

**Mgr Hanna Nosal**

### **Alkyd resins synthesis using new and renewable raw materials**

Alkyd resins make a group of polymers which is known since the early 20 - th century. They are widely applicable in the production of coating materials like paints, lacquers, enamels, etc.

Alkyd resins are produced with the use of vegetable oils, in most cases linseed oil or soya oil, and petrochemical compounds like pentaerythritol and phthalic anhydride. The synthesis process involves two steps. In the first of them (alcoholysis), the vegetable oil is subjected to the transesterification reaction with some selected polyols in the presence of an alkaline catalyst. The alcoholysis product is then converted in the polycondensation process with an acidic component, in most cases with phthalic anhydride. It is one of key challenges for the contemporary chemical engineering to develop new types of polymer materials for the production of which renewable raw materials would be used. Hence, it is necessary to search for new supplies of raw materials for the synthesis of alkyd resins with the widest possible share of naturally occurring resources.

This study presents three selected new methods for modification of alkyd resins with the use of renewable raw materials. The principal purpose of this research was to investigate the effects of the raw materials used on the course of the polymer synthesis and on the properties of the obtained products.

The first method for modification of alkyd resins was based on the use of a new fatty raw material – camelina oil – in the synthesis. This oil is obtained from the seeds of a plant which is called camelina sativa and which can be cultivated in the soils hardly usable for the crops intended for the production of foods (barren soils and/or those devastated by the industrial activity). Thus, camelina oil is recognised as vegetable oil the production of which is not competitive against the production of foods. That makes one of general assumption for sustainable development in the chemical industry.

Raw vegetable oils, inclusive of camelina oil as used in this study, must undergo initial purification before they can be used in the synthesis of alkyd resins. Hence, an efficient method was developed for purification of raw camelina oil at the first stage of the research programme. The method comprised oil degumming, deacidification and decolourization processes. After

purification, camelina oil showed a low content of free fatty acids (0.60% m/m), low acid value (0.2 mg KOH/g) and the content of phosphorus compounds below 10 ppm. The pre-processed camelina oil was then fed to the synthesis of alkyd resins. The process also involved standard reacting substances – pentaerythritol, phthalic anhydride and maleic anhydride. The research results demonstrated that the change in the fatty raw material noticeably affected the course of individual synthesis stages and consequently the properties of the resin obtained from that raw material. The differences in the obtained findings may result from different fatty acid profiles for the vegetable oils used. For that reason, the synthesis conditions and the relative volumes of the reacting substances were adjusted in the research in such a way as to produce the camelina-based resin with the physical-chemical properties possibly close to those of the product derived from a standard fatty raw material – linseed oil.

Considerable structural modifications in alkyd resins are also possible when polyols with various structures are employed in the synthesis. For that reason, another method for modification of alkyd resins was based on the use in the polymer synthesis of polyols which had been produced by oligomerisation of glycerol, i.e. on the use of mixed oligomers with various oligomerisation degrees. Also, the commercial dimer of glycerol, i.e.  $\alpha,\alpha$  - diglycerol – oligomer of glycerol with the oligomerisation degree  $n = 2$ , was used for reference.

It was first of all needed to produce oligoglycerol with the content of diglycerol as high as possible in order to reach that goal. The effects of the following parameters were verified to optimise oligomerisation of glycerol: temperature, concentration of a catalyst, and reaction time. The optimum parameters which made it possible to obtain polyol with a high content of diglycerol were found as: 0.1% m/m LiOH as a catalyst, synthesis time – 7 h, and temperature – 245°C. Polyol produced in that way was employed in the successive stage of the studies on the synthesis of alkyd resins.

The resin synthesis tests involved oligoglycerol, glycerol, commercial diglycerol and pentaerythritol in order to verify usability of the obtained oligoglycerol. The results indicated that the type of polyol, and in particular the number of hydroxyl groups and their locations within a polyol molecule, essentially affected both the course of individual stages of the resin synthesis process and the properties of the obtained products. It was found in the research that the lower polyol molecule was, the faster the alcoholysis reaction was, and the obtained resin offered lower viscosity.

As regards performance parameters of the obtained products, the use of oligoglycerol as polyol in the synthesis of alkyd resins was found to yield the products with the quality which was satisfactory for most applications. Some performance properties were even better (shorter

cross - linking time) than for glycerol - based resins. However, the products offered slightly longer cross-linking times and inferior scratch resistance than the products obtained from pentaerythritol (more expensive raw material).

The third method for structural modifications of alkyd resins which was employed in this research was based on the use of a modifier (epoxidized vegetable oil) with improved functionality in the synthesis. Epoxidized derivatives of vegetable oils make valuable modifiers of various polymers, and principally epoxy resins. So far, however, there are no reports available on their use in the synthesis of alkyd resins.

In the first place, tests were conducted to optimise conditions for the synthesis of epoxidized camelina oil. The work was directed on establishing the effects on the volumes of the reacting substances used, process temperature and time of epoxidation on the conversion of unsaturated bonds present in camelina oil. Carefully selected epoxidation parameters made it possible to produce camelina oil with a high degree of epoxidation (0.45 mol/100 g). Linseed oil was also subjected to epoxidation under the same conditions and the product offered the epoxide equivalent of 0.52 mol/100 g.

Within further research on the synthesis of alkyd resins, some part of camelina oil was replaced by epoxidized camelina oil or by epoxidized linseed oil – for the purpose of comparison, and glycerol was used as a polyol component. The alcoholysis reaction was found to open more than 70% of oxirane rings which were initially present in epoxidized vegetable oils. The higher percentage of epoxidized vegetable oil was added to the synthesis, the higher hydroxyl number was found for the alcoholysis products. The obtained results confirmed also that the amount of a modifier used and the contents of oxirane rings in epoxidized vegetable oils affected the course of the polycondensation process. Different structures of raw materials modified the structures of the obtained products and their properties. The acid numbers and viscosity values of the final products were higher for higher amounts of reactive functional groups in the modifier employed. When epoxidized vegetable oil is present in the reaction system, the polymer chain may propagate in the polycondensation process not only through the reaction of hydroxyl groups of glycerol with carboxyl groups of phthalic anhydride or maleic anhydride (these were used in the research) but also through the reaction of carboxyl groups of those anhydrides with functional groups which are present in hydrocarbon chains of the modifier used. The polymer structure obtained in that way is highly branched, hence carboxyl groups of acid anhydrides as used in the synthesis may find it harder to approach hydroxyl groups in monoglycerides of fatty acids. So, the esterification reaction may be

expected to proceed more slowly because of steric hindrance. That is reflected by higher viscosities and higher acid numbers for the products which contain epoxidized oil added.

The modification considerably affected also the performance properties of the obtained alkyd resins. The presence of compounds with reactive epoxy groups in the alkyd resins contributed to the production of the materials with shorter cross-linking times and better scratch resistance than the reference resin in the production of which no modifier was used.

Summing up the modification methods of alkyd resins as suggested in this thesis with the use of renewable raw materials, one may declare in the full conviction that the suggested new modification methods of the supplies/resources of raw materials to expand the share of renewable feeds make promising routes for the synthesis of alkyd resins. When renewable raw materials are used, it is possible to produce alkyd resins with the properties comparable to and in some cases even surpassing those of standard products.

*Hei*

14.08.17 ✓

*Noel Heine*