

Kinetic Study on the Polyesterification and Copolymerisation Process of Unstyrenated and Styrenated Palm Kernel Oil Based Alkyd Resin

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Abstract

The kinetics of the preparation of unstyrenated and styrenated palm kernel oil based alkyd resins were studied using polycondensation and copolymerization process. Three alkyd resins A, B, and C of medium oil length were prepared using phthalic anhydride, maleic anhydride, and glycerol at stipulated ratios. The prepared alkyd resins were copolymerized with styrene using benzoyl peroxide as an initiator at 150°C for 3 hr. The kinetic behavior of the polyesterification and copolymerization process and the resulting alkyd resins and styrenated alkyd resins were studied as a function of viscosity and the reaction time using integral method of analysis. The results showed that the resins A and B followed the first order reaction while resin C followed the second order reaction with rate constants of $13 \times 10^{-3} \text{ min}^{-1}$, $30 \times 10^{-3} \text{ min}^{-1}$, and $3 \times 10^{-3} \text{ (Pa.S)(min)}^{-1}$ respectively. For styrenated alkyds, kinetic study confirmed that styrenated alkyd A followed the first order kinetics and styrenated alkyds B and C followed the second order kinetics with rate constants of $8 \times 10^{-3} \text{ min}^{-1}$, $6 \times 10^{-4} \text{ (Pa.S)(min)}^{-1}$, and $6 \times 10^{-4} \text{ (Pa.S)(min)}^{-1}$ respectively.

Keywords: Kinetics; Copolymerization; Polyesterification; Palm kernel oil; Surface coating

Introduction

Alkyd resins are any of a large group of thermoplastic resins that are essentially polyesters made by heating polyhydric alcohol with polybasic acids or their anhydride and used chiefly in making protective coatings and gold weathering properties [1]. These resins are useful as film forming agents in paint, varnished and enamel and as thermosetting plastics that can be moulded into solid objects. Therefore, alkyd resins are one of the important ingredients in the synthetic paint industry. Despite the growing popularity of acrylic, polyurethane and epoxy resins, alkyd resins remain highly favoured among paint producers for its variability of compositions and better value for money [1]. Alkyd resins were originally made by reaction of phthalic anhydride and glycerine. But these products were too brittle to make satisfactory coatings. The use of dry oils in combination with the brittle alkyds resulted in the air-drying coatings which revolutionized the chemical coating industry. The oil or fatty acid portion of the alkyd is one of the factors which determine the paint formulator's choice of resin to be used. In other words, the lower the phthalic content of an alkyd, the higher the amount of oil used. These drying oils, which are regarded as standards in surface coating industry are still very scarce and expensive. Moreover, their alkyds are prone to yellowing due to high unsaturation.

Preliminary investigations have revealed the potential sources that could meet the country's requirement of vegetable oil for alkyd production when properly developed [2], and palm kernel oil is one of them. Palm kernel oil has become one of the major edible oils in the world. It is classified as non-drying oil because of its low iodine value. The limited unsaturation in the fatty acid chain of this oil is responsible for its inferior curing properties compared to other drying oil based resins. Therefore, modification of these resins with highly unsaturated styrene is needed in the curing process. Consequently, there are very little reports on the kinetics of alkyd resins formation especially for non-drying oil and alkyd resins modification. The importance of the kinetic studies of alkyd resins formation cannot be overemphasized, as such knowledge is useful in classification of polymerization reactions and polymers and studying the conditions necessary for synthesis of high molecular weight alkyds [3]. The determination of the correct reaction order is very important since the calculation of activation

energies must be related to correct order of reaction and in addition to its direct contribution to alkyd fundamentals, knowledge of activation energies is of value in the design and control of alkyd processes [4].

The kinetic studies on alkyd resins formation has been the subject of disagreement among research workers. Due to the complexity of alkyd polymerization mechanism, and other reasons related to the uncertainty of the monomer structure, detailed kinetics model capable of yielding accurate prediction of reaction motion and product quality in alkyd reactor is basically lacking. This problem has been well-emphasized in reaction engineering literatures and no satisfactory solution has been reported. Kienel et al. [5] could not explain the glycerol-phthalic anhydride reaction by simple second or third - order equations, whereas in fatty acid - modified polyester, Berryman [6] claim second kinetic applies. However, Tawn [7] favours third order kinetic but only where the degree of reaction is 70-80%. Solomon and Swift [8] who studies 50% oil length alkyd resins found the reaction did not follow either second or third-order kinetic. Aigbodion and Okieimen [9] studies the kinetics of the preparation of rubber seed oil alkyd and found that the initial reaction rates follow second order kinetics with deviation at the later stage of reaction. Igwe and Ogbobe [10] carried out similar study, using melon seed, rubber seed oil, linseed and soyabean oil. The studies showed that the polyesterification reactions did followed a second order kinetics during the early part of the reaction. However, a second order kinetics was obtained after 150 minutes of conversion of monomers to products at the later stages of the reaction during which time the degree of polymerization is greater than five. Ekpa and Isaac [3] carried out similar study using coconut, soyabean and palm kernel oil. The studies

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showed that the polyesterification reactions follow a second order kinetics with slight deviation from linearity at the onset of the reaction.

It appears from the fore-going that there is no generally established kinetic study in the alkyd resins study. This has been attributed to the undetermined alkyd monomer architecture, specifically, kinetics study of non-drying oil alkyds has not been reported. The aim of the current study, therefore, is to use integral method of analysis to study the kinetics of styrenated and unstyrenated non-drying palm kernel oil.

Kinetic modelling

Theory of End-group Analysis, Extent of Conversion (P_n) and Average Degree of Polymerization (X_n) of Biopolymers have been reviewed by Isaac and Ekpa [10]. The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups [11]. Thus, the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base, i.e., monitoring the acid value. Considering a simple esterification reaction below ("Equation 1"), the rate of polymerization, R , can then be expressed as the rate of disappearance of carboxyl groups, $-d[\text{COOH}]/dt$ ("Equation 2").



$$R = \frac{-d[\text{COOH}]}{dt} = K [\text{COOH}] [\text{OH}] \quad (2)$$

For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric [11,12], and "Equation 2" can be written as:

$$-\frac{d[A]}{dt} = K[A]^2 \quad (3)$$

$$-\int \frac{d[A]}{[A]^2} = K \int dt \quad (4)$$

Where $[A]$ is the concentration of - OH groups or - COOH groups. However, "Equations 2 and 3" show that synthesis of biopolymers follows second order reaction, with K as the second order rate constant. By integrating "Equation 4", we have a second order rate constant.

$$-\int \frac{d[A]}{[A]^2} = K \int dt \quad (5)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = Kt \quad (6)$$

Where $[A]_o$ is the initial concentration at $t=0$ and $[A]_t$ is the concentration after time, t , of hydroxyl or carboxyl groups respectively. It is convenient at this point to express "Equation 6" in terms of the extent or fraction of reaction (P_n) defined as the fraction of the hydroxyl or carboxyl functional groups that have reacted at time t [11,12]. However, "Equation 7" gives P_n , which is also referred to as the extent or fraction of conversion.

$$P_n = \frac{[A]_o - [A]_t}{[A]_o} \quad (7)$$

This implies

$$[A]_t = [A]_o - [A]_o P_n = [A]_o (1 - P_n) \quad (8)$$

Substituting for $[A]_t$ in "Equation 6" and rearrangement, we have

$$\frac{1}{1 - P_n} = [A]_o Kt + 1 \quad (9)$$

Hence, "Equation 9" is a second order rate equation with K as second order rate constant. Hence, "Equation 9" indicates that a plot

of $1/(1 - P_n)$ versus t should be linear. This behaviour has been generally observed in polyesterification [11]. Several authors have plotted this graph during kinetic studies of rubber seed, coconut, soyabean, castor and palm kernel oils alkyds preparation [3,4,9,13-15] and observed deviations from linearity (second order) either at the early stage of the reactions or towards the end of the reactions.

The deviation from second order kinetics of polyesterification reaction was attributed to occurrence of chain branching at relatively short intervals along the polymer chain [3,9]. In addition, Onukwuli and Igbokwe [15] attributed this to the periods of reaction of the primary - OH and the secondary - OH leading to the formation of linear and three dimensional molecules respectively.

Odian [11] and Fried [12] define (X_n) as the average number of structural units per polymer chain.

$$X_n = \frac{1}{(1 - P_n)} \quad (10)$$

This "Equation 10" relating the degree of polymerization to the extent of reaction was originally set forth by Carothers and is often referred to as Carothers equation [11]. The extent of the reaction (P_n) and number-average degree of polymerization (X_n) were calculated from the end-group analysis of aliquots of the reaction mixture withdrawn at various intervals of time using the relationships in "Equations 7 and 10" respectively. The values of P_n and X_n for both MESO and COSO biopolymer samples, as well as acid values, pH and water of esterification obtained were plotted with reaction time. Also, rates of polymerization of biopolymers were calculated using "Equation 9" (end-group analysis) and based on the amount of water of polycondensation evolved at each stage of reaction.

Materials and Methods

Materials

Laboratory-grade phthalic anhydride with assay 99.7%, maleic anhydride with assay 99.0%, glycerol with assay 99.7%, styrene with assay 99.5%, xylene with assay 98%, benzoyl peroxide with assay 96%, and manganese (drier) from British Drug House (Poole, UK) were used in the preparation of the alkyds and styrenated alkyds. The palm kernel oil (PKO.) was purchased from Head Bridge Market, Onitsha, and Anambra State in a refined form and used without further purifications. Distilled water was used throughout the analytical procedures.

Methods

Preparation of Alkyd Resin: Three different alkyds were prepared with dehydrated palm kernel oil, glycerol, phthalic anhydride, maleic anhydride using lithium hydroxide as catalyst using the formulations shown in Table 1. The reactions were carried out in a three necked round bottom flask titled with a motorized stirrer, a dean-stark trap titled with water-cooled condenser and nitrogen in let tube at a temperature of 230-250°C. Xylene was also employed as the azeotropic solvent. Two stages were involved.

State 1 (Alcoholysis): At this stage, the measured quantity of dehydrated palm kernel oil was poured into the flask and heated to about 120°C to remove moisture. The heating was achieved with a heating mantle. Thereafter, the measured quantity of glycerol was added and the temperature was raised to 230°C. After 30 minutes, a small quantity of the aliquot was taken to check for its solubility in methanol. Alcoholysis was completed when the solubility test in methanol was positive. The reaction mixtures were cooled to about 140°C.

Stage 2 (Esterification process): At this stage, the measured quantity of phthalic anhydride, maleic anhydride and xylene was added into the flask and heated with a heating mantle. The temperature was gradually raised to about 230°C and maintained at a range of about 230-250°C for about 3 hr. Aliquots were withdrawn from the reaction mixture at time intervals of 30 minutes to check for drop in acid value. The reaction was then discontinued as soon as the acid value of the mixture attained the value of about 10 mg KOH/g.

Preparation of Styrenated Alkyd Resin: The styrenated alkyds were prepared by post co-polymerization of the alkyd resin. The alkyds were withdrawn into 100 ml flask and heated in the presence of an initiator, benzoyl peroxide, under reflux at 120°C for 3 hr.

Kinetic study

Integral method was used in data analysis. For this purpose, first - (Eq. (11)), second - (Eq. (12)) and third - order (Eq. (13)) rate equations were tested for each reaction.

$$kt = \ln n - \ln n_0 \quad (11)$$

$$kt = \frac{1}{n} - \frac{1}{n_0} \quad (12)$$

$$2kt = \frac{1}{n^2} - \frac{1}{n_0^2} \quad (13)$$

Where k is the rate constant, t time, n viscosity and n_0 is viscosity of the initial reaction mixture.

To test Eqs. (1) - (3), $\ln n$, $\frac{1}{n}$ and $\frac{1}{n^2}$ were plotted against t , respectively. In fitting a straight line to experimental data, the regression analysis was applied and in each case coefficient of determination (R^2) was determined.

Results and Discussion

The viscosity of alkyd resins determined during the polyesterification stage of the alkyd resin synthesis was used in analysis of kinetic study. The integral method was used in data analysis and for this purpose, first, second and third order rate equations were tested for each reaction of resins, A, B, and C. The rates of the reactions were estimated from change in viscosity with respect to time as shown in Figures 1-9. Reaction orders and rate constants are presented in Table 2. The results in Table 2 showed that the synthesis of alkyd resins (i.e., A and B) followed the first order equation while resin C followed the second order equation based on the values of coefficient of determination (R^2). A close look at the values of R^2 showed that synthesis of palm kernel oil-modified resin could follow first or second order kinetics depending on the time of reaction. From the figures, it is evident that the plot is linear at earlier stage of the reaction which confirmed the first order kinetics. However, a second order kinetics is generally obtained after 100 minutes of conversion of reactants to products, which represent the later stage of the reaction. This late stage of the reaction represents the greater part of the reaction time and it is here that one is most concerned with the application of conventional control test such as acid value to a practical alkyd synthesis.

The calculated rate constants for first order reaction of resins A and B are $13 \times 10^{-3} \text{ min}^{-1}$ and $30 \times 10^{-3} \text{ min}^{-1}$; while for second order reaction of resin C, its rate constant is $3 \times 10^{-3} \text{ (Pa.S)(min)}^{-1}$. Many authors have reported similar observation for alkyds prepared from other oils [4,9,15]. Rate constant in polyesterification reactions depends majorly on the reaction mixture, change in temperature, and removal of water of polyesterification [9]. For first and second order reaction, rate constant depends on the initial concentration of the reactants (acid value). The

decrease in acid value as the reaction proceed leads to increase in the viscosity of the reaction mixture and subsequently leads to increase in the rate of reaction. The high rate of the first order reaction of resin B shows that the reaction occurs at faster rate more than the other resins. The viscosity increased during the copolymerization reaction. Rates of the reaction were estimated from changes in viscosity as shown in Figures 10-18. Reaction orders and rate constants are given in Table 3. The result in Table 3 showed that the copolymerization of styrene with alkyd resin A is first order reaction based on the values of R^2 . The value of coefficient of determination (R^2) is highest in first order reaction followed by second order reaction and least in third order reaction. But for the copolymerization of styrene with alkyd resin B and alkyd resin C, the reactions are said to be second order reactions based on the values of R^2 .

These differences in order of reactions between resins A, B and C copolymerized with styrene could be possibly explained by:

1. Decrease in volume due to the consumption of styrene.
2. Fractional kinetics may apply, possibly because of the difficulty associated with the removal of water of reaction.
3. Under copolymerization condition may exist.
4. Some of the double bonds in styrene structure may not be available for reaction.

Efforts were made to compare these possibilities with the previous works found in the literature but it does not provide desired results. This is because the kinetic study of styrenated alkyds via copolymerization process of non - drying palm kernel oil - modified alkyd resins have not receive adequate research attention but future work will review this in detail.

Conclusions

The results from this research revealed that the kinetic study of resins A and B followed the first order reaction while resin C followed the second order reaction with rate constants of $13 \times 10^{-3} \text{ min}^{-1}$, $30 \times 10^{-3} \text{ min}^{-1}$, and $3 \times 10^{-3} \text{ (Pa.S)(min)}^{-1}$ respectively. For styrenated alkyds, kinetic study confirmed that styrenated alkyd A followed the first order kinetics and styrenated alkyds B and C followed the second order

Resin type	Oil length (%)	Glycerol (g)	LiOH (g)	PA (g)	MA (g)
Resin-A	50	50	0.5	50	-
Resin-B	50	50	0.5	25	25
Resin-C	50	50	0.5	15	35

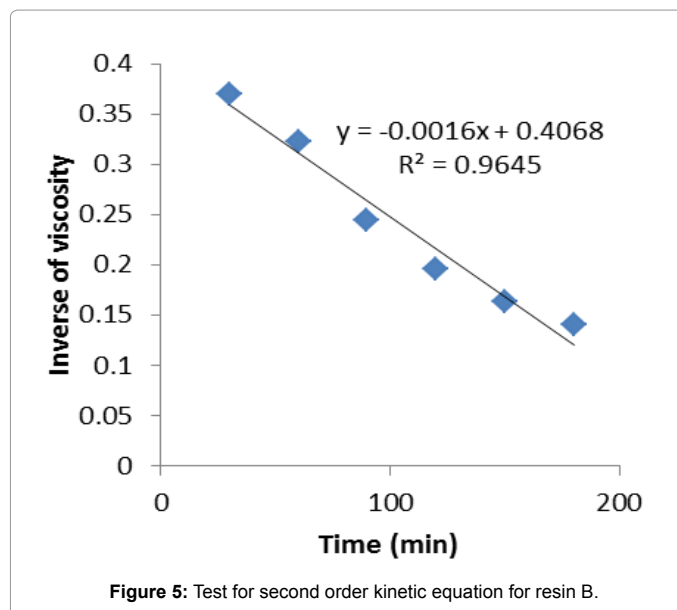
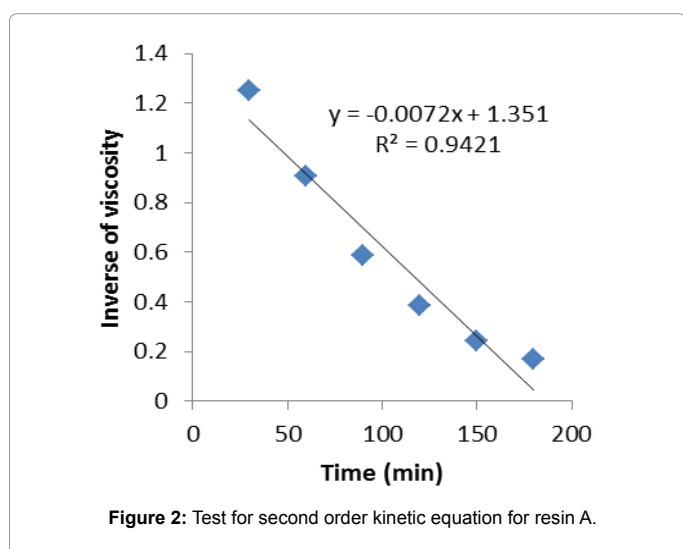
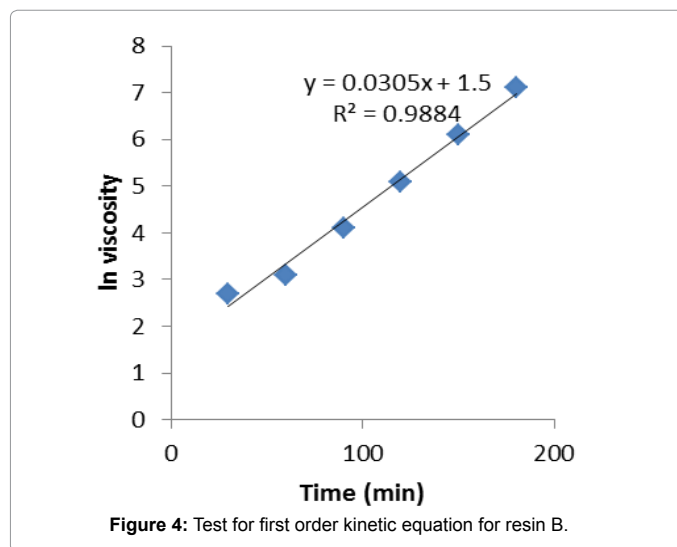
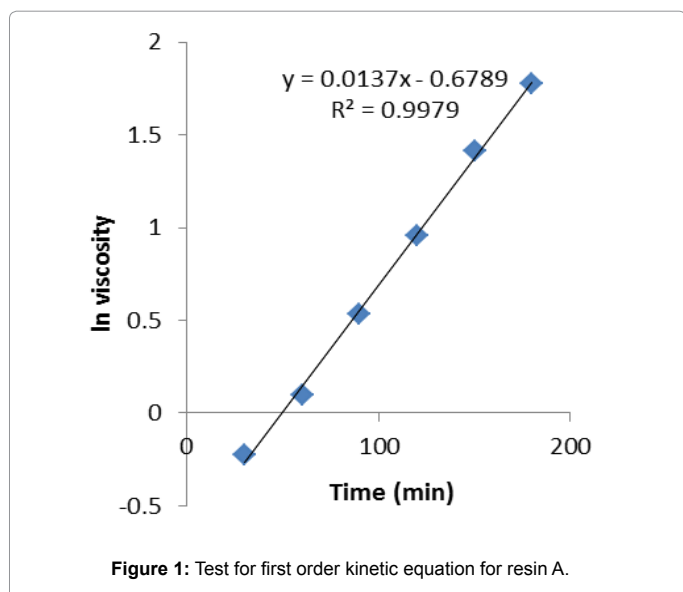
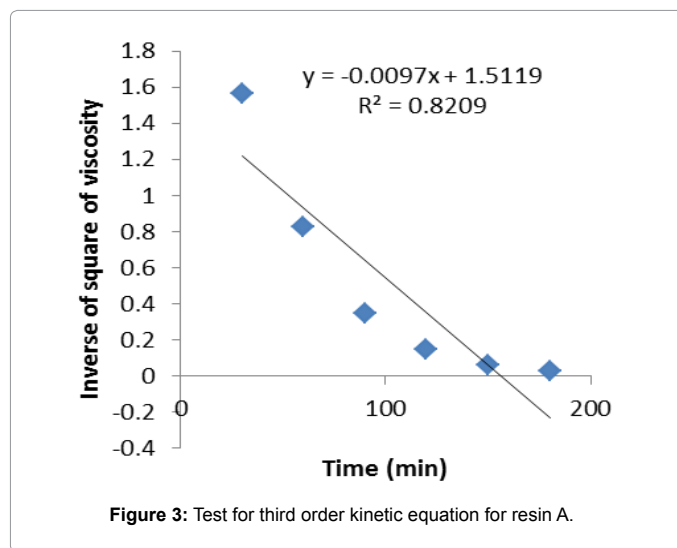
Table 1: Recipe of the preparation of resin.

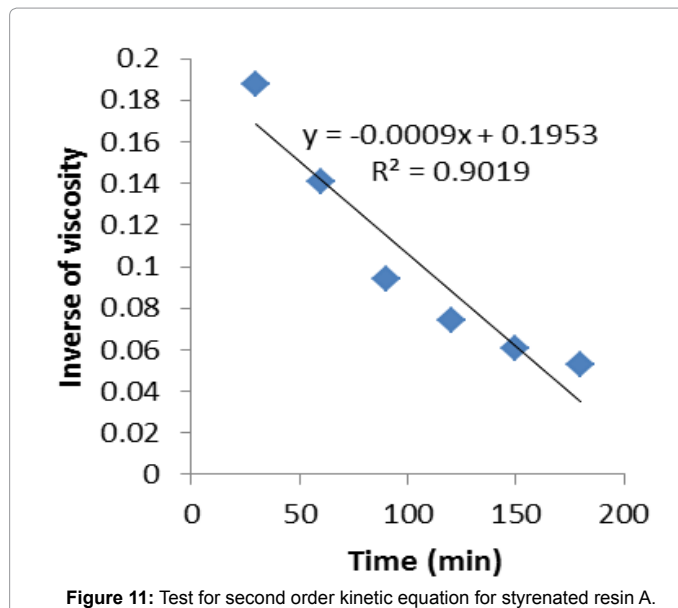
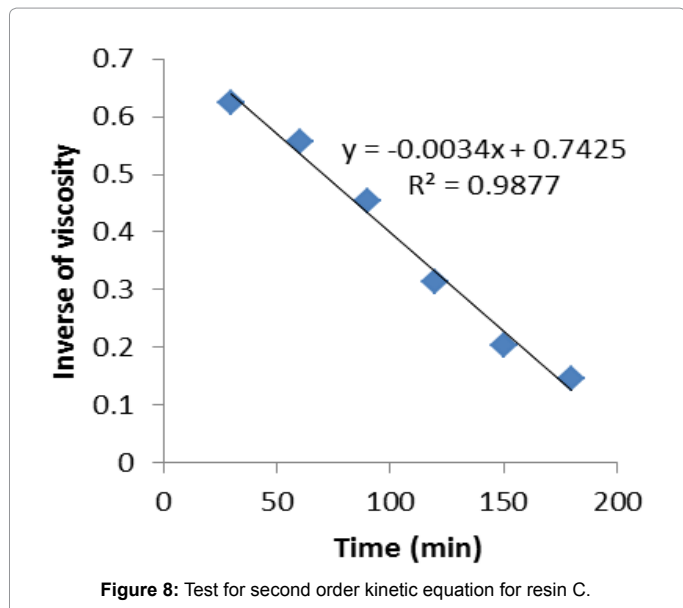
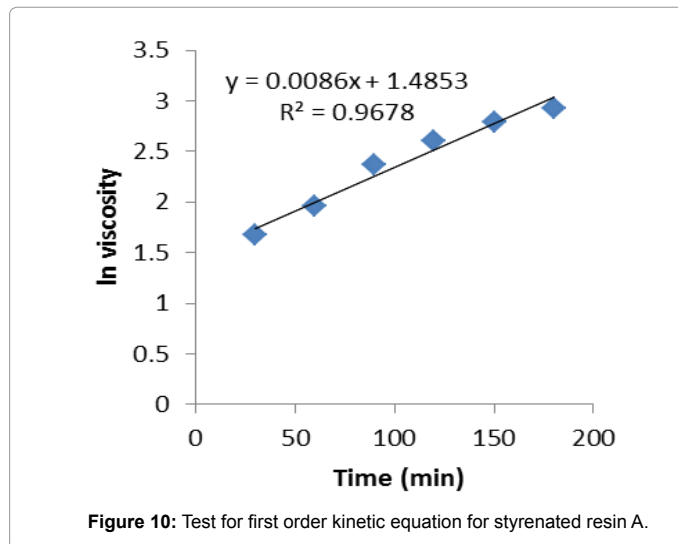
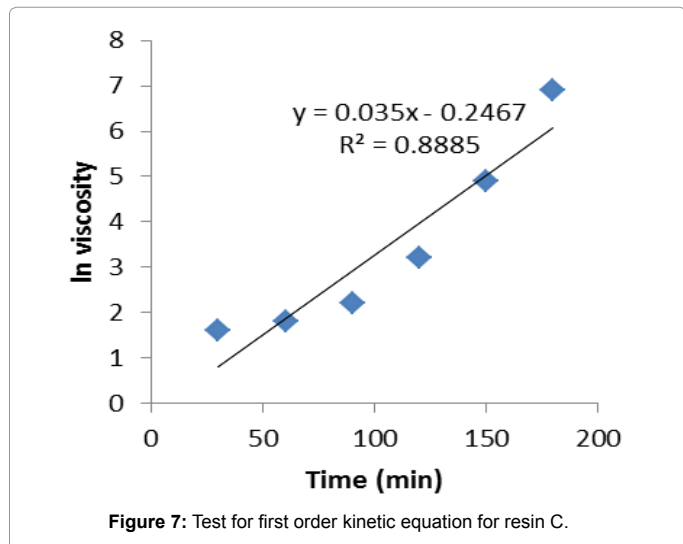
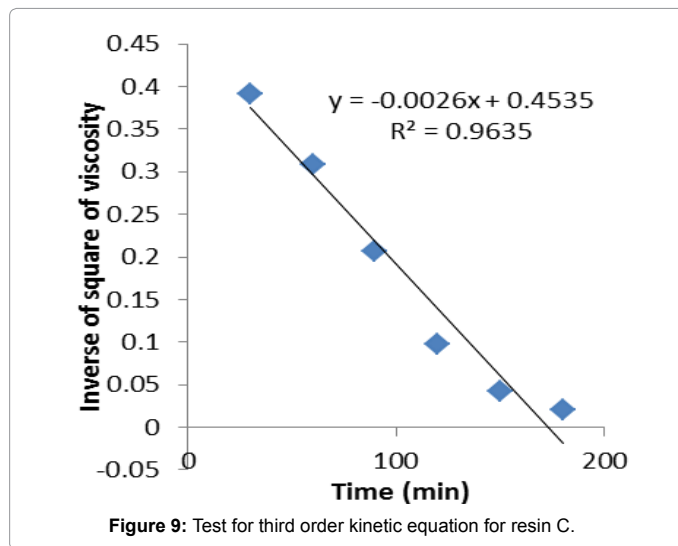
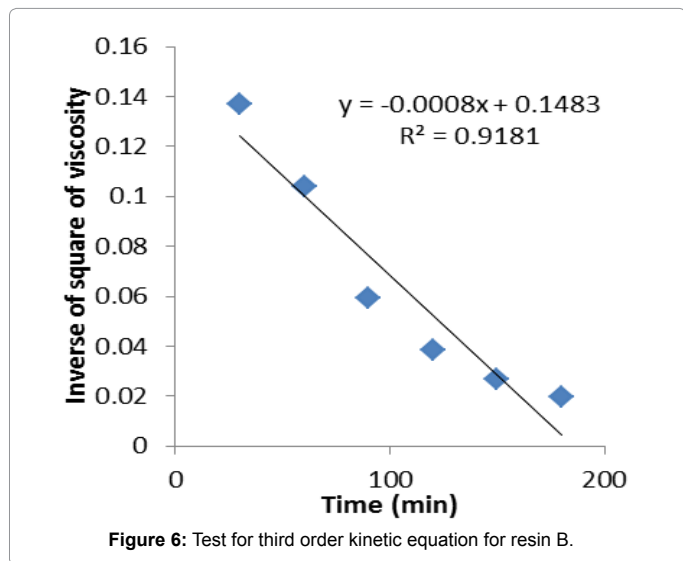
Components	Order of Reaction (n)	Rate of reactions (Pa.s/min)	Rate Constant (k)	R^2
Resin-A	1	0.013	$13 \times 10^{-3} \text{ (min)}^{-1}$	0.997
	2	0.007	$7 \times 10^{-3} \text{ (Pa.s)}$	0.942
	3	0.009	$4.5 \times 10^{-3} \text{ (Pa.s)}^2 \text{ (min)}^{-1}$	0.820
Resin-B	1	0.03	$30 \times 10^{-3} \text{ (min)}^{-1}$	0.988
	2	0.001	$1 \times 10^{-3} \text{ (Pa.s)}$	0.964
	3	0.0003	$1.5 \times 10^{-4} \text{ (Pa.s)}^2 \text{ (min)}^{-1}$	0.918
Resin-C	1	0.035	$35 \times 10^{-3} \text{ (min)}^{-1}$	0.888
	2	0.003	$3 \times 10^{-3} \text{ (Pa.s)(min)}^{-1}$	0.987
	3	0.002	$1 \times 10^{-3} \text{ (Pa.s)}^2 \text{ (min)}^{-1}$	0.963

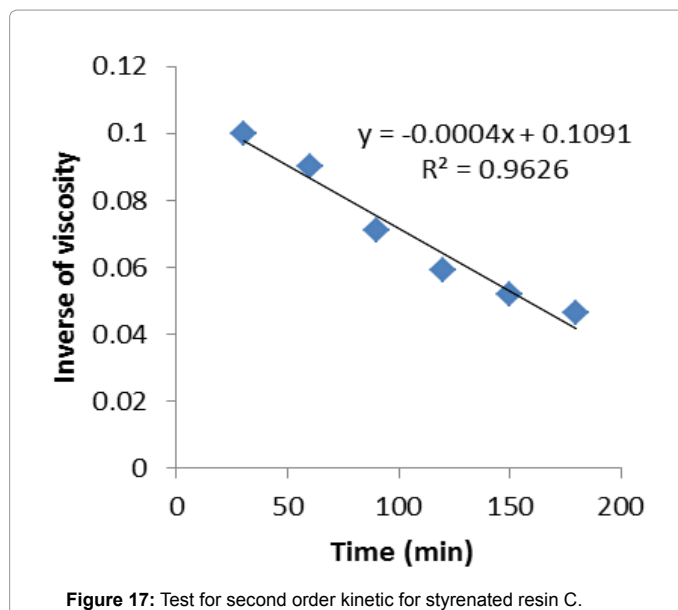
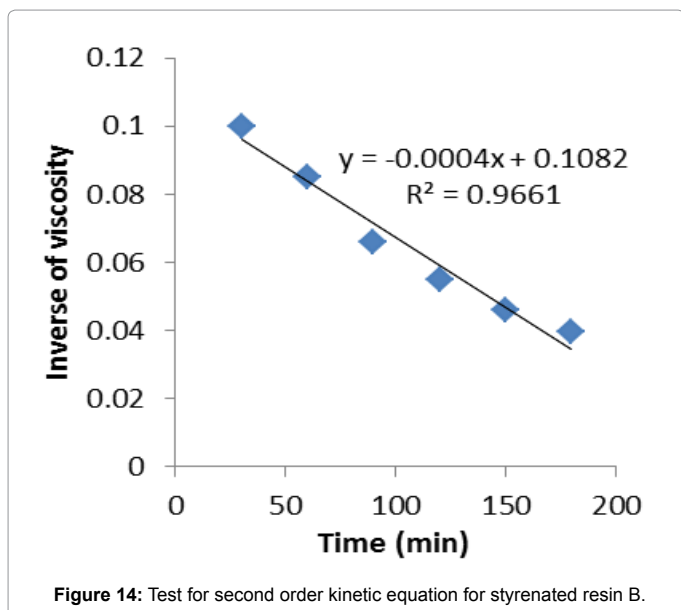
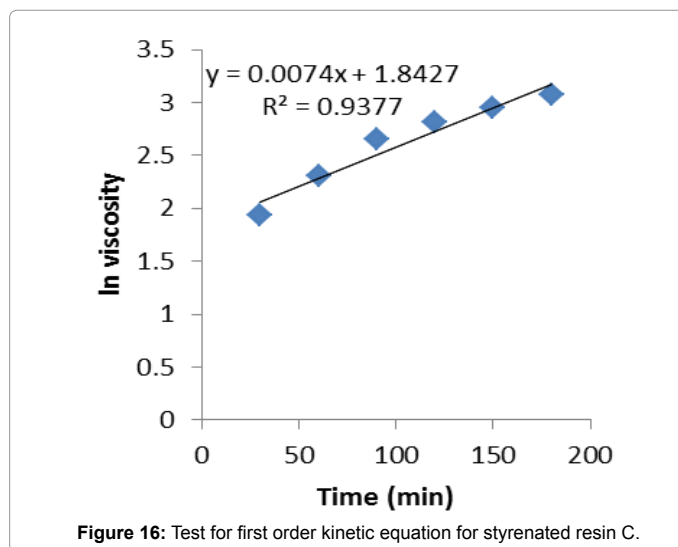
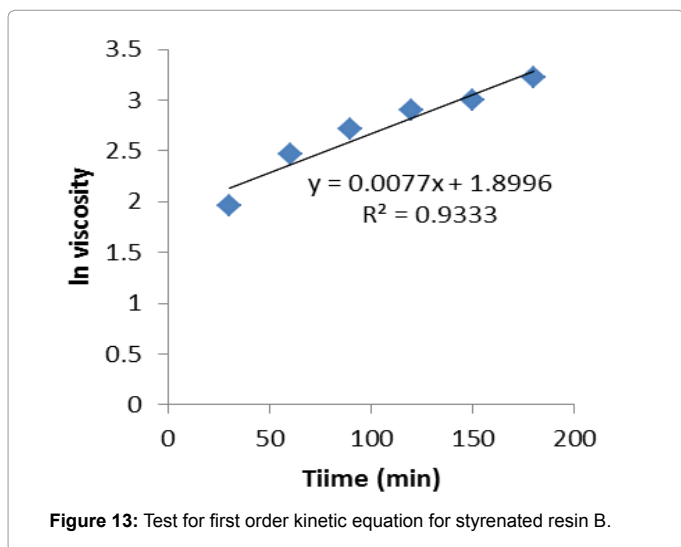
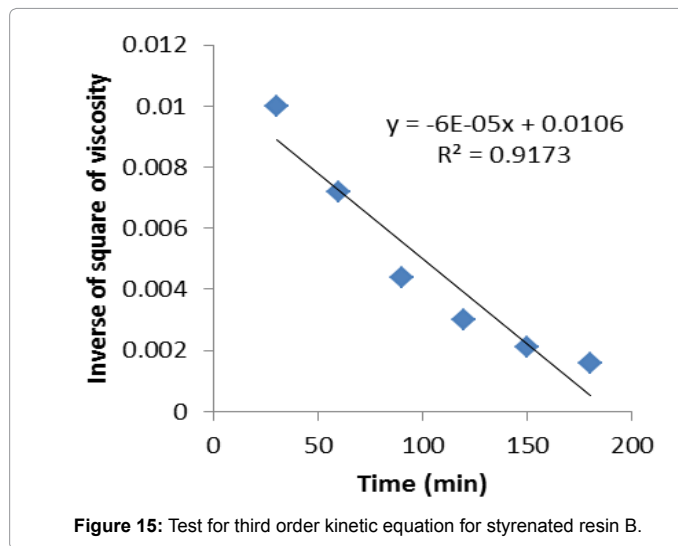
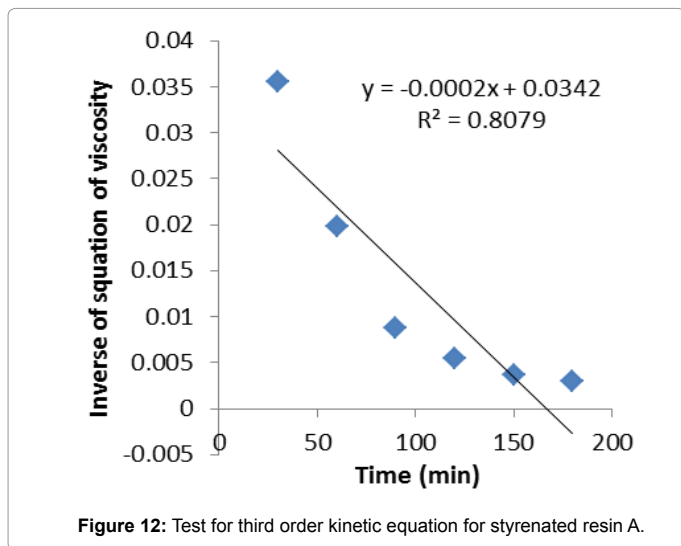
Table 2: Results for kinetic study of alkyds resins.

Components	Order of Reaction (n)	Rates of reaction (Pa.s/min)	Rate Constant (k)	R ²
SA	1	8×10^{-3}	$8 \times 10^{-3} (\text{min})^{-1}$	0.967
	2	7×10^{-4}	$7 \times 10^{-4} (\text{Pa.s})(\text{min})^{-1}$	0.901
	3	5.9×10^{-5}	$2.95 \times 10^{-5} (\text{Pa.s})^2 (\text{min})^{-1}$	0.807
SB	1	7×10^{-3}	$7 \times 10^{-3} (\text{min})^{-1}$	0.933
	2	6×10^{-4}	$6 \times 10^{-4} (\text{Pa.s})(\text{min})^{-1}$	0.966
	3	6×10^{-5}	$3 \times 10^{-5} (\text{Pa.s})^2 (\text{min})^{-1}$	0.917
SC	1	7×10^{-3}	$7 \times 10^{-3} (\text{min})^{-1}$	0.937
	2	6×10^{-4}	$6 \times 10^{-4} (\text{Pa.s})(\text{min})^{-1}$	0.962
	3	6×10^{-5}	$3 \times 10^{-5} (\text{Pa.s})^2 (\text{min})^{-1}$	0.774

Table 3: Results for kinetic study of styrenated resins. R²=coefficient of determination; SA, SB and SC=Styrenated alkyd resins A, B and C respectively.







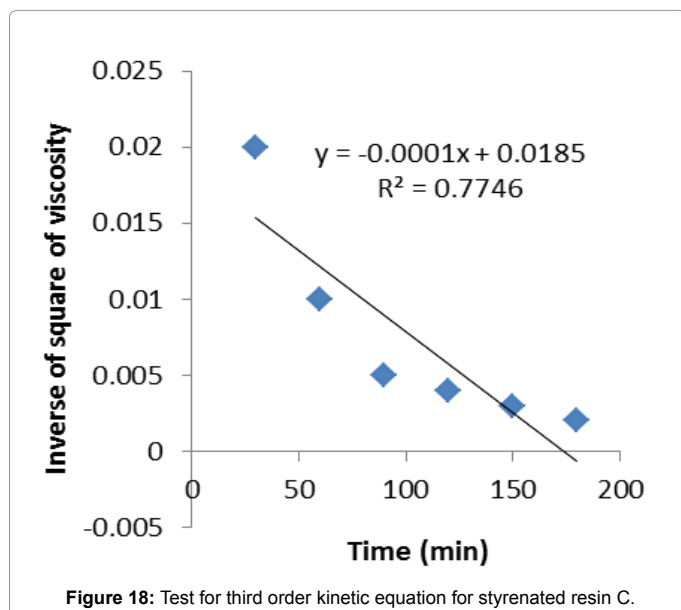


Figure 18: Test for third order kinetic equation for styrenated resin C.

kinetics with rate constants of $8 \times 10^{-3} \text{ min}^{-1}$, $6 \times 10^{-4} (\text{Pa.S})(\text{min})^{-1}$ and $6 \times 10^{-4} (\text{Pa.S})(\text{min})^{-1}$ respectively. It can be concluded that palm kernel oil based alkyd resins and its styrenation could be best explained by first and second order kinetics.

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