

# Alkyd-derived Urethane Acrylate Oligomers in UV Curable Coatings; Synthesis and Properties

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## Introduction

Urethane acrylates are well known oligomers and commonly used as major components in UV curable coating formulations<sup>1a-b</sup>. They are of interest because of their ability to introduce toughness in terms of the combination of high modulus and good elasticity into a UV cured film. Urethane acrylate oligomers are typically prepared from the reaction of a hydroxy-acrylate with a multi-functional isocyanate and a hydroxy-functional prepolymer. They are generally more expensive than corresponding acrylate ester oligomers due to the cost of the isocyanate involved in the preparation. Consequently, any means of reducing cost of a urethane acrylate is of great interest.

Alkyds have formed the basis of general purpose coatings for many years<sup>2a-c</sup>. Part of the attraction in the use of these materials stems from their inexpensive nature due to their availability from natural, renewable resources. This is especially true today in light of the substantial increases in the cost of petrochemically derived resources. Literature reveals limited use of alkyds as components in UV curable formulations<sup>3a-c</sup>. In most cases alkyds have been used as simple blends along with conventional monomers, photoinitiators, and other additives. However, alkyds can be viewed as hydroxy-functional prepolymers and as such are suitable for use in urethane acrylate oligomers. Therefore, the use of alkyds as starting materials appeared to us to be an obvious means of reducing cost of urethane acrylates by reducing, at least in part, dependence on petrochemical resources.

This report details some of our studies on the use of alkyd-derived urethane acrylate oligomers in UV curable coatings<sup>4a-b</sup>. Synthesis and liquid properties of the oligomers are described along with selected properties of the UV cured films derived from model coatings based on these oligomers.

## Results and Discussion

In formulating UV curable coatings DSM Desotech has for many years employed the use of urethane acrylate oligomers. Our interest in urethane acrylate modified alkyds arose from our interest in developing a novel class of oligomers having versatile properties for use in both hard and soft coatings and optimally at lower cost. Because alkyds are derived from oils as renewable resources, we viewed this as an opportunity not only to develop a novel, versatile class of materials but also to lower cost by reducing dependence on petrochemical resources.

## What is an Alkyd

The word “alkyd” is descriptive of the composition and is a conjunction of the words “alcohol” and “acid.” Therefore, in its most basic sense an alkyd is a polymer of an alcohol and an acid and is often regarded as an “oil-modified” polyester. It is the oil modification that truly distinguishes an alkyd from a typical polyester because the fatty acid component present in the oil imparts very unique properties not normally associated with polyesters. Alkyds were originally prepared by the reaction of alcoholized oils (glyceride esters) with phthalic anhydride. Figure 1 represents a simplified structure of an alkyd.

### **Alkyd Synthesis**

As stated above, in order for the polymer forming reaction to occur the oil, a tri-ester of glycerine, must first be converted to a multi-functional hydroxy compound. This conversion can be accomplished by either alcoholysis of a natural oil or by direct esterification of a multi-functional alcohol with a naturally occurring fatty acid. Once prepared, the oil-based hydroxy compound can then be polymerized with multi-functional carboxylic acids and optionally with other alcohols. This sequence of step is depicted in figure 2.

### **Urethane Acrylate Synthesis**

Figures 1 and 2 indicate that stoichiometry in the polymer forming reaction can be suitably adjusted to influence the molecular weight of the resulting alkyd and also to ensure the polymer is hydroxy-functional. Therefore, the alkyd can easily be prepared for suitable use in the synthesis of a urethane acrylate oligomer. Figure 3 illustrates the use of an alkyd in the synthesis of a urethane acrylate oligomer based on isophorone diisocyanate (IPDI) and 2-hydroxyethyl acrylate (HEA).

Implicit in the sequences described in figures 1-3 is the versatility provided by the use of alkyd-derived urethane acrylate oligomers. The molecular weight of the alkyd diol can be controlled by stoichiometry as can the molecular weight of the resulting urethane acrylate oligomer. Furthermore, the composition of the alkyd can be varied dependent upon the nature of the oil or fatty acid, the presence of co-reacting diols, and the composition of the diacids. Similarly, the composition of the urethane can be influenced by the type of isocyanate and the hydroxy-acrylate.

### **Oligomer Design Study**

Our study began with the synthesis of a series of alkyd diols in which a number of compositional variables were changed. We chose to vary the type of oil or fatty acid (soya or coconut), the type of “glyceride” monoester (glycerine, trimethylol propane (TMP), or pentaerythritol (PE)), the content of “glyceride” present in the alkyd polymer (0-100 mole percent), and the type of co-reacting diol (neopentyl glycol (NPG) or 2-butyl-2-ethyl-1,3-propanediol (BEPD)). Held constant in this series were the types and mole ratios of acids used (isophthalic acid (IPA) and adipic acid (ADA), 2:1) and the molecular weight of the alkyd polymer (1000 g/mole).

These alkyds were then used to prepare a series of urethane acrylate oligomers in which the type of isocyanate was varied (isophorone diisocyanate (IPDI) or toluene diisocyanate (TDI)). The molecular weight of the urethane was kept constant at approximately 1600 g/mole and all oligomers were terminated with 2-hydroxyethyl acrylate (HEA).

Each of the oligomers was then used in a simple model UV curable coating formulation. The oligomers were used in identical formulations so that the effect of the compositional variables could be directly determined without fear of being masked by changes in the formulation. Two types of model coating composition were selected and are summarized in table 1. For this study we limited our choice to compositions giving hard coating films, and as can be seen the compositions are very simple, containing only oligomer, monomer, and photoinitiator. Coatings prepared according to the compositions in table 1 were cast onto Mylar as 75 micron wet films and cured under a nitrogen atmosphere with a medium pressure mercury lamp (Fusion Systems D bulb), at a dose of 1 joule-cm<sup>-2</sup>.

Table 1. Model UV Coating Formulations

Composition (wt %)	Low BPAEDA	High BPAEDA
Urethane acrylate oligomer	55	55
Isobornyl acrylate (IBOA)	30	30
Ethoxylated bisphenol-A diacrylate (BPAEDA)	5	10
Hexanediol diacrylate (HDDA)	10	
Trimethylolpropane triacrylate (TMPTA)		5
Darocur <sup>®</sup> 1173	3 pph	3 pph

The critical responses we sought to examine were the liquid viscosity of the polymeric alkyd diol and the corresponding urethane acrylate, and the tensile modulus, water sensitivity, oil sensitivity, hydrolysis resistance, and oxidative color development of the resulting cured films. Unfortunately, space considerations preclude reporting all our results. Instead, results of selected performance properties will be reported.

### Structural Effect on Alkyd Viscosity

Monoglyceride was prepared from coconut oil alcoholized with glycerine according to the sequence described in step one of figure 2. This monoglyceride diol was used to prepare of series of alkyd polymers using either neopentyl glycol (NPG) or 2-butyl-2-ethyl-1,3-propane diol (BEPD) as a co-reacting diol along with isophthalic acid (IPA) and adipic acid (ADA) in a 2:1 mole ratio. The overall hydroxyl:carboxyl ratio was selected to result in a polymer of 1000 g/mole number average molecular weight. Figure 4 depicts the effect of incorporating the monoglyceride at varying mole ratios on the liquid viscosity of the resulting alkyd diol. A dramatic reduction in viscosity with increasing glyceride content is observed along with the fact that use of NPG as a co-reacting diol results in slightly higher viscosity compared to BEPD.

### Structure Effect on Cured Film Tensile Modulus

The alkyd polymers of figure 4 were converted into urethane acrylate oligomers as described above and the oligomers were used to make model coating as described in Table 1 above. Figure 5 describes the effect of monoglyceride content on the tensile modulus of cured films from the Low BEAEDA model formulation. The figure indicates a general trend to lower modulus with increasing glyceride content and also indicates that use of NPG gives higher modulus than BEPD. For the BEPD series of alkyds, the levels of 50 and 75 mole percent glyceride seem to be suspicious and should probably be reproduced.

### Structure Effect on Sensitivity to Mineral Oil

Figure 6 describes the effect of monoglyceride content on sensitivity to mineral oil. Mineral oil resistance is a concern in alkyds because of the presence of the oleophilic fatty acid component of the oil. Total sensitivity is reported in terms of the combination of absorption and extraction of the cured film by oil following immersion for 21 days at room temperature. The figure shows the increasing sensitivity of alkyds containing NPG with increasing glyceride content, and this would be the expected trend. However, the BEPD series of alkyds shows very unusual behavior and actually would be expected to be more sensitive than the NPG series because BEPD has a much higher hydrocarbon content than NPG. The unusual behavior could be due to the fact that the total sensitivity of these films is very low for both series. Total sensitivity less than 5 percent is normally regarded to be very good. Therefore, we can conclude that sensitivity to mineral oil in either series of alkyd-based oligomers can be expected to be very good.

### **Structure Effect on Hydrolytic Stability**

Because alkyds contain ester groups in both the main chain polymeric backbone and the pendant side groups, their resistance to hydrolysis can be suspect. For this reason, hydrolytic stability of cured films was of interest. Figure 7 describes the dependence of hydrolytic stability on the level of glyceride incorporated into the alkyd diol. Hydrolysis resistance is reported as a percentage loss in equilibrium modulus following exposure of the cured film to a chamber at 85°C and 85% humidity for 30 days. Normally, a loss of 25% or less in equilibrium modulus is regarded as good stability. The graph indicates there is no particular dependence of hydrolytic stability on glyceride content, but we can conclude that all coatings have good hydrolysis resistance.

### **Summary**

Alkyd diols became of interest for use as starting materials in the synthesis of UV curable urethane acrylate oligomers. Their interest arose from their prospect of being a novel class of materials capable of offering a great deal of versatility in the design of properties demonstrated by the oligomers. In addition to such versatility, the fact that they are derived from renewable natural resources, independent of petrochemical supply, offered the potential for lower raw material cost.

In this report, the synthesis of hydroxy-terminated alkyd prepolymers from coconut oil, glycerine, isophthalic acid, adipic acid, and either neopentyl glycol or 2-butyl-2-ethyl-1,3-propane diol was demonstrated. The prepolymers were used to prepare urethane acrylate oligomers from isophorone diisocyanate and 2-hydroxyethyl acrylate. The corresponding oligomers were then used in two very simple UV curable model coating formulations in order to determine the effect of alkyd diol compositional variation on liquid and cured film properties.

The viscosity of the liquid prepolymer was found to be reduced with increasing incorporation of monoglyceride. Cured film modulus was also generally found to be reduced as the amount of glyceride was increased. Overall resistance to attack by mineral oil was found to be very good, even though the trend with respect to the level of glyceride incorporated was unclear. Similarly, resistance to hydrolysis showed unclear dependence with respect to the amount of glyceride, but the overall resistance was very good.

From these results we can conclude that the use of alkyd diols in synthesis of urethane acrylate oligomers for UV curable coatings is feasible, capable of providing versatility in the design of various performance properties, and capable of providing very good overall chemical resistance and mechanical properties.

## References

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## SIMPLIFIED PHTHALIC ALKYD STRUCTURE

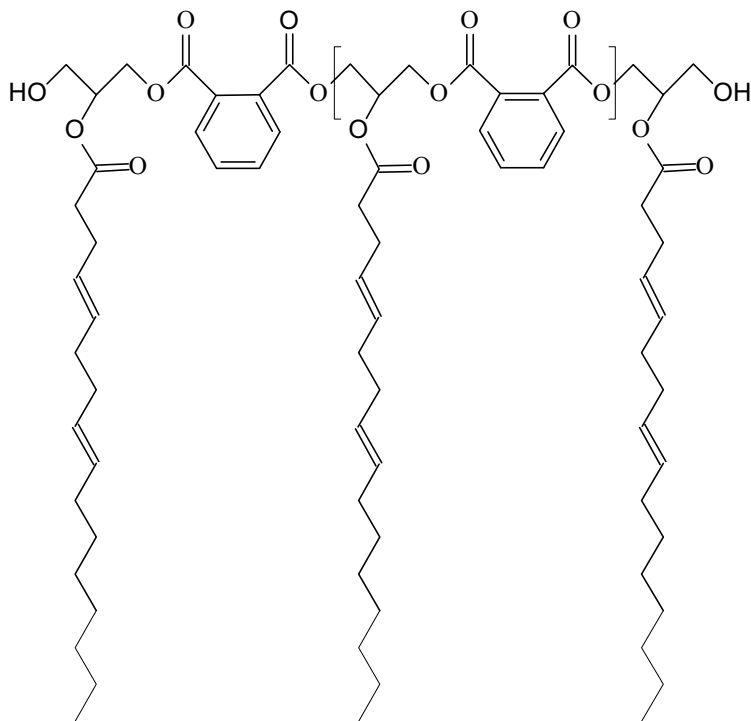
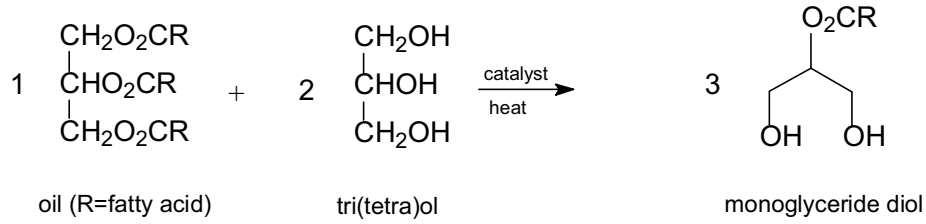


Figure 1. Structure of a simplified phthalic alkyd

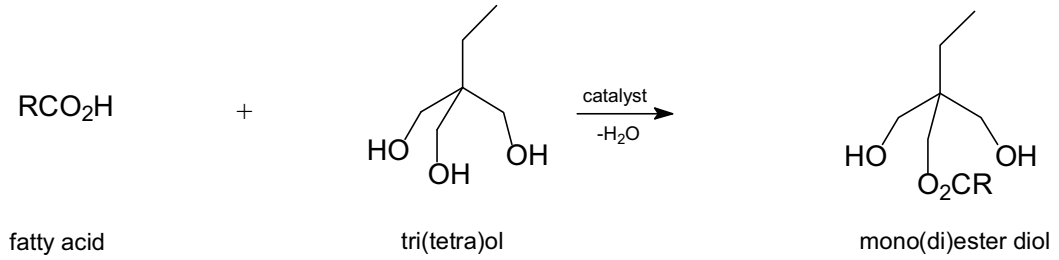
## GENERAL ALKYD SYNTHESIS REACTION SCHEME

### Glyceride Synthesis

Alcoholysis method



Direct esterification method



### Alkyd Synthesis

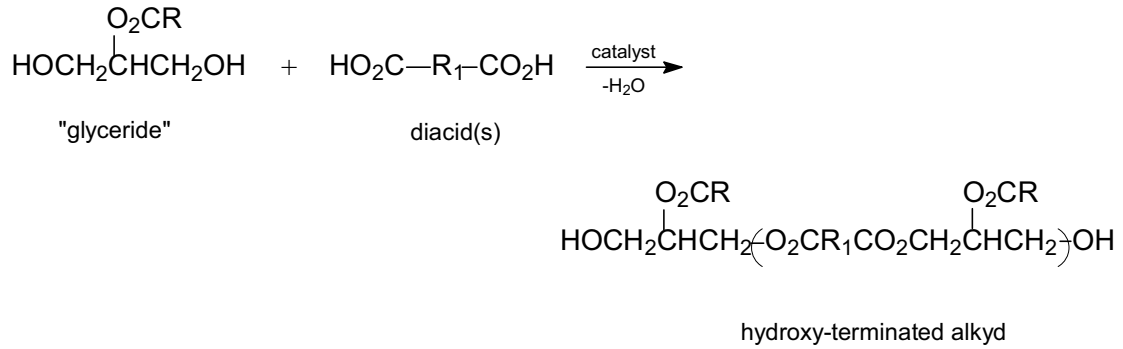


Figure 2. Alkyd synthesis reaction scheme

### Alkyd Urethane Acrylate Synthesis

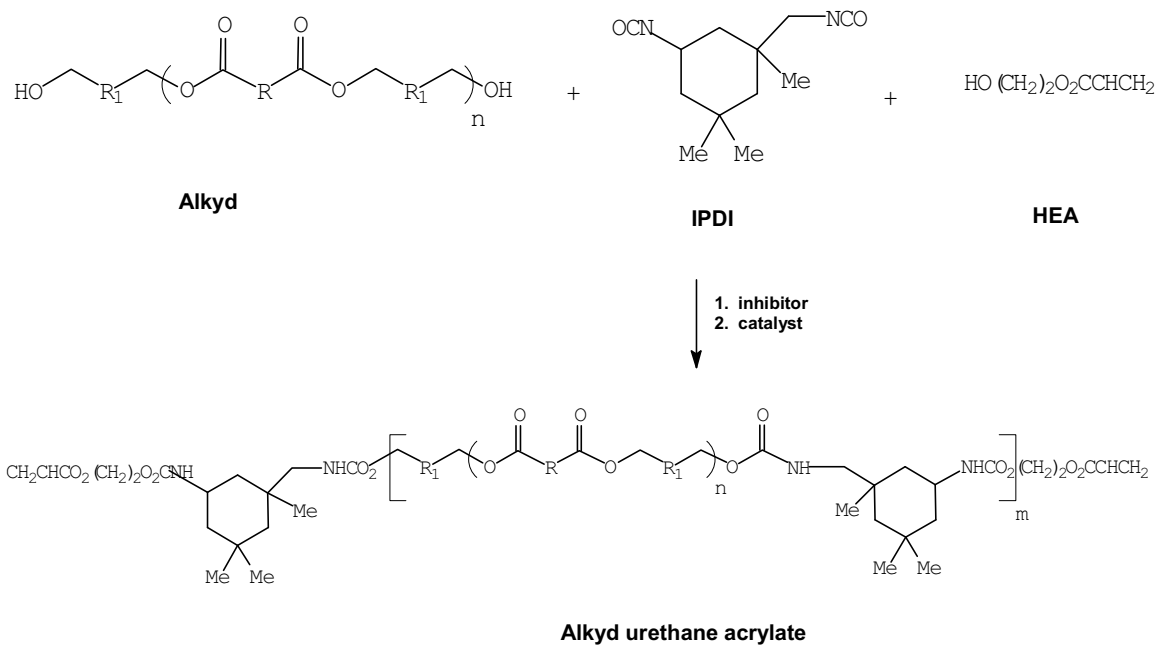


Figure 3. Alkyd urethane acrylate reaction scheme

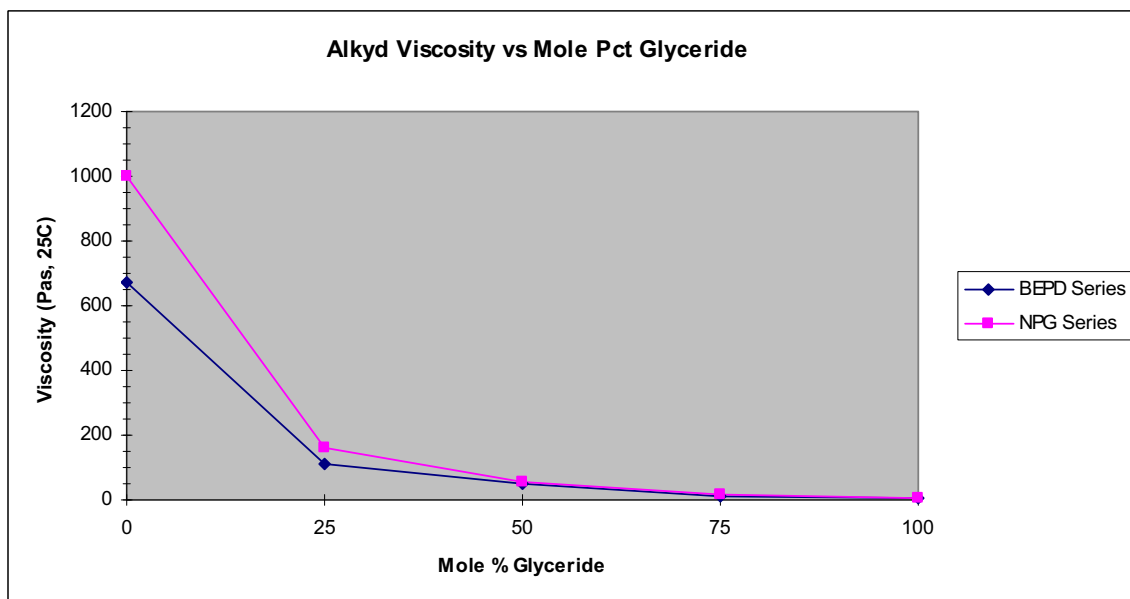


Figure 4. Effect of monoglyceride content on alkyd diol liquid viscosity



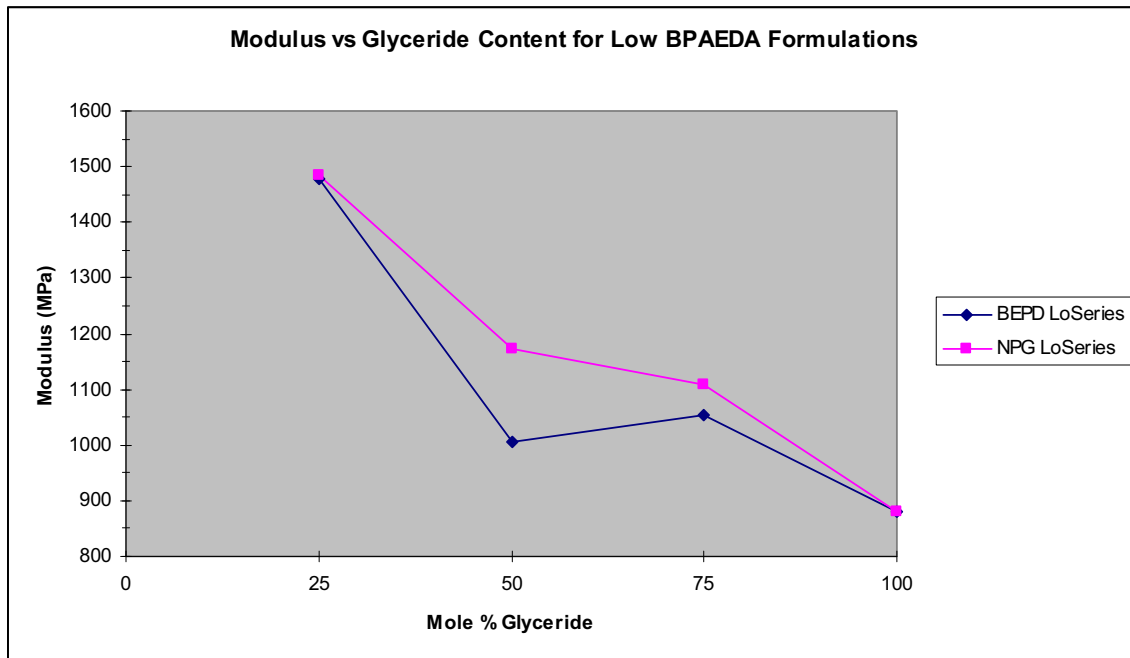


Figure 5. Effect of monoglyceride content on cured film tensile modulus

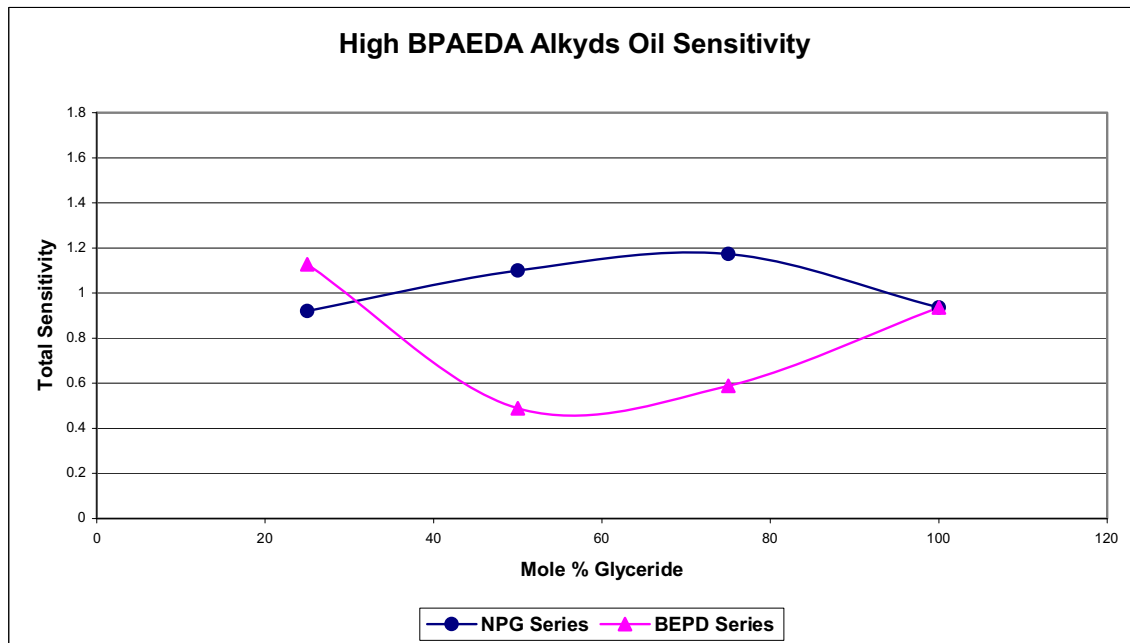


Figure 6. Effect of monoglyceride content on cured film sensitivity to mineral oil

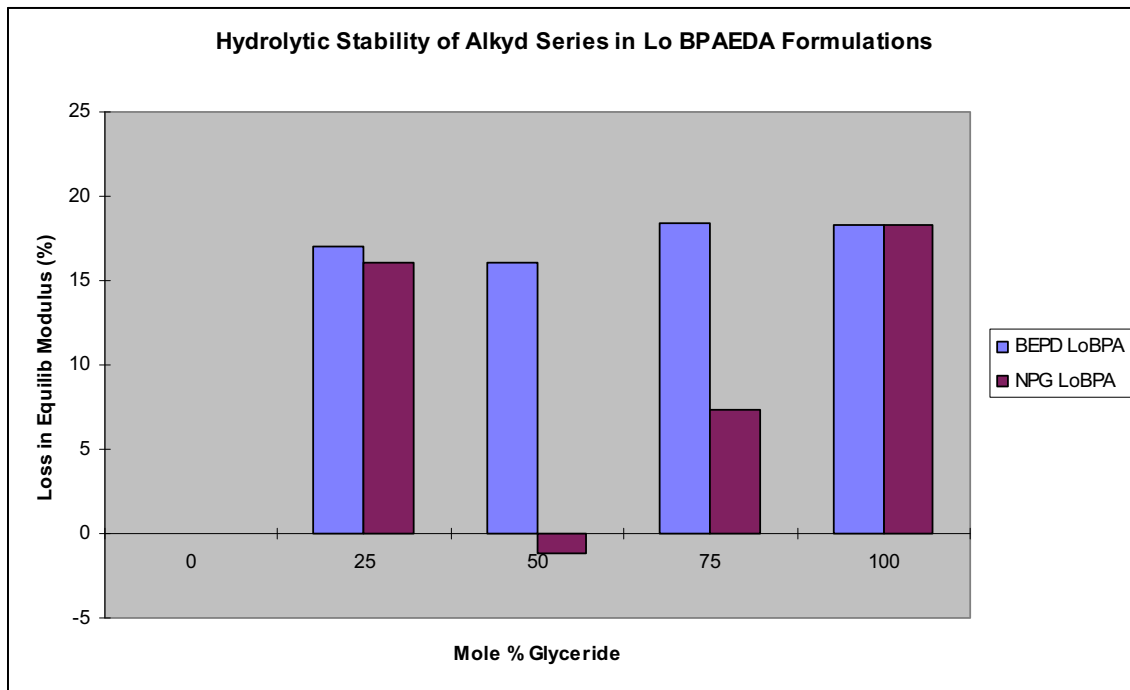


Figure 7. Effect of monoglyceride content on hydrolysis resistance