

Determination of Solution Viscosity Characteristics of Rubber Seed Oil Based Alkyds Resins

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ABSTRACT: Three medium oil alkyd samples of different oil length [(I) 45%, (II) 50%, and (III) 55%] were synthesized with rubber seed oil. Dilute solution viscosity measurements were carried out on the alkyd in acetone and in toluene. The parameters investigated include intrinsic viscosity $[\eta]$, Huggins constant (k_H), and Mark-Houwink Sakurada constants (κ and α). The $[\eta]$ values for the alkyd samples were found to be larger in acetone than in toluene. The K_H values showed a regular order in acetone but not in toluene. The K_H values showed no regular order in their variation with the oil content of the alkyd samples and the solvent, but the values obtained are higher in acetone than in toluene. Cor-

relation of molecular weight (M) with $[\eta]$ was also examined. $[\eta]$ was observed to increase with the increase in the molecular weight of the resins. The α values obtained are in reasonable agreement with the reported ranges of α values in good solvent. The characteristics examined suggest that acetone is a better solvent for rubber seed oil alkyd resin than toluene. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3073–3075, 2006

Key words: viscosity; synthesis; solution properties; molecular weight

INTRODUCTION

One of the problems confronting polymer processors is caused by the differences in the flow characteristics of resins and material variables.¹ The capillary rheometer has been used to obtain flow data, which stimulate actual processing condition.² When a resin is known to process satisfactorily under certain operating condition, the intrinsic viscosity and the molecular weight are determined and could be used as standard for other incoming resins. Many practical and theoretical applications of alkyd solutions manifest themselves daily in the surface coatings industry.³ Knowledge of solution behavior of alkyds is important for adjusting properties of finished alkyds for optimum performance as their practical usefulness can be realized only in solution in suitable solvent systems, for instance, solution viscosity of surface coatings determines their mode of application either by brushing or spraying and is equally important in the design of processing equipment.⁴ Similarly, polymer fractionation is performed in the solution state.^{5,6} The solvents are selected in such a way that they allow the complete dissolution of the alkyd and also evaporate at a reasonable rate, which leaves an intact film after

application. Several tests are performed in commercial alkyds to determine their solution properties for the purpose of effective handling, design of processing and storage equipment, and establishing processing conditions. Methods of characterizing alkyd resins include viscosity measurements and comparative values of molecular weights.⁷

In this study, the viscosity and molecular weight of rubber seed oil alkyd resins and their fractions in toluene and acetone were evaluated with a view to determining some solution properties such the Huggins constant, K_H , intrinsic viscosity, $[\eta]$, and the Mark-Houwink Sakurada constants (α and κ). These constants are useful in ascertaining the degree of aggregation of molecules in solution.⁸

METHODS

Materials

Rubber seed oil used on the preparation of alkyds was obtained by solvent extraction. Phthalic anhydride and glycerol, from British Drug Houses (BDH), were used in the preparation of alkyd resins. Toluene and acetone of analytical grade obtained from BDH were used in the viscosity measurements. Microanalytical reagents camphor from BDH was used in the Rast method.

Synthesis of alkyd resin

Three medium oil alkyd samples of different oil lengths [(I) 45%, (II) 50%, and (III) 55%] were synthe-

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TABLE I
Recipe for the Formulation of Alkyd Samples

Ingredients	Alkyd samples		
	I	II	III
Rubber seed oil (g)	136.18	151.13	164.8
Phthalic anhydride (g)	101.02	91.28	83.31
Glycerol (g)	62.78	57.60	51.60
Oil length (%)	45	50	55
Alkyd constant	1.00	1.00	1.00

sized. All the alkyd samples were formulated to alkyd constant of about 1.00.^{9,10} The recipe used in the preparation of the alkyd is shown in Table I.

Fractionation of alkyd

The alkyd samples were fractionated by fractional precipitation through the addition of *n*-heptane as nonsolvent to the solution of the alkyds (5% W/V) in toluene.⁷

Viscosity measurements

Viscosity measurements were carried out with solutions of the alkyds and their fractions in acetone and toluene using an Ubbelohde 50 viscometer. Three additional dilutions were made in the viscometer, allowing efflux times to be measured at concentrations of 2.5, 2.0, 1.5, and 1.0 g/100 cm³. Viscosity measurements were carried out at temperature of 30 ± 0.5°C.

The specific viscosity η_{sp} was calculated using the formula

$$\eta_{sp} = \eta_r - 1 = t/t_0 - 1 \quad (1)$$

where t and t_0 are the efflux times of alkyd solution and pure solvent, respectively. $[\eta]$ for the finished alkyds were obtained graphically by plotting the viscosity number, η_{sp}/C , versus concentration, (C) , and extrapolating to zero. The values of K_H were calculated as follows from the Huggin-kremer viscosity relationship:

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2C \quad (2)$$

Determination of molecular weight

Molecular weights of the alkyd samples and their fractions were determined by Rast method.¹¹

RESULTS AND DISCUSSION

Dilute solution viscosity measurements have been carried out on rubber seed oil alkyd resins. The results in Table II show that $[\eta]$ values of the alkyd sample are larger in acetone than in toluene. It has been established that the intrinsic viscosity is affected by solvent polymer

interaction.^{12,13} The better the solvent, the greater the extent of solvent associated with a polymer molecule, the more the coil expands, and therefore, the higher the intrinsic viscosity. The larger intrinsic viscosity values obtained in acetone could possibly be due to the formation of hydrogen bonding in the acid–base interaction which could promote molecular extension. The more polar the solvent, the larger the apparent size of the molecule. This more extended state of the molecule is indicated by the high intrinsic viscosity. It therefore seems from this result that acetone is a better solvent than toluene for rubber seed oil alkyd resins. The intrinsic viscosity obtained in this study was compared with previous studies⁷ where solutions of the resins were made in methyl ethyl ketone and dimethyl formamide. It is observed that acetone has a higher intrinsic viscosity than the other solvents. Though evaporative loss of acetone at the experimental level may affect reproducibility, acetone could be a better hydrogen bond acceptor and thus reduces the viscosity more effectively than the other solvents by reducing intermolecular hydrogen bonding.

The results in Table II also show K_H of the alkyd samples. The values of K_H showed a regular order in acetone, as they are observed to increase with increase in the oil length but not in toluene. It is well known that the values of K_H are influenced by molecular weight distribution, molecular shape and configuration, polarity, and the degree of interaction of the polymer molecule with the solvent.¹³ The K_H obtained in this study suggest that acetone may be a better solvent than toluene for rubber seed oil alkyds.

In the characterization of polymers, knowledge of the molecular weight is indispensable because the application properties such as mechanical properties are related to the molecular weight. Table III shows the intrinsic viscosity of the alkyd fractions and their molecular weights. The average molecular weight of alkyd samples and their fractions are of the order of 10². The average molecular weight of alkyd fractions IIF₁ and IIIF₁ are somewhat higher than the average molecular weight of the corresponding unfractionated samples. This could probably be due to the fact that these fractions contribute less to the average molecular weight of the final alkyd because it has been estab-

TABLE II
Intrinsic Viscosity of the Alkyd Samples in Acetone and Toluene

Alkyd samples	Intrinsic viscosity (η) at 30°C (cm ³ /g)	
	Acetone	Toluene
I	0.052 (0.463)	0.047 (0.546)
II	0.048 (0.863)	0.044 (4.914)
III	0.046 (1.245)	0.032 (3.906)

Values of the Huggins constant, K_H , is in parenthesis.

lished that the value of the molecular weight of the final alkyd is influenced by the molecular weight of the fraction, which constitute the largest proportion of the alkyd samples.⁷ In other words, the molecular weight of the final alkyd resin is closest to the molecular weight of the largest fraction.

Intrinsic viscosity of polymers is often correlated with molecular weights. The relationship between intrinsic viscosity and molecular weight, M , is expressed by the Mark-Houwink equation 3

$$[\eta] = KM^\alpha \quad (3)$$

where K and α are the Mark-Houwink constants for a given polymer, solvent, and the temperature. The results in Table III show that the intrinsic viscosity increased with the increase in molecular weight of the alkyd in both solvents. This is in agreement with the Mark-Houwink equation 3. The values of K and α express the solvent power of different solvents of a given polymer. The values calculated for the different alkyd samples are given in Table IV. From the results, the values of K range from 6.28×10^{-3} to 5.30×10^{-4} for solution of the alkyd samples in acetone, while that of toluene ranged from 8.75×10^{-4} to 2.7×10^{-5} . These results show no regular variation of K with respect to oil length of the alkyd samples. However, the values are larger in acetone than in toluene for all the samples. It is well known that the value of K is an indication of the homogeneity of the alkyd.¹⁴ In other words, the higher the value of K , the more homogeneous the alkyd. Therefore, the results from this study show that the alkyd samples are more homogenous in acetone than in toluene.

It has been reported that the value of α approaches 0.8 in a good solvent and 0.5 in a poor solvent, but generally lies between 0.6 and 0.8 for dilute polymer solutions.¹³ However, extensive studies on various polymer-solvent systems have shown that α values of

TABLE III
Intrinsic Viscosity of Alkyd Fractions in Acetone and Toluene and Their Molecular Weight

Alkyd samples	Molecular weight	Intrinsic viscosity $[\eta]$ at 30°C (cm ³ /g)	
		Acetone	Toluene
IF ₁	496.25	0.240	0.120
IF ₂	441.11	0.155	0.075
IF ₃	360.90	0.140	0.054
Unfractionated	520.25	0.052	0.047
IF ₁	661.67	0.128	0.115
IF ₂	496.25	0.072	0.096
IIIF ₃	283.57	0.045	0.068
Unfractionated	580.64	0.048	0.044
IIIF ₁	767.14	0.226	0.123
IIIF ₂	567.14	0.154	0.096
IIIF ₃	283.57	0.104	0.068
Unfractionated	710.26	0.046	0.032

TABLE IV
Values of the Mark-Houwink Sakurada Constants, K and α , for the Alkyd Samples in Acetone and Toluene

Alkyd samples	Acetone		Toluene	
	K	α	K	α
I	5.30×10^{-4}	0.838	2.7×10^{-5}	1.446
II	2.19×10^{-3}	0.609	5.24×10^{-5}	1.187
III	6.28×10^{-3}	0.749	8.75×10^{-4}	0.846

well over 1 are possible for rigid polymers.¹³ The results in Table IV show α values less than 1 in acetone, which are in reasonable agreement with the reported ranges of α values in good solvent.

CONCLUSIONS

Despite the potential of rubber seed oil alkyd resins as binders for surface coatings, there is little information about their dilute solution properties. The properties obtained in this study are simple quality control measures useful for maintaining the consistency of polymer resins to obtain a product with good stability and satisfactory performance. This study shows that rubber seed oil alkyd resins are more soluble in polar solvent like acetone than in nonpolar solvent like toluene.

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