SBOP (15 : 85)	S	2	2	4	3
PB-M15	MSOP : SBOP (50 : 50)	S	3	3	4	3
PB-M16	MSOP : SBOP (85 : 15)	NS	—	—	—	—

[a] 24-h surface dry, followed by 48 h tack-free dry; S = satisfactory, NS = not satisfactory.
Abbreviations: CB = chemical blend; RSO = rubber-seed oil; MSO = melon-seed oil; LSO = linseed oil; SBO = soyabean oil.

From Table III, all long-oil physical blends of rubber-seed oil polyesters with linseed oil polyesters or soyabean oil polyesters show satisfactory air-drying performance. Again, rubber-seed oil polyester resin can substitute 85% of linseed-oil polyester resins or soyabean-oil polyester resins in the preparation of long-oil air-drying polyester resins. The chemical blends and physical blends are observed to have shown identical good drying properties.

In the long-oil polyester resins of melon-seed oil–linseed oil blends, melon-seed oil was found to substitute linseed only up to 50% as opposed to 85% substitution by rubber-seed oil. This result shows the superiority of rubber-seed oil over melon-seed oil in the preparation of long oil air-drying polyester resins. Rubber-seed oil is a drying oil (iodine value = 135.4), while melon-seed oil (iodine value = 113.4) is a semidrying oil.

In the long polyester resins prepared from melon-seed oil–soyabean oil blends, melon-seed oil could substitute soyabean oil only up to 15% as opposed to 85% substitution by rubber-seed oil. This again, confirms the superiority of rubber-seed oil over melon-seed oil in the preparation of long-oil–modified polyester resins. Also, as linseed oil has an iodine value of 148.9 as opposed to 127.6 for soyabean oil, the blends of linseed oil should be expected to perform better than soyabean oil, and this was confirmed by the experimental results.

The physical blends of polyesters of melon-seed oil with polyesters of linseed oil or soyabean oil showed that melon-seed oil polyesters could only mix up to 50% with linseed oil, or 15% with soyabean oil. These results show that the compatibility of melon-seed oil polyesters with those of linseed oil polyesters or soyabean oil polyesters were poor, and that chemical and physical blends have identical drying performance as was observed for rubber-seed oil polyesters.

Table IV shows that the medium-oil polyesters of melon-seed oil and rubber-seed oil dried as well as those of linseed and soyabean oils.

All the polyester resins prepared from the blends of rubber-seed oil; with linseed oil or soyabean oil show satisfactory drying properties, indicating acceptable compatibility of the oil mixtures, and thus the capacity of rubber-seed oil to completely substitute linseed oil or soyabean oil in the preparation of medium drying-oil–modified polyester resins. The physical blends of the polyesters of rubber-seed oil with linseed oil or soyabean oil gave satisfactory air-drying performance, indicating good compatibility of the polyester mixtures.

In the preparation of medium-oil polyester resins, melon-seed oil could substitute 50% of linseed oil and 50% of soyabean oil. In the physical blends of polyesters of melon-seed oil with linseed oil, melon-seed oil could substitute 50% of linseed oil polyester. With soyabean oil polyesters, substitution is also possible up to 50%. These results show better substitution of the conventional oils (linseed, soyabean) by melon-seed oil in the preparation of medium-oil drying polyester resins than was found for the long-oil–drying polyester resins. Furthermore, the physical blends of medium-oil polyesters of melon-seed oil with soyabean oil were observed to show better drying properties than the physical blends of the long-oil polyester resins of the two.

The Media Resistance Tests

The water and acid resistance of the synthesized polyester resins were generally good except for the poor water resistance obtained with blends of polyesters of melon-seed oil with soyabean oil CB-M_{15} and PB-M_{15}. All the formulations failed the alkali resistance test. This confirms the fact that polyesters generally have low alkali resistance.

CONCLUSIONS

It can be inferred without any ambiguity that rubber-seed oil provides an outstanding complete substitution for the conventional drying oils (linseed, soyabean) in the manufacture of long- and medium-oil polyester resins. The earlier work of Muralidharan Nair et al.[1] on the possible use of rubber-seed oil in the synthesis of polyester resins is further confirmed. Melon-seed oil was found to be an acceptable substitute for linseed and soyabean oils to the extent of 50% each in the synthesis of long-oil–length polyester resins. It was also found to substitute for 15% of linseed and 50% of soyabean oils in the synthesis of medium-oil–length polyester resins.

REFERENCES

1. Muralidharan Nair, N.; Unnikrishnan, K. G.; Unnikrishnan, M.; Nair, C. S. B. Paintindia 1981, 5.
2. Khandelwal, S. M.; Gogte, B. . Paintindia 1976, 26, 15.
3. Mondhe, O. P. S.; Rao, J. T. Colourage 1993, 40, 51.
4. Abd El-Ghaffer, M. A.; Gomaa, A. Z.; Moustafa, M. Surface Coat Int 1994, 77, 96.
5. Eka, O. U. West Afr Biol Appl Chem 1977, 20, 45.
6. Igwe, I. O. M.Sc. Thesis, University of Nigeria, Nsukka (1989).
7. Girgis, P.; Said, F. J Sci Fd Agric 1968, 19, 615.
8. Achife, E. C. M.Sc. Thesis, University of Nigeria, Nsukka (1988).
9. Attah, J. C.; Ibemesi, J. A. J Am Oil Chemists Soc 1990, 67, 25.
10. Fasina, A. B. Proceedings, 1st Annual Technical Conference of Polymer Institute of Nigeria, Owerri, 1990.
11. Newfield, B. Seminar, Department of Pure And Industrial Chemistry, University of Nigeria, Nsukka (1982).
12. Cocks, L. V.; Rede, C. V. Laboratory Handbook for Oil and Fat Analysis; Academic Press: London, 1966, p. 331.
13. ASTM 1959. Test for Iodine Value of Drying Oils and Fatty Acids, Part 20, 1973, p. 748.