Low Viscous Unsaturated Polyester Resin for Monomer Free UP-Resins

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Summary: It was possible to develop comonomer free unsaturated polyester resins for the application in electrical industry. By testing model compounds and mixtures of model compounds it was possible to find the optimised structure of the resin molecule with respect to the position of the copolymerizable double bonds. By choosing the proper composition of the other components of the resin, e.g. the glycols and modifying dicarboxylic acids, it was also possible to manufacture low viscous resins.

Keywords: crosslinking, curing of polymers, esterification, polycondensation, polyesters, reactivity, resins, unsaturated polyester resin, viscosity

Introduction

The insulating system of an electrical machine consists of the primary insulation and the secondary insulation. The primary insulation is the wire enamel fulfilling the main insulation purpose of the whole system. The secondary insulation has only a small contribution to the electrical insulation itself. The main purposes are

- Mechanical reinforcing the magnet winding, especially in rotating parts of the machine
- Improving heat transfer resulting from the ohmic resistance of the windings
- Protection against mechanical and chemical attack on the primary insulation
- Last but not least supporting the electrical insulation power of the primary insulation.

As a standard today electrical machines normally run at temperatures of 155°C, some special machines at even higher temperatures. Therefore the secondary insulation has to be able to withstand such temperatures without losing the ability to fulfil the above mentioned requirements during the lifetime of the equipment.

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For a long time, and in many parts of the world even today, the secondary insulation was built by varnishes curing at relatively high temperatures. Since the 1960ies in Europe and especially in Germany these varnishes were gradually replaced by unsaturated polyester resins. The advantages of such systems over varnishes are:

- No need to use solvents which have to be removed by time and energy consuming evaporation processes
- The filling of the gaps in the windings is much better as there is no material loss during the curing as with a varnish in which about 50% of the material in the winding has to be removed
- As a radically initiated curing process the reactivity is much higher as in varnishes resulting in much shorter curing cycles at lower temperatures

As there is no need to use a solvent to have the insulating resin in an applicable form UP resins theoretically are 100% systems. Therefore the impact on environment should be neglectable.

In reality the possibility of adjusting the viscosity of the system by addition of an excess of comonomer, mainly styrene, and the necessity to cure at elevated temperatures to have stable resins at ambient temperature leads to losses of styrene during curing. In order to reduce the VOC in technical processes it is necessary to clean the exhaust air from the evaporated styrene. To avoid the costly installation of such cleaning systems many efforts have been made to reduce the evaporation, mainly by using other comonomers as styrene with lower vapour pressures, for instance by using diallylphthalate or highly boiling acrylates. For various reasons such products did not gain a considerable market share.

Another strategy to reduce the VOC content to nearly zero would be the use of comonomer free unsaturated polyesters. The total amount of unsaturated polyester resins used in electrical insulation is very small compared to the huge amounts going into other business, but nevertheless it is useful to reduce the impact on environment even in such comparatively small areas of use.

Requirements for a Monomer Free Unsaturated Polyester Resin

An unsaturated polyester resin consists of a polyester containing unsaturated double bonds usually introduced by the unsaturated dicarboxylic maleic or fumaric acid. This unsaturated base resin normally is highly viscous or even solid at ambient temperature. Therefore it cannot be used for impregnating any object. On the other hand this base resin is hardly curable at normal conditions because the tendency of the ester double bonds to homopolymerize is quite low. Therefore a copolymerizable monomer is added, in which the base resin is soluble. By adding various amounts of this comonomer, mostly styrene, the viscosity can be adjusted as it is needed.

An unsaturated polyester without a copolymerizable monomer has to fulfil the following requirements:

- It has to be curable under economic conditions
- It has to be low viscous to allow the application
- The resin should be a one pot system with long potlife at ambient and slightly increased temperatures
- The potlife of the resin activated by the hardener has to be in a range allowing a production without problems

From the beginning of the work there was no doubt that it would not be possible to develop a polyester fulfilling the legal requirements of a polymer with viscosities in the range of the normal monomer containing UP resins. Otherwise it would have been necessary to pass the whole time consuming and expensive procedure for the testing of new chemicals. It was believed from the beginning that the resin had to be heated to reduce the viscosity for application. Therefore the question of potlife at increased temperature up to 40°C to 60°C became more important.

Solution of the Problem of Copolymerisation; Reactivity of Model Compounds

It had been possible to find two types of double bonds which are able to copolymerize. One of them is the standard unsaturation of UP resins, the maleic/fumaric unsaturation. The other one results from an adduct of cyclopentadiene with a functional group allowing a condensation reaction. It is possible to incorporate these two types of double bonds into one resin without a copolymerisation during the polycondensation of the polyester. The copolymerisation of the double bonds can be started by radicals, for instance from peroxides or UV radiation.

There are two strategies possible: It is possible to incorporate both copolymerizable double bonds in one resin. The other possibility is to make two resins, one containing the double bond from the cyclopentadiene adduct and the other resin containing the double bond from the maleic/fumaric acid alone. This strategy resembles the well known mixing of resin and hardener for instance in polyurethane or epoxy resins with the difference that in the case of monomer free UP-resins an additional initiator has to be added.

It became very quickly obvious that the reactivity strongly depends on the number of double bonds, the position of them in the molecule and on the ratio of them. Therefore it was necessary to find out these parameters in order to get molecules with the right reactivity on one hand and the good stability needed for the pot life on the other hand. So we decided to synthesise model compounds and mixing them to find the optimum in reactivity by measuring their reactivity by determining the time of gelation (as the aim is the production of a duroplastic system) and the reaction enthalpy of curing by thermal analysis.[1,2]

The model compounds contain

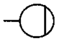
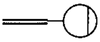
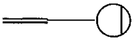
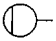
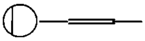
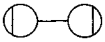
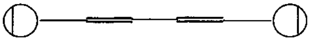
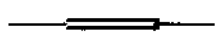
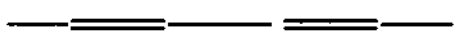
- the double bond of the adduct of the cyclopentadiene symbolised by 
- the double bond of maleic/fumaric acid symbolised by ═══
    - in direct neighbourhood to the adduct 
    - in a certain distance to the adduct 
    - in different number in the molecule ═══——— ═══

Table 1 shows the first group of model compounds and their behaviour under curing conditions after activation with tert.-butyl perbenzoate.

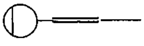
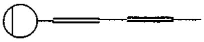
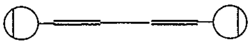
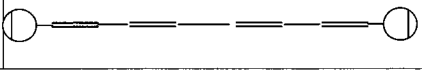
Table 1. Model compounds with no or low reactivity determined by gel time measurement and DSC measurement.

Number	Model compound	Reactivity by Gel Time	DSC Measurement [J/Mol]
1		**No crosslinking**	**8600**
2		**No crosslinking**	**8700**
3		**No crosslinking**	**11500**
4		**Very low reactivity**	**52500**
5		**Good reactivity**	**84300**
6		**No crosslinking**	**28000**
7		**Very low reactivity**	**23100**

The double bonds of the cyclopentadiene adduct show no reactivity by gel time measurements, even when two groups are in one molecule. The addition of one maleic/fumaric double bond makes the molecule slowly curable, while the addition of two such double bonds increases the reactivity considerably. Two maleic/fumaric double bonds without the addition product show a very low reactivity. The measurement of the reaction enthalpy of all model compounds shows that they are reactive, but the reaction does not lead to the desired crosslinking in every case.

Table 2 shows the results of the reactivity measurements of the second group of model compounds. In these compounds the maleic/fumaric double bonds are in the direct neighbourhood of the cyclopentadiene adduct.

Table 2. Reactivity of model compounds with maleic/fumaric double bonds directly linked to the cyclopentadiene adduct.

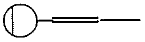
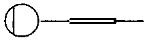
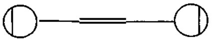
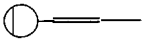
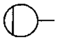
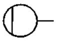
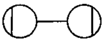
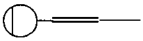
Number	Model compound	Reactivity by Gel Time	DSC Measurement [J/Mol]
1		No crosslinking	31500
2		Low reactivity	52300
3		↓ Increasing reactivity	90200
4			112000
5			120500

It is necessary to fix the maleic/fumaric double bond directly to the cyclopentadiene adduct to get a good reactivity in the sense that the material is crosslinked by the curing process. In this sense it is necessary to have at least one adduct with linked maleic/fumaric double bond plus one more maleic/fumaric double bond to have crosslinking. Good reactivity in the sense of crosslinking is obtained with two adduct groups with linked maleic/fumaric double bond as in 3. Further increase of the number of maleic/fumaric double bonds increases the probability of crosslinking and therefore the reactivity characterised by reduced gel time.

Reactivity of Mixtures of Model Compounds

The second strategy to mix model compounds which are not readily homopolymerizable is interesting in the respect of resin manufacture. If both copolymerizable groups are present in one resin there is the danger of uncontrolled reaction during the manufacturing of the resin. Table 3 shows such mixtures. In this case there was no measurement of reaction enthalpy made. Only the possibility of crosslinking was of interest and therefore determined by gel time measurement.

Table 3. Reactivity of mixtures of model compounds which do not crosslink alone.

Number of Mixture	Ratio molar	Model compounds	Reactivity by Gel Time
1	1 1	 	No crosslinking
2	1 1	 	No crosslinking
3	1 2	 	No crosslinking
4	1 1	 	No crosslinking
5	1 1	 	No crosslinking
6	1 1	 	No crosslinking
7	1 1	 	No crosslinking

As the table shows this strategy is not working. Therefore it was necessary to incorporate both reactive types of double bonds in one resin.

Optimisation of the Polyester

As the previous investigations had shown it is necessary to have the double bond of the cyclopentadiene adduct directly linked to a maleic/fumaric double bond and additional maleic/fumaric double bonds in the resin to get a good crosslinking characteristics. Fortunately the system showed such a good stability that under certain precautions it is possible to make polyesters which fulfil the legal requirements for a polymer (number average molecular weight >1000 and a molecular weight distribution) and which can be crosslinked by the addition of radical producing compounds like peroxides. The cured resin also fulfilled the requirements for the application in the manufacturing of electrical machines and the resin has an interesting curing characteristics. The Arrhenius plot shows a good linearity in the temperature range above about 100°C and also below about 80°C. In the temperature range between 80°C and 100°C there is a change in the curing mechanism so that the energy of activation below 80°C is much higher than above 100°C. Therefore it is possible to apply the resin at elevated temperatures up to 80°C to reduce the viscosity without getting problems with the pot life.

Nevertheless it was necessary to try to reduce the viscosity of the resin at ambient temperature by choosing the right composition of the polyester. This can be done by changing the glycols and by introducing modifying dicarboxylic acids in place of parts of the maleic/fumaric acids. Of course this will lower the reactivity of the resin as the probability for crosslinking is reduced. Nevertheless it could be shown that partial exchange of the maleic/fumaric acid by adipic acid greatly reduces the viscosity of the resin.

The second way of influencing viscosity is to vary the glycol used in the polycondensation. Unfortunately it was not possible to use a statistic test plan to reduce the number of tests. There are too many possibilities. In the many test batches it was possible to find an optimised composition of different glycols in one resin which led to a resin that was applicable at even slowly raised temperature. Fig. 1 shows the viscosity range vs. temperature which is usable.

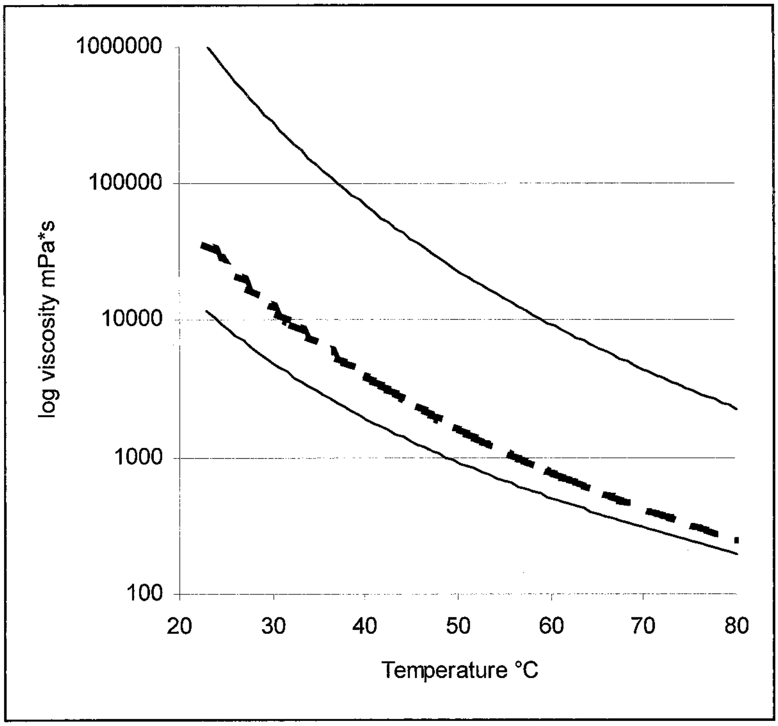


Fig. 1. Usable viscosity range of monomer free unsaturated polyester resins. Dotted line: Upper viscosity limit for standard applications.

A further reduction of viscosity was possible by reducing the acid number. The standard acid number of the polyesters is in the range of about 20 to 25 mg KOH/g. A further reduction by improving the degree of condensation leads to a rapid increase in viscosity as the molecular weight is increased. Therefore the carboxylic end group is esterified with methanol or ethanol until the acid number becomes lower as 5 mg KOH/g. This leads to a further reduction in viscosity of about 20%.

Conclusion

It was possible to develop a monomer free unsaturated polyester which

- can be manufactured by standard polycondensation procedures without reacting although the resin contains two types of copolymerizable double bonds
- can be processed in activated state at elevated temperatures without premature gelling
- can be cured by standard conditions to produce a material fulfilling the requirements for the construction of electrical machines
- has very low emissions during the curing process compared to standard UP resins.

To do this it was necessary to synthesise model compounds to find out which configuration of the two different double bonds gives the best results in reactivity. In this special case reactivity means the possibility to form a duroplastic resin. The other task was to optimise the composition of the polyester with regard to viscosity.

Due to the much higher viscosity compared with the standard UP resins some of the application processes have to be modified.

[1] Horn, Nicole, Modellversuche zur Aufklärung des Härtungsmechanismusses comonomerenfreier ungesättigter Polyester Diplomarbeit im Studiengang Chemieingenieurwesen Fachhochschule Hamburg 1998
[2] Bunardi, Wenli, Wechselwirkungen bei der kombinierten thermischen und UV-Härtung bei monomerenfreien UP-Harzen Diplomarbeit im Studiengang Chemieingenieurwesen Fachhochschule Hamburg 1999