ISSN 2394-9651

International Journal of Novel Research in Physics Chemistry & Mathematics
Vol. 2, Issue 3, pp: (1-5), Month: September-December 2015, Available at: www.noveltyjournals.com

Kinetic Studies on Polyesterification Process of Cloisite® 20 Organoclay Modified Dehydrated Castor Oil (DCO) Fire Retardant Alkyd Resin

[1]Onukwuli O.D, [2]Madiebo E.M.

[1, 2] Chemical Engineering Department, Faculty of Engineering, Nnamdi Azikiwe University, Awka

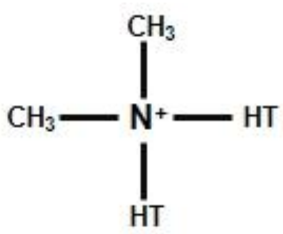
Abstract: **Kinetics studies of cloisite® 20 Organoclay Modified Dehydrated Castor Oil (DCO) Fire Retardant Alkyd Resin were studied using the first, second and third order chemical reaction equation. The DCO modified alkyd resin macromolecule was synthesized through alcoholysis-esterification interface using glycerol, phthalic and maleic anhydride, PA and MA. Eight samples of fire retardant resin were produced. Sample I,II,III,IV,V and VI contains 1, 2, 4, 6, 8 and 10% weight of cloisite® 20 organoclay. Sample VII and VIII contain 4% of each of cloisite® 20 with 100% PA and 3:1 ratio of MA and PA respectively. The viscosity profile of the alkyd system was monitored and confirmed to increase as the reaction progress which implies that alkyd products are formed. However, there tends to be decrease in the order of reaction when compared to other work on alkyd resin kinetics. This is attributed to the presence of cloisite® 20 which could mask the reaction site in the alkyd reaction system. It was also found that first, second and third order reaction equation can be used to explain the reaction path of cloisite® 20 modified resin.**

Keywords: **alkyd resin, cloisite® 20, reaction order, esterification.**

1. INTRODUCTION

One of the importance of most chemical processes is determination of its reaction rate especially when such process is of practical importance. This is the typical case of the esterification processes of cloisite® 20 modified dehydrated castor oil fire retardant alkyd resin. Modifying alkyd resin with cloisite® 20 impact an prove end use properties like hardness and fire retardancy. The determination of the correct reaction order is of great importance, 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 [1]. Alkyd resin has a variety of applications in coating industries where they are used as binders.

Cloisite® 20 is a natural montmorillonite modified with a quarternary ammonium salt. It is used mainly as an additive for plastics to improve various physical properties such as reinforcement etc. It is represented schematically as shown below



Where HT is hydrogenated tallow (65% C18; 30%C16; 5% C14) the organic modifier (2M2HT) is Bis (hydrogenated tallow Alkyl), dimethyl quaternary ammonium salts.

International Journal of Novel Research in Physics Chemistry & Mathematics
Vol. 2, Issue 3, pp: (1-5), Month: September-December 2015, Available at: www.noveltyjournals.com

The kinetics of alkyd resins has been investigated by many researchers by checking the acid value profile as the reaction progresses via determining the acid value of aliquots of the alkyd reaction mixture withdrawn at various time intervals. It can also be monitored by checking the viscosity to ascertain where to stop the reaction before it turn to gel. It is well known that the rate constant in esterification reactions is dependent on the proportion of the reactants, speed of agitation of the reaction mixture, changes in temperature and removal of water of esterification [2], these factors jointly represents the viscosity profile of the alkyd system. These research seek to investigate the reaction path of cloisite® 20 modified dehydrated castor oil fire retardant alkyd resin and to understand any short comings of incorporating cloisite® 20 organoclay in the resin.

2. EXPERIMENTAL

2.1 Materials Preparation and Characterization:

The castor oil seeds were dehulled to obtain the cotyledon (mesocarp). The cotyledon were sun dried for one week to reduce the moisture content to the minimal. The dried cotyledons were milled and the oil extracted by solvent method using soxhlet extractor. Refined castor seed oil was mixed with 0.8g of sulfuric acid in a conical flask and heated to 260-300 ^{o}C in an inert atmosphere of nitrogen. The temperature was maintained for about one hour and a vacuum of 4-6 mmHg applied. At the end of this period, the source of heat was removed and the dehydrated oil allowed to cool. The characteristic of the crude oil and neutralized oil were determined according to AOCS standard [3]. The physico-chemical properties (specific gravity, acid value free fatty acid content, refractive index, saponification value, colour and iodine value) were determined using the American oil Chemists Society methods [3]

2.2 Preparation of Castor Oil Alkyd Resin:

A three-necked glass vessel was used for the reactions. The vessel was placed on a magnetic heater with stirrer. An inert atmosphere was confirmed in the reaction chamber by a continuous flow of nitrogen gas. The details of the ingredients are listed in Table 1.

Alcoholysis: In alcoholysis, oil, glycerol and catalyst (CaO) were taken in the reaction chamber, and heated at 230^{o}C. The end point of the reaction was confirmed by the complete dissolution of the reaction products into methanol at a ratio of 1:3. After that, the reaction products were cooled to 120^{o}C.

Esterification: In esterification process, PA, MA and cloisite® 20 were added to reaction products of the alcoholysis. The temperature was maintained at 230-260^{o}C. A continues monitoring of the reaction system was initiated to monitor the acid value. The end point of the reaction was confirmed by measuring and thus confirming the acid value of the products to be less than 10 after which the liquid resin were kept for further testing. The characteristics of the fire retardant alkyd resin were determined according to AOCS [3]. Viscosity was determined by Brookfield viscometer, RVT Model (#Spindle 3, RPM 20).The process flow diagram is shown in fig. 1.

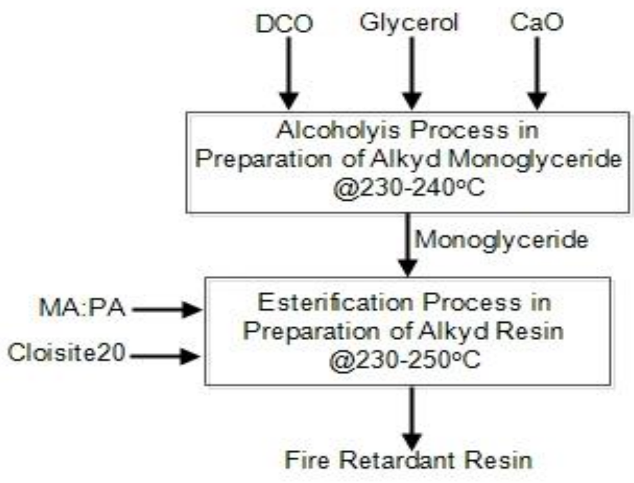


Fig.1: Process flow diagram for fire retardant resin

International Journal of Novel Research in Physics Chemistry & Mathematics
Vol. 2, Issue 3, pp: (1-5), Month: September-December 2015, Available at: www.noveltyjournals.com

Table.1: Recipe for fire retardant alkyd Resin

Alkyd Resin	Oil (g)	Glycerol (g)	CaO (g)	PA (g)	MA (g)	Mass ratio (PA:MA)	Cloisite20 Wt%
I	100	20	0.05	25	25	50:50	1
II	100	20	0.05	25	25	50:50	2
III	100	20	0.05	25	25	50:50	4
IV	100	20	0.05	25	25	50:50	6
V	100	20	0.05	25	25	50:50	8
VI	100	20	0.05	25	25	50:50	10
VII	100	20	0.05	12.5	37.5	25:75	4
VIII	100	20	0.05	50	-	100:0	4

2.3 Kinetic Study:

The kinetic models of the esterification reaction was investigated using rate of change of viscosity with time interval of 30, 60, 90, 120 and 150mins. The data obtained were fitted using first, second and third order reaction equation. The equation is as follows.

First order reaction

$$In\mu = kt + In\mu_o \text{ ....} (1)$$

Second order reaction

$$1/\mu = kt + 1/\mu_o \text{ ....} (2)$$

Third order reaction

$$1/\mu^2 = 2kt + 1/\mu_0^{\ 2} \text{ ....} (3)$$

Where μ and μ_o is the final viscosity and initial viscosity. T is the time and k, the rate constant.

3. RESULTS AND DISCUSSIONS

Kinetic models of the alkyd samples investigated using OriginPro 9.1. The adjusted R-square was utilized to measure the best fitted data since it also accounts for degree of freedom. The estimation of the rate constant k follows a linearization approach that resulted from comparing data set from each alkyd samples using different kinetic models; first, second and third order reactions. The viscosity profile is used to measure the rate yield of the resin.

The alkyd samples show no linearity at the early stages of reaction up to 60mins of reaction (fig 1). Linearity started at the 60 mins of reactions of the alkyd samples (I-VIII). Samples I, II, III, IV and VIII follows first order reaction with rate constant k given as 7.57×10^{-3}, 7.23×10^{-3}, 6.8×10^{-3}, 6.67×10^{-3} and 16.3×10^{-3} Pa.s/min respectively. Sample V follows second order reaction with rate constant, k, as -1.4×10^{-3} Pa.s/min while samples VI and VII follows third order reactions with rate contstant, k, as -0.3×10^{-3} and -1.04×10^{-3} Pa.s/min respectively. An attempt to compare other kinetics studies of other author show that [3] reported on the kinetics of the preparation of rubber seed oil alkyds and found that the initial reaction rates followed second order kinetics with deviation at the later stage of reaction with the rate constant in the order of 10^{-5} (mg KOH)$^{-1}$ min^{-1}. The differences in the order of rate constant might be attributed to the presence of cloisite® 20. Though cloisite® 20 which is incorporated into the resin improves fire retardant properties of the resin, it is regarded as an impurity since it does not take part in the reaction. This is synonymous with Neal (2000) who reported that any starting material that do not take part in the reaction is an impurity, hence can hinder reaction rate. It can also be deduced that kinetic reactions of alkyd resin can be explained by first, second and third order reaction equation.

Novelty Journals
ISSN 2394-9651
International Journal of Novel Research in Physics Chemistry & Mathematics
Vol. 2, Issue 3, pp: (1-5), Month: September-December 2015, Available at: www.noveltyjournals.com

Table.2: Characteristics of the kinetic model

Kinetic model characteristics	Alkyd Samples							
	I	II	III	IV	V	VI	VII	VIII
Reaction order	1st	1st	1st	1st	2nd	3rd	3rd	1st
Reaction rate 10^3(Pa.s/min)	7.57	7.23	6.8	6.67	-1.4	-0.3	-1.04	16.1
Adj. R^2	0.9867	0.9887	0.9882	0.9717	0.9821	0.9837	0.9945	0.9717

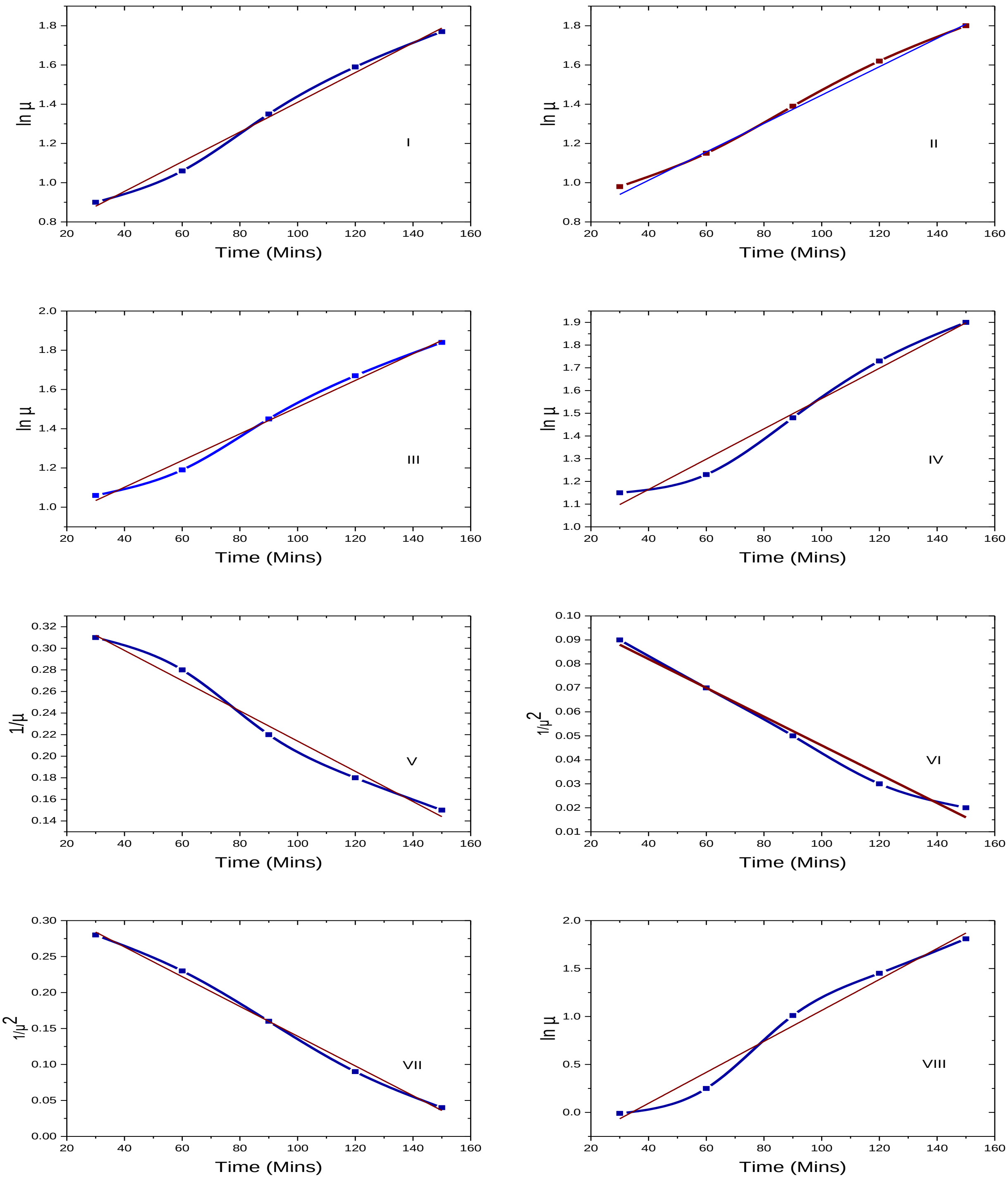


Fig.1: Kinetic models of the esterification process of fire retardant resin samples I-VIII

International Journal of Novel Research in Physics Chemistry & Mathematics
Vol. 2, Issue 3, pp: (1-5), Month: September-December 2015, Available at: www.noveltyjournals.com

4. CONCLUSION

It can be concluded from this Kinetics studies of cloisite® 20 modified dehydrated castor oil alkyd resin that incorporating cloisite® 20 in the resin system slows down reaction rate and hence rate constant.

REFERENCES

[1] Igwe, I. O and O. Ogbobe (2001) A study on kinetics of alkyd resin formation. J. Chem. Soc. Nig., 26: 75-80.

[2] Aigbodion, A.I and F.E.Okiemen (1996) Kinetics of the reaction preparation of rubber seed oil alkyds resin. Eur. Polymer J., 32: 1105-11081.

[3] A.O.C.S. (2011) Official Methods and Recommended Practices of the American Oil Chemist's Society, 4th ed., AOCS, Champaign.

[4] Neal, G Anderson (2000) Practical Process Research and Development. Academic press p238.