Preparation and molecular weight determination of soya-beans and benni-seed oil-modified alkyd resins

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Abstract

Alkyd resins were prepared into four different sets by varying the percentage concentration of the glycerol content. Various properties such as the viscosity, Surface drying time, solubility and color of the alkyd resins were evaluated for the various sets. The alkyd resin with the highest glycerol content was the most viscous, brownish in color and having the highest molecular weight this is due to the ratio 1:3 oil to glycerol content.

Keywords: Soybean oil; Benni-seed oil; Alkyd; Resin.

1. Introduction

Alkyd resins are durable synthetic resins widely used in paints and adhesives. Alkyd resins are widely used in the coatings and paints industry and they have become indispensable raw materials that are used for the production of industrial and household finishes [1].

Oil-modified alkyds are prepared through a condensation–polymerization reaction between fatty acids or oils, polyhydric alcohols and a dibasic acid or anhydride. In the two-stage process shown in Eqs. (a) and (b) below, oil is initially subjected to a reaction with glycerol to obtain a monoglyceride precursor, which in the second step, is reacted with phthalic anhydride to obtain the alkyd resin.

$$\text{Monoglyceride} + \text{phthalic Acid} \longrightarrow \text{Alkyd resin} \qquad (b)$$

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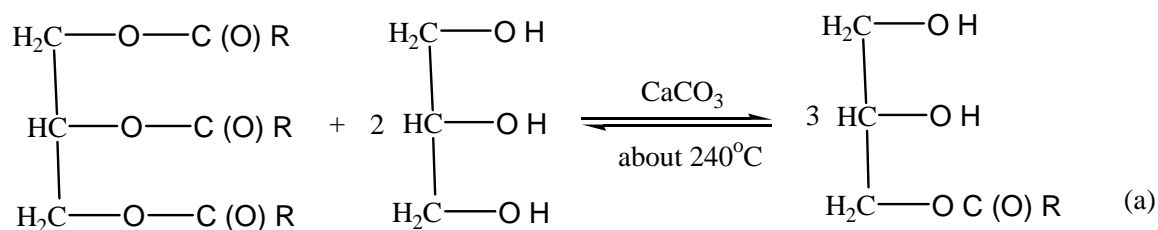
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$CaCO_3$ are additives used as fillers, they help to either reduce the thermal expansion coefficient of the base polymer to improve the dielectric properties or to soften the polymer [2].The oil chosen for the production of alkyds usually has a significant effect on the properties of the finished alkyd resins [3].

Soyabean bean plants are grown generally throughout Asia, Europe, America and tropics (Nigeria inclusive), the mixture of the oil has been analyzed and found to contain fatty acids such as linoleic acid in the range of 56.2%,linolenic acid: 4.3%, oleic acid: 12.4%, palmitic acid: 13.9% and stearic acid: 3.49% [5]. Benniseed known as sesame oil has been analysed and found to contain fatty acids such as linoleic acid in the range of 39–56%, oleic acid: 32–54%, palmitic acid: 7–11% and stearic acid: 2-6%[4]. Studies has been carried out on varying the % composition of Tobacco seed oil,it was reported that the viscosity of the various alkyd resin decreases as the % composition of oil increases, evaluation of some various properties such as viscosity, drying time and solubility were reported [6].

The aim of this paper is to produce various alkyds by varying the % composition of glycerol present in the alkyds. Studies on the viscosity, molecular weight, solubility, and surface drying time were also carried out.

2. Experimental

2.1. Materials

The various seeds (soyabeans and benni-seed) were dried, crushed and the tobacco seed oil was extracted using n-Hexane in a Soxhlet extractor. The yield for sesame was found to be 51% while that of Soyabean was found to be 16%. The yield quoted in the literature for sesame seed was 50-55% while that of soyabean was 18-20% [3]. Analytical/technical grade phthalic anhydride, glycerol and calcium carbonate were obtained from commercial sources and used in the preparation of alkyd resin.

2.2. Physicochemical properties

Some physicochemical properties of soyabeans and benni-seed oil (e.g., acid value, saponification value, iodine value, density and viscosity) were determined according to relevant standards. Standard test methods used for the determination of physical and chemical properties of oils:

Physical and Chemical Properties	Standard methods
Iodine value (centigrams I/g oil)	AOCS CD1-25 1993 (AOAC, 1993)
Saponification value (mgKOH/g oil)	AOCS CD3-25 1993 (AOAC, 1997)
Acid value (mg KOH/g)	PEARSON (1976)
Density (g/cm^3)	ASTM D4052-91 (ASTM, 1995)
Viscosity (poise)	PEARSON (1976)
Free fatty acid	PEARSON (1976)
Peroxide value	PEARSON (1976)

The iodine value indicates a level of unsaturation that enables the oil to be classified as semi-drying. The degree of unsaturation in the oil determines the drying property of the resulting alkyds [1]. The peroxide values of both oils are low this values indicates that the shelf life will be longer.

2.3. Preparation of alkyds

Four different alkyds having glycerol contents of 43% w/w, 58% w/w, 66% w/w and 70% w/w were prepared using a two-stage alcoholysis - polyesterification method [11]. The alkyds were labeled as follows: T-AKD 1 (43% glycerol); T-AKD 2 (58% glycerol); T-AKD 3 (66% glycerol); T-AKD 4 (70% glycerol).

Table 1
Some physicochemical properties of soyabean and benni-seed oil.

Properties	Literature	Result Benniseed oil	Result Soyabean oil
Acid value (mg KOH/g)	4(virgin oil) 0.6(non-virgin oil)	1.4	1.0
Saponification value (mgKOH/g)	187-195(BSO) 189-192(SSO)	185.95	192.24
Iodine value (g I_2/100 g)	106.6 (BSO) 112.5 (SBO)	126.24	120.23
Density (g/cm^3)	0.9138(BSO) 0.9133(SSO)	0.9120	0.9130
Viscosity (poise)	-	1.231	1.210
Peroxide value (m Eq/kg)	10(max) for both.	2.1	1.7
Refractive index	1.466-1.470	1.4730	1.432
Free fatty acid	-	0.7042	0.4527

In preparing each of the alkyd, a known mass of glycerol was heated to a temperature between 240°C and 260°C. SBO/BSO (16.0 g) and $CaCO_3$ (0.5g) were added while maintaining the temperature at about 260°C. The amounts of the various ingredients are shown in Table 2. The completion of alcoholysis was monitored by taking samples of reaction mixture every 5 min. This sample was mixed with anhydrous methanol in a 1:1 volume ratio. When the mixture gave a clear solution, it indicated the end of alcoholysis process [11,12]. After the completion of the alcoholysis stage, 4g of phthalic anhydride was added while reaction continued at about 260°C. Nitrogen gas was used to blanket the surface of the reaction mixture. When the acid value was about 15, the reaction was quenched. It is to be noted that acid value is a measure of the amount of free acids present in the oil and it is the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of sample. In the polymerization, it was observed that when the ratio of oil to glycerol was 1:1 not all the oil were consumed, but when it was 1:2 or 1:3 all the oil was used up.

Table 2
Formulations of the different alkyd resins.

	Alkyd 1 (43% glycerol content)	Alkyd 2 (58% glycerol content)	Alkyd 3 (66% glycerol content)	Alkyd 4 (70% glycerol content)
BSO/SBO (g)	16.00	16.00	16.00	16.00
Phthalic anhydride (g)	4.00	4.00	4.00	4.00
Glycerol (g)	16.00	28.00	39.00	48.00
Silicate(g)	0.50	0.50	0.50	0.50

BSO=benni seed oil, SBO= soya bean oil

3. Results and discussion

3.1. Physicochemical properties of Benni-seed and soya bean oil

The properties of the BSO/SBO obtained by solvent extraction are shown in Table 2. The iodine value indicates a level of unsaturation that enables the oil to be classified as semi-drying. The degree of unsaturation in the oil determines the drying property of the resulting alkyds [1]. Our iodine value is high compared to the value cited in the literature [14] while there are differences in saponification value and density; we attribute these differences for the same raw material to their different geographical origins.

3.2. Evaluation of alkyd resins

In order to test for solubility, 5 g of each resin was dissolved in 10 ml of each of methanol and turpentine; the resin–solvent mixture was allowed to stand for 5 h with intermittent stirring. All the alkyds were partially soluble in turpentine; methanol appeared to be the best solvent for all the alkyd resins. M-AKD 4 is more viscous than the other resins, it took the longest time to dissolve (5 hrs 30mins in Methanol); this is probably due to a high extent of polymerization in the preparation of this resin and the amount of the glycerol present. The viscosity measurements of the alkyd solutions (5 g in 15 cm^3 turpentine) were taken with a Ubbelohde capillary viscometer in accordance with a literature method [6].

Table 3a
Some physical properties of the alkyds using Soyabean oil.

Sample	Viscosity(cP)	Drying Time surface(s)	Colour
Alkyd 1	19.5	279	Brown
Alkyd 2	22.7	243	Deep brown
Alkyd 3	26.5	225	Yellowish brown
Alkyd 4	31.5	185	Chocolate

Table 3b
Some physical properties of the alkyds using Benniseed oil.

Sample	Viscosity(cP)	Drying Time surface(s)	Colour
Alkyd 1	20.2	290	Brown
Alkyd 2	21.7	254	Chocolate
Alkyd 3	27.1	263	Rich brown
Alkyd 4	33.1	197	Brown

The solution viscosity depends on the solvent viscosity, temperature and solute concentration.

3.3. Molecular weight determination

A simple and commonly used technique for assessing the molecular weight of a polymer, viscometry is employed [16]. In this technique, the time is measured for a dilute solution of polymer to flow through a capillary. Through measuring the times at various polymer concentrations and comparing with the time obtained for the neat solvent, it is possible to obtain a value for the intrinsic viscosity (or limiting viscosity number) [η], which can be related to the

molecular weight using the Mark–Houwink–Sakurada relationship given below. Where M is the viscosity average molecular weight while K and a are constants.

$$[\eta] = KM^a$$

Interestingly, the value for *a* is determined directly by polymer–solvent interactions, where $k=2.72\times10^{-5}$ and a=0.96 [15]. The specific viscosity (η_{sp}) at different concentrations was then measured and the intrinsic viscosity ($[\eta]$) was obtained by extrapolating the linear plot of η_{sp}/c vs. c to the zero concentration. The viscosity average molecular weight (M_v) was then calculated using the Mark–Houwink equation, $[\eta] = KM_v^a$ [17,18].

For determination of the molecular weight, Methanol was used as the solvent to determine the flow rate of the alkyds produced so that the intrinsic viscosity can be calculated as shown below.

Table 4a
Values for the specific viscosity [η_{sp}] obtained using Methanol as solvent in Soyabean oil (SBO).

Concn. (g/50ml)	Alkyd 1	Alkyd 2	Alkyd 3	Alkyd 4
0.04	0.031	0.034	0.030	0.020
0.06	0.044	0.042	0.046	0.030
0.08	0.051	0.046	0.078	0.046
0.10	0.058	0.053	0.131	0.065
0.12	0.065	0.062	0.219	0.090

The linear plot of η_{sp}/c vs. c for alkyds 1&2, 3&4 using soya bean oil (SBO) are given in figures 1 and 2 respectively.

Table 4b
Values for the specific viscosity [η] obtained using Methanol as solvent in Benniseed oil (BSO).

Concn. (g/50ml)	Alkyd 1	Alkyd 2	Alkyd 3	Alkyd 4
0.04	0.021	0.012	0.051	0.040
0.06	0.048	0.028	0.087	0.066
0.08	0.065	0.046	0.130	0.132
0.10	0.084	0.065	0.178	0.190
0.12	0.128	0.109	0.219	0.245

The linear plot of η_{sp}/c vs. c for alkyds 1&2, 3&4 using Benni seed oil (BSO) are given in figures 3 and 4 respectively.

Table 5
The molecular weight of soyabean oil Alkyds and benniseed oil alkyds are presented in the table below.

Alkyds	1	2	3	4
Benniseed	8.9×10^3	19.6×10^3	30.6×10^3	44.0×10^3
Soyabean	18.2×10^3	32.6×10^3	44.5×10^3	55.1×10^3

Molecular Weight of Alkyds using Benni-seed oil
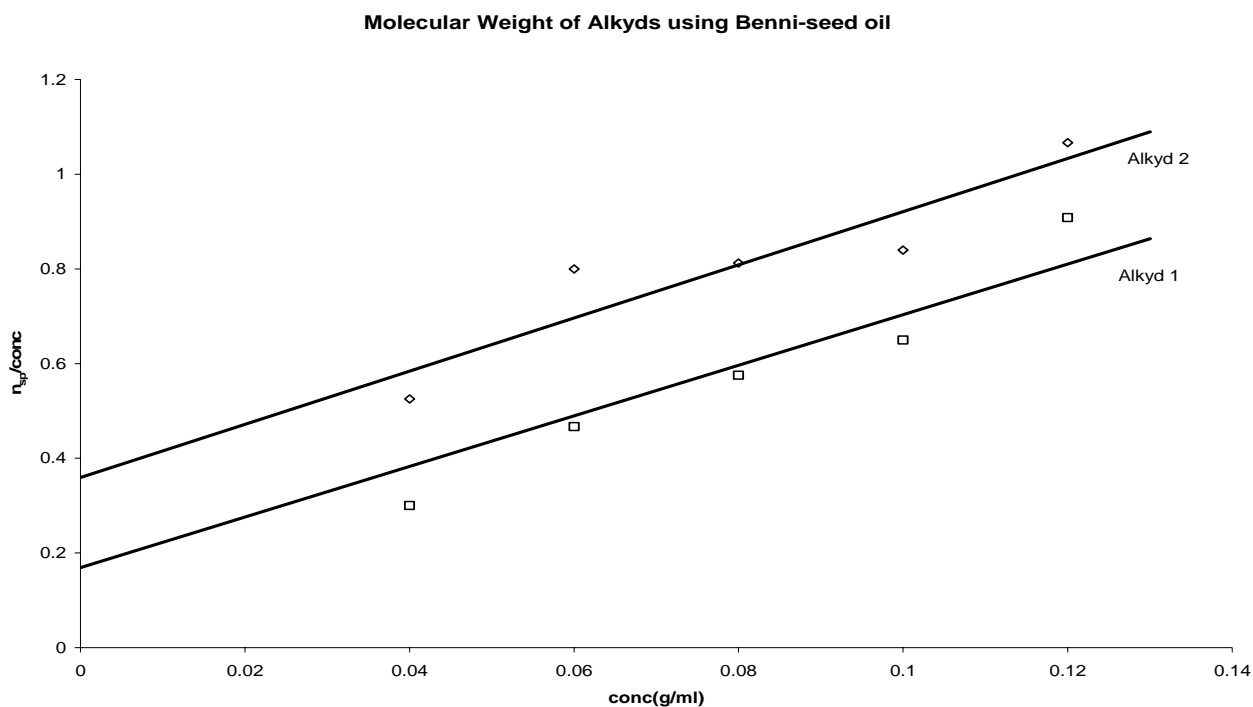
Fig. 1. The linear plot of η_{sp}/concentration vs. concentration (g/50ml) for Alkyds 1 and 2 using BSO.

Molecular weight for Alkyd using Benni-seed oil
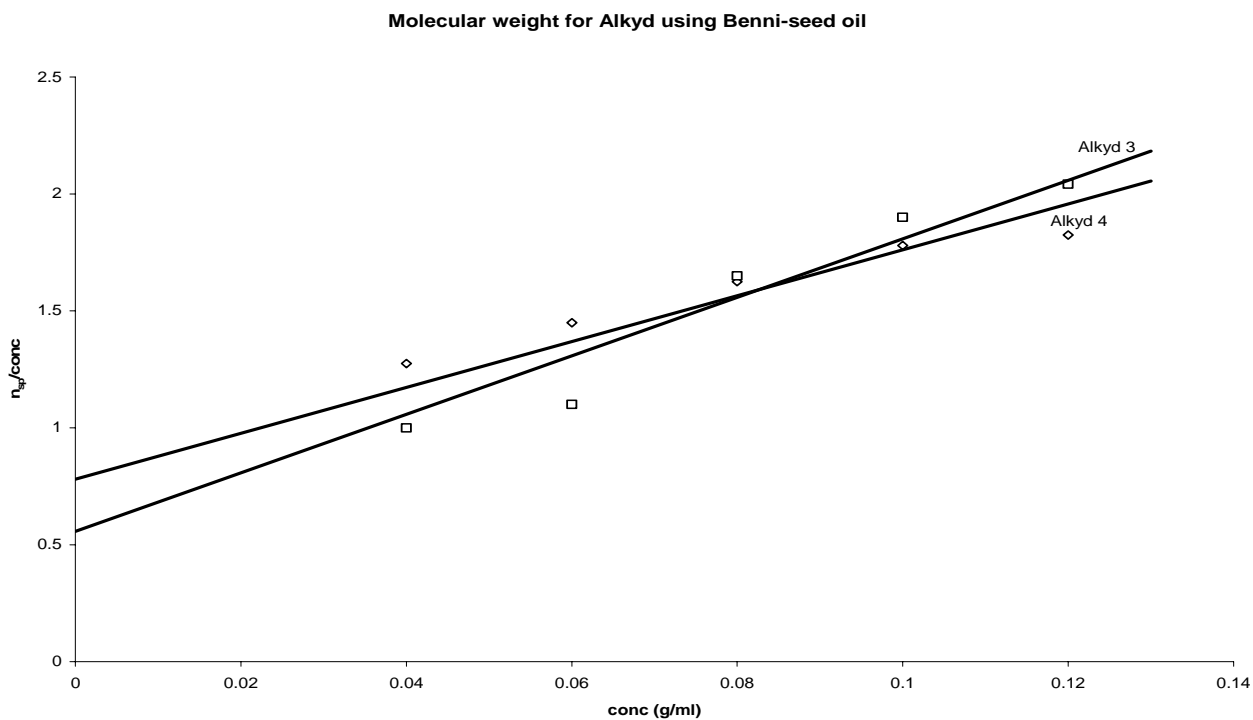
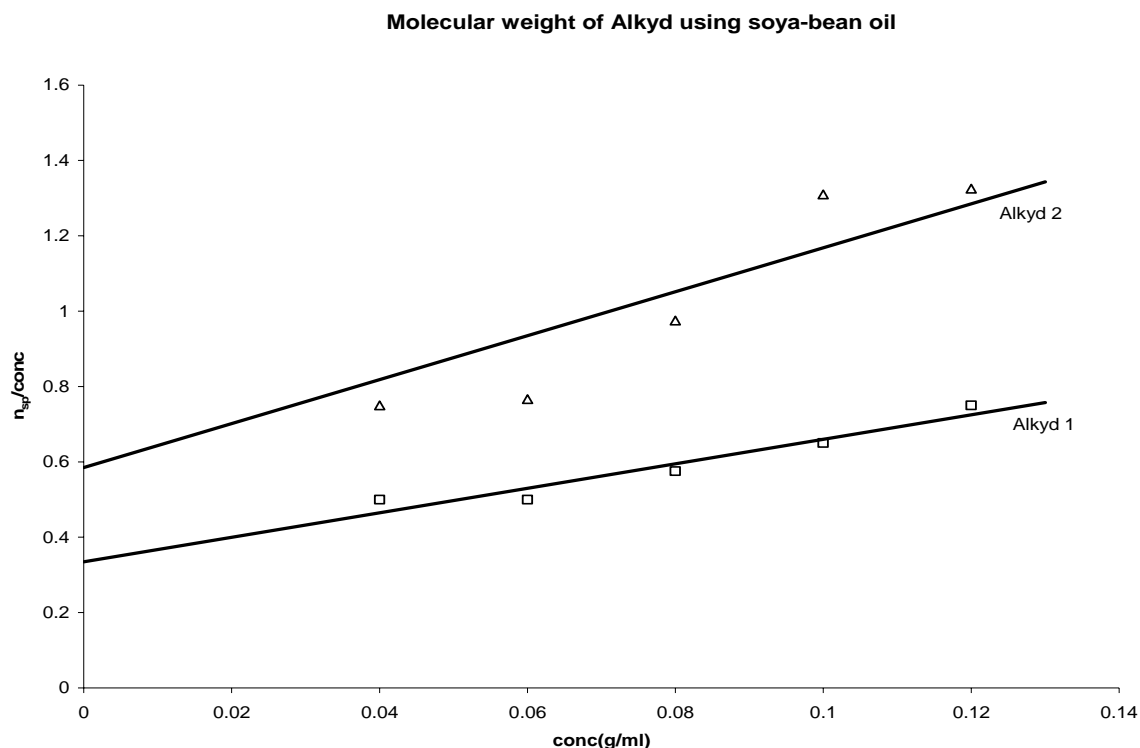**Fig. 2.** The linear plot of η_{sp}/concentration vs. concentration (g/50ml) for Alkyds 3 and 4 using BSO.

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Molecular weight of Alkyd using soya-bean oil

Fig. 3. The linear plot of η_{sp}/concentration vs. concentration (g/50ml) for Alkyds 1 and 2 using SBO.
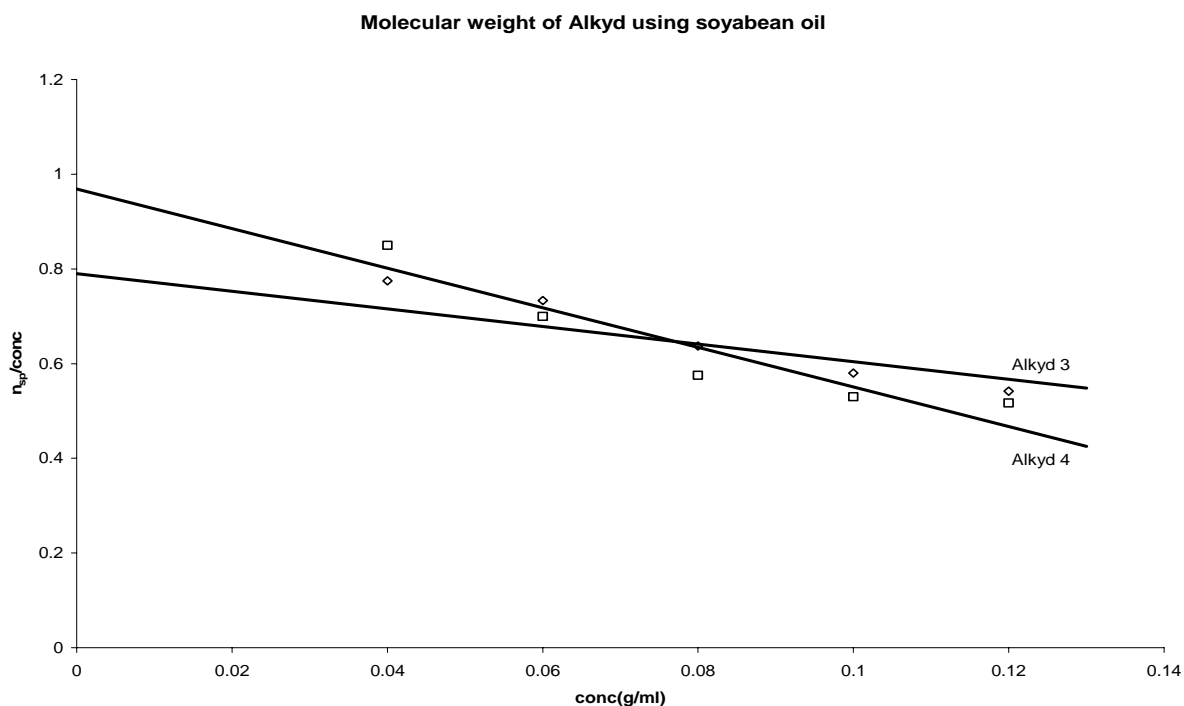
Molecular weight of Alkyd using soyabean oil

Fig. 4. The linear plot of η_{sp}/concentration vs. concentration (g/50ml) for Alkyds 3 and 4 using SBO.

Table 5 shows that the molecular weight increases as the glycerol content increases Knowledge of the average molecular weight of finished alkyds is of utmost importance in their practical application[19]. From the experimental results it was found that the higher the molecular weight the shorter the drying time, higher viscosity takes relatively shorter time to air-dry [6]. From the above table viscosity shows a direct relationship with the molecular weight of

the alkyds. Based on this result, it can be inferred that alkyds containing higher glycerol content up to 40% and above could be used in air-drying coatings, the higher the molecular weight the higher the non-volatile matter (solid content) and the shorter the drying time.

4. Conclusion

Various Alkyds were prepared by varying the glycerol contents. It was discovered that the higher the molecular weight the shorter the drying time.

Reference

[1] Kirk-Othmer, In: Encyclopedia of Chemical Technology,vol. 1, second ed. Interscience Publishers, New York, 1963.

[2] S. Tadmor and C.G. Gogos, Principles of polymer Processing. A wiley- Interscience Publication, 1979.

[3] F.D. Gunstone, Fatty Acid and Lipid Chemistry. Chapman and Hall, London, 1996.

[4] K.D. Weiss, Progress Polym. Sci. 22 (1997) 203–245.

[5] U. Usta, Biomass and Bioenergy 28 (2005) 77–86.

[6] D.S. Ogunniyi, T.E. Odetoye, Bioresource Technology 99 (2008) 1300–1304.

[7] ASTM, Designation: D4052-91. Annual Book of ASTM Standards, vol. 05.02. ASTM, Philadelphia, PA, (1995a) 684–687.

[8] AOAC, Section A: Commercial Fats and Oils. American Oil Chemists Society (AOCS) Official Method CD1-25 for Iodine Value. Assoc. Off. Anal. Chem., Washington, 1993.

[9] AOAC, Commercial Fats and Oils. American Oil Chemists Society (AOCS) Official Method CD3-25 for Saponification Value. Assoc. Off. Anal. Chem.,Washington, 1997.

[10] D. Pearson, The chemical Analysis of Foods, Churchhill Living Stone, 7th Edition, 1976.

[11] D. Stoye, Alkyd Resins,Resins for Coatings: Chemistry, Properties and Applications. Carl Hanser Verlag, Munich, 1996.

[12] C.O. Akintayo, K.O. Adebowale, Progress in Organic Coatings, 50 (2004)138–143.

[13] E. Bekele, Seminararbeit im Rahmen der Vorlesung O¨ lpflanez-Zu¨chtung, Anbau, 2000.

[14] P.N. Giannelos, F. Zannikos, S. Stournas, E. Lois, G. Anastopoulos, Industrial Crops and Products 16 (2002) 1–9.

[15] P.J. Flory, Principles of Polymer Chemistry; Cornell University Press, New York, 1953.

[16] L.I. Hosier, S. Alun Vaughan, R. Geoffrey Mitchell, Jintana   Siripitayananon, J. Fred Davis, Practical Approach in polymer Chemistry: Polymer Chemistry, Oxford University Press,1st ed, 2004.

[17] W. Wang, S. Bo, S. Li, W. Qin, Int. J. Biol. Macromol. 13 (1991) 281-285.

[18] A.I. Gamzazade, V.M. Shaishk, A.M. Sklyer, E.V. Stikova, S.A. Pavlova, S.V. Rogozhin, Acta Polym. 36 (1985) 420-426.

[19] S.H. Maron, J.B. Lando, Fundamentals of Physical Chemistry, Macmillan, 1974.