SYNTHETIC MODIFICATION AND CHARACTERISATION OF UNSATURATED POLYESTERS

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ACADEMIC DISSERTATION

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ABSTRACT

Synthetic modifications of unsaturated polyester resins have been done in order to achieve lower styrene emission, better styrene solubility and lower processing viscosity. Two concepts were used; introduction of liquid crystalline segments into the unsaturated polyester and end-capping the unsaturated polyester with poly(ethylene glycol)s of various molar mass. The cross-linking reaction of unsaturated polyesters and the formed network was studied with low-resolution NMR and solid-state 13C-NMR spectroscopy, rheological methods and thermal analysis.

Liquid crystalline unsaturated polyesters were possible to synthesise, and it was also possible to prepare lyotropic solutions of unsaturated polyesters in styrene. The thermal properties of the liquid crystalline polyesters depended on the substituents. Rigid substituents gave higher glass transition temperature compared to the polyesters with more flexible substituents. The polyesters exhibited nematic liquid crystalline phases above their glass transition temperatures.

By modification with monofunctional poly(ethylene glycol) end groups it is possible to enhance styrene solubility, and possible to prepare room temperature processable and curable resins with a styrene content as low as 20 wt %. The mechanical properties of the cured samples varied from soft to hard, depending on the molar mass of the end group. Modification of unsaturated polyesters in this way is a possibility to get unsaturated polyester resins with lower shrinkage, reduced brittleness and increased flexibility.

Low-resolution ^{1}H-NMR spectroscopy was used to follow the curing reaction in unsaturated polyester resins. Three components with different proton mobility could be identified during the curing of unsaturated polyester resins; very mobile, less mobile, and immobile ones. The most mobile component with T_2 around 3 s corresponded to unpolymerized styrene, and the less mobile component with a T_2 around 150 ms corresponded to free polyester prepolymers. The mobility of these both components decreases during the cross-linking reaction, as the network is formed. The immobile component with T_2 around 0.04 ms corresponded to the cured resin polymer network. The NMR results correlated well with the results from the DSC analysis and the viscoelastic measurements. Low-resolution NMR can also be used for the determination of residual monomer content in unsaturated polyesters.

The network structure of cured unsaturated polyester resins was studied with solid-state ^{13}C-NMR spectroscopy. Four different structures could be identified, fumarate-styrene-fumarate (FSF), styrene-styrene-fumarate (SSF), fumarate-styrene-styrene (FSS) and styrene-styrene-styrene (SSS). The styrene sequence lengths increased with increasing styrene content and increasing styrene/maleic anhydride molar ratio in the polyester prepolymer. The number of monad (FSF) sequences increased when the styrene content decreased. The number of diad (SSF, FSS) and n-ad (SSS) sequences increased with increasing styrene content. The amount of unreacted fumarate units in the cured resin was high; in the resins with styrene content less than 40 wt % not more than every second fumarate had reacted. Postcuring, which did not have an effect on sequence distributions, but the amount of unreacted fumarate units decreased.

LIST OF PAPERS

This thesis is a summary of the following publications, which will be referred to by their Roman numerals:

I. Skrifvars, M. and Schmidt, H.-W., Unsaturated *para*-linked aromatic LC-polyesters: Thermotropic and lyotropic systems, J. Appl. Polym. Sci. 55 (1995) 1787 - 1795

II. Skrifvars, M., Hyvärinen, S. and Sundholm, F., Thermal and liquid crystalline properties of unsaturated polyesters containing rigid segments, Polym. Polym. Compos. 7 (1999) 289 - 293

III. Schulze, U., Skrifvars, M., Reichelt, N. and Schmidt, H.-W., Modification of unsaturated polyesters by poly(ethylene glycol) end groups, J. Appl. Polym. Sci. 64 (1997) 527 - 537

IV. Hietalahti, K., Root, A., Skrifvars, M. and Sundholm, F., Crosslinking of unsaturated polyester resins studied by low-resolution ^{1}H-NMR spectroscopy, J. Appl. Polym. Sci. 65 (1997) 77 - 83

V. Hietalahti, K., Skrifvars, M., Root, A. and Sundholm, F., Correlation of viscoelastic properties with low-resolution ^{1}H-NMR measurements of crosslinking unsaturated polyesters, J. Appl. Polym. Sci. 68 (1998) 671 - 680

VI. Hietalahti, K., Root, A., Skrifvars, M. and Sundholm, F., A solid-state ^{13}C nuclear magnetic resonance study of cured, unsaturated polyester resins, J. Appl. Polym. Sci. 73 (1999) 563 - 571

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1 INTRODUCTION AND BACKGROUND

Unsaturated polyester resins are one of the most important matrix resins for commodity glass fibre reinforced composites. They are obtained in a two step process; first unsaturated and saturated acids or anhydrides are reacted with diols in a polycondensation reaction, secondly the resulting linear polyester prepolymer is dissolved in styrene into a syrup - like resin. The resin is finally processed into a rigid thermoset in a free radical co-polymerisation between styrene and the double bonds in the polyester chain. The basic chemistry of unsaturated polyesters has remained very much unchanged for the last 40 years, although material development has been otherwise rapid.

During the end of the 1980's the environmental problems caused by styrene emission from the processing of unsaturated polyesters were debated a lot in the society, especially in the Nordic countries. The producers of unsaturated polyesters started therefore to search actively for alternatives to styrene, and started to develop additives inhibiting styrene emission. Today much of the styrene debate has silenced, instead the development of unsaturated polyesters is focused on resin formulations for resin transfer moulding (RTM) and vacuum infusion processing, on resins with superior surface quality, on halogen-free flame retarded resin, and on resins with improved mechanical properties, such as toughness.

This thesis deals with the development of unsaturated polyester resins, which started in 1989 at Neste Chemicals Technology Centre in Porvoo, Finland. The work began with a study of the emission of styrene and *p*-methyl styrene during the lamination [1], and continued with studies concerning delamination in low styrene emission (LSE) resins [2,3] and morphology of LSE resin laminates [4]. Further a lot of effort was put on gaining knowledge about process factors causing styrene emission during spray lay-up lamination, in order to decrease styrene emission and exposure. [5]

These studies showed clearly that the styrene emission cannot be avoided as long as the basic chemical composition is kept unchanged. Structural modifications are therefore needed. One possibility is the introduction of liquid crystalline properties into the unsaturated polyester chain. This was studied during a stay at the Materials Department, at the University of California in Santa Barbara, USA during 1992 and 1993, (Paper I) and continued at the Laboratory of Polymer Chemistry at the University of Helsinki (Paper II). An other option which came up was the possibility to end-cap unsaturated polyesters with poly(ethylene glycol)s, which was studied in collaboration with the macromolecular group at the University of Bayreuth in Germany during 1995 (Paper III).

The cross-linking reaction is fundamental for an efficient processing of unsaturated polyesters, and therefore a co-operation project was started in 1995 with the Laboratory of Polymer Chemistry at the University of Helsinki. Rheological and nuclear magnetic resonance (NMR) studies of the cross-linking reactions and the cured resin were performed, and the obtained data were correlated to data from methods used in the industry. (Paper IV, V and VI).

2 AIM OF THE WORK

The experimental work in this thesis deals with two important topics in polymer chemistry: tailoring of polymer properties by synthetic methods, and correlation of the chemical structure and end-use properties.

The aim of the synthetic work was to tailor the chemical structure of the unsaturated polyester in order to achieve lower styrene emission and improved mechanical properties. Two concepts were used; introduction of liquid crystalline segments into the unsaturated polyester (Paper I and II) and end-capping the unsaturated polyester with poly(ethylene glycol)s of varying molar mass (Paper III).

The resin viscosity is an important factor when targeting low styrene emission in unsaturated polyesters. It is generally known that the viscosity of a liquid crystalline melt or solution is lower than that of an isotropic one. [6] The lower viscosity of the polyester prepolymer would then make it possible to reduce the styrene content. Additionally it was known from the literature that the combination of liquid crystalline properties with the properties of a thermoset, should give interesting properties such as reduced shrinkage upon curing, increased fracture toughness, and improved mechanical properties perpendicular to the orientation direction. [7]

Introduction of flexible poly(ethylene glycol) end groups was done in order to influence the solution behaviour and the mechanical properties of the resin. The end-capping of the polar end groups with poly(ethylene glycol) compounds was expected to improve the flexibility of the cured material. The intermolecular interaction of the polymers should also change considerably. Instead of hydrogen bonds, which are responsible for the aggregation and the high viscosity of the polyester prepolymer dissolved in styrene, van der Waals interactions should be present. The reduction of the polar interactions between the chains was expected to give lower viscosity, which should make it possible to reduce the styrene content.

The aim of the analytical work was to follow the cross-linking reaction and to characterise the formed network with NMR spectroscopy, rheological methods and thermal analysis, and further to correlate this data with mechanical properties. The crosslinking reaction is a fundamentally important stage in the processing of an unsaturated polyester into a composite product. It is therefore necessary to have available proper methods for the characterisation of the cross-linking reaction. Low-resolution NMR spectroscopy is used in the food industry for routine analysis [8], and has also been applied to monitor the molecular mobility of unsaturated polyesters [9]. In Papers IV and V data from low-resolution NMR measurements on polyesters with different compositions were compared with data from thermal analysis and rheological measurements. The aim was to correlate structural characteristics such as molar ratio of styrene to double bonds in the polyester chain, molecular mass, styrene content, and the degree of cis-trans isomerisation with the molecular mobilities. The formed network was further characterised with solid-state ^{13}C-NMR in Paper VI. The aim of this paper was to study the influence of styrene content on the length of styrene sequences and to estimate the amount of unreacted double bonds. The styrene content was also correlated to the glass transition temperature and the mechanical properties. These relationships are important to understand when developing new polyester resin formulations.

3 UNSATURATED POLYESTERS

The first unsaturated polyester resins of similar type as used today were synthesised in the 1930's. Carlton Ellis found that unsaturated polyester prepolymers could be mixed with styrene, and copolymerised into a rigid polymer. These resins became commercially important the next decade when they were reinforced with glass fibres giving structural products with high mechanical strength and low density. Today unsaturated polyesters are one of the most important matrix resins for composite materials. [10]

A composite is defined as a combination of at least two chemically distinct phases, the matrix and the reinforcement, which at the microscopic scale are separated by a distinguishable interface. In the composite the unsaturated polyester holds the reinforcement in place, it transfers the external loads to the reinforcement, and protects the reinforcement from the environment. If individual fibres are fractured, the matrix will redistribute the load to the surrounding fibres, thus preventing the complete failure of the material. The composite product will exhibit a broad range of mechanical, chemical, thermal and physical properties, depending on the composition of the unsaturated polyester. [11]

Important product areas for unsaturated polyesters are marine, automotive, electric and electronic, building, construction, sport and leisure, domestic and sanitary appliances, furniture as well as military applications. A special use is in gel coats, which are used as coloured and protecting surface coatings in composites. Unsaturated polyester resins are very versatile as the processing into a composite product can be done using several techniques; hand lay-up and spray lay-up lamination, casting, compression molding, pultrusion, resin transfer moulding (RTM), vacuum infusion and filament winding. [12]

3.1 Chemical composition

The basic chemistry of linear unsaturated polyesters is rather simple. [13] A mixture of unsaturated and saturated dicarboxylic acids is reacted with diols in a melt polycondensation. Monofunctional alcohols and acids are also used in some formulations to tailor the properties. The most traditional composition is maleic anhydride, *o*-phthalic anhydride and 1.2-propanediol, which are cheap raw materials. Other common raw materials are fumaric acid, isophthalic anhydride, terephthalic acid, adipic acid, ethylene glycol, diethylene glycol, dipropylene glycol, neopentyl glycol and bisphenol A. The properties of the final product can be varied almost endlessly by changing the composition of the unsaturated polyester using these raw materials. Generally aromatic groups improve the hardness and the stiffness while aliphatic chain components increase the flexibility. The most common raw materials and their influence on end-use properties are listed in Table I. **[14]**

The unsaturated polyester prepolymer is finally blended with styrene to a reactive resin solution, in which form the resin is sent to the end-user. The styrene acts both as a crosslinking agent, and as a viscosity reducer so that the resin can be processed. In conventional unsaturated polyesters the styrene content varies between 38 and 45 wt %.

The adjustment of the molar ratio of the unsaturated dicarboxylic acid and the saturated dicarboxylic acid (maleic anhydride respective phthalic anhydride) is an important method to tailor the properties of the resin. This ratio controls the reactivity of the unsaturated polyester and also the cross-linking density of the final network. This structural tailoring concept was used in all papers except Paper I in this thesis. If the saturated dicarboxylic acid is used in a molar excess the reactive unsaturated bonds will be distributed in the polyester chain sparsely, and the reactivity of the unsaturated polyester will be lower. If the unsaturated dicarboxylic acid is used in a molar excess will the reactive double bonds be distributed much more densely, and the reactivity will be higher, as there will be a larger number of reactive sites in each polyester chain. This will also give a much denser network in the cured resin, which will result in a brittle material with poor mechanical properties. For this reason commercial unsaturated polyesters are usually formulated using an excess of saturated acid.

Table I. Common components used in unsaturated polyester resins and their influence on the properties of the final product. [14]

COMPOUND	PROPERTIES
Maleic anhydride	• Branched polyesters compared to those from fumaric acid • Lower degree of unsaturation compared to those from fumaric acid
Fumaric acid	• Increased reactivity of polyesters
Phthalic anhydride	• Polyesters with low molecular masses • Improved hardness and stiffness in cured resins • Good compatibility with styrene
Terephthalic acid	• Improved hardness and stiffness in cured resins • Increased heat deflection point
Isophthalic acid	• Higher molecular masses • Excellent physical and chemical properties • Improved hardness and stiffness in cured resins
Adipic acid	• More flexible chains • Soft products • Increased toughness • Reduced water and weathering resistance
Ethylene glycol	• Reduced solubility of unsaturated polyester in the vinyl monomer • Increased rigidity
Propylene glycol (1.2-propanediol)	• Good compatibility with styrene
Diethylene glycol	• More flexible chains • Soft products • Increased toughness • Reduced water resistance
Neopentyl glycol	• Good corrosion, UV, water, and chemical resistance
Hydrogenated bisphenol A	• Good corrosion, water, and chemical resistance

The unsaturated polyester has typically a molecular mass between 1000 and 5000. The molecular mass is regulated by the diol/dicarboxylic acid ratio, according to the principles of Carothers. [15] Usually the diol is in excess, as the used diols are liquids, while the dicarboxylic acids and anhydrides are solids. An excess of solid reactants can cause a problem in the form of sublimation of the reactants during polycondensation. A high molecular mass will give a higher hardness, tensile and flexural strength of the final cured material. If the molecular mass is too low, the mechanical properties of the cured resin will be poor. A too high molecular mass increases the viscosity of the resin solution, which will cause problems with the processing of the resin. Air entrapment in the laminate, poor wetting of the reinforcement, long mould filling times and processing times are typical practical problems due to the resin viscosity.

3.2 Manufacturing of unsaturated polyesters

Almost all commercial production of unsaturated polyesters is done by the melt polycondensation of unsaturated and saturated acids or anhydrides with glycols. No solvents are used, and the formed water is continuously removed, in order to force the esterification reaction towards completion. The condensation temperature is typically between 170 and 230 °C. At the end of the condensation, vacuum is often applied in order to remove remaining water from the viscous melt. The total reaction time can be from 8 h up to 25 h, and the reaction is followed by acid number titrations and viscosity measurements. Azeotropic polycondensation in the presence of organic solvents such as xylene or toluene can also be used. The reaction takes place at lower temperatures and it is possible to avoid losses of volatile reactants. The drawbacks are longer reaction times and environmental problems with solvent removing and recycling.

The unsaturated polyesters studied in the enclosed papers were all made by polycondensation, except the unsaturated polyesters in Paper I and II. In these papers, the polyesters were made by an interfacial condensation reaction of fumaroyl dichloride, aliphatic acid dichlorides and aromatic diols. This method cannot be used for large-scale production of unsaturated polyesters, it is strictly a method for the laboratory.

3.3 Crosslinking of unsaturated polyesters

In order to get a rigid, structural material the prepolymer-styrene solution is cross-linked by the user into a rigid thermoset in a free radical copolymerization between the styrene monomer and the polyester double bonds originating from the unsaturated dicarboxylic acid. The copolymerisation is initiated by peroxides activated by a redox reaction with cobalt salts or thermally. During the crosslinking the resin undergoes gelation, which is a dramatic physical change. The viscosity increases rapidly, the resin becomes elastic and begins to behave as a rubber. The extent of reaction, at which an infinite molecular network starts to form, is called the gel point, and the time to achieve it is the gel time. The chemical reaction continues in the gel state, and more polyesters are linked to the network. Each polyester will finally be linked to each other at several points in the network, and one gigantic molecule is formed. The crosslinking reaction is a highly exothermic reaction, and the temperature can increase up to 100 - 200 °C, depending on the resin composition, laminate thickness, and the initiator system. The crosslinking reaction is not complete, however. Even when the final solid state is achieved there will be unreacted styrene monomers and double bonds left. This residual reactivity can be removed by postcuring simply by heating at a temperature above the glass transition temperature of the crosslinked unsaturated polyester. This process of network formation is often named in the literature as curing, and the degree of cure is taken as the crosslinking density.

Methods for the determination of crosslinking

The crosslinking reaction is a very important stage in the processing of unsaturated polyester into a composite product. In order to achieve good product quality the crosslinking reaction should occur in a controllable manner. It is also necessary to carefully follow the reaction, and to check the degree of cure after the completion of the processing. There are several techniques available to characterise the crosslinking of an unsaturated polyester resin. They can be divided into methods based on the changes in physical properties of the resin, and methods based on the changes in chemical properties of the resin. [16]

Physical properties, which change during cure include shear and torsional modulus, hardness, dielectric constant, and viscosity. Change in shear modulus can be measured by curometers, which are based on oscillatory motion of needles, paddles, disks or other geometries in a curing resin. One example is the thermal scanning rheometer used in Paper III. Viscosity measurements are used to follow the earlier stages of the cross-linking, and are particularly useful for the determination of the processability of the resin. Both steady shearing flow measurements [17] and oscillatory shearing flow measurements [18] have been used. The industry uses several empirical techniques for cure monitoring, for example the cure can be followed with a stop-watch while mixing the resin in a beaker, or by measuring the maximum temperature generated by the cross-linking reaction with a thermoelement embedded in the resin. Hardness is a common empirical method to determine the degree of cure in cured laminates, for example by using the Barcol impressometer. Dielectric cure monitoring is based on the measurement of changes in dielectric properties of the resin, and can be used both for the liquid and solid-states of the resin.

Among the chemical techniques, differential scanning calorimetry (DSC) is the most important. DSC involves the measurement of the heat of reaction (exothermal heat) which is liberated in the curing reaction of the thermoset. The technique can be used for the simulation of the curing process in a composite. The analysis is based on the assumptions that the exothermal reactions monitored are those of the curing reaction, and that the heat generation is directly proportional to the rate of cure. Several other factors (heating rate, sample preparation, atmosphere, resin properties and thermal history) also affect the data analysis. Spectroscopic techniques can also be used, such as FT infra-red spectroscopy and low-resolution proton NMR spectroscopy, as will be described in Papers V and VI.

3.4 Low styrene emission resins

The free styrene monomer in the unsaturated polyester resin is an environmental and occupational health problem due to evaporation and emissions, which occur during the processing of the resin. In 1992 it was found that about 75 % of the workers in the reinforced plastic industry in Finland are exposed to styrene concentrations exceeding the current occupational exposure limit of 20 ppm. [19] Much improvement of the work environment has been made by using proper ventilation systems together with styrene absorbing collection systems, by improvement of the work practice and the housekeeping, by using personal respiratory protection and by using low styrene emission (LSE) resins in the industry.

There are three technical approaches for LSE resins; *emission suppressed resins* that contain styrene emission inhibiting additives; *monomer substituted resins* where styrene has been replaced with an other monomer, and *high-solid resins* where the styrene content has been reduced. [1]

Emission suppressed resins

The emission suppressed resins are based on paraffin or wax compounds, which form a film on the laminate surface, thus preventing the styrene emission. Paraffin is insoluble in the unsaturated polyester, and separates after the lay-up to form a thin layer on the resin surface, as shown in Figure 1. [4] The main draw-back is that these additives cannot hinder the styrene emission during the spraying or the rolling phase of a lamination, as the film formation occurs only under static conditions. The film acts also as a release agent, and reduces greatly the interfacial bonding in the laminate, as is discussed in Chapter 3.5.

To improve interfacial bonding, adhesion promoters or bonding agents have been introduced. They probably create sufficient surface area for good interfacial bonding, by increasing the miscibility between the unsaturated polyester and the paraffin. Some compounds, which are mentioned in the patent literature, are listed in Table II, but it is not known if these are used commercially. [20]

Monomer substituted resins

The most obvious solution to the styrene emission problem would be to replace styrene with a compound with a lower vapour pressure. Any compound that fulfils the requirements for the free radical cross-linking reaction could be used instead of styrene. The most promising styrene substitutes are para-methylstyrene and vinyltoluene[*]. By IR absorption measurements of the emission from a resin containing these solvents it has been shown that the solvent emission during the rolling phase can be reduced to one third compared to the emission from a styrene containing unsaturated polyester. [1] Due to a much higher price, less commercial availability and also a rather strong smell compared to styrene substituted resins have not found any greater use.

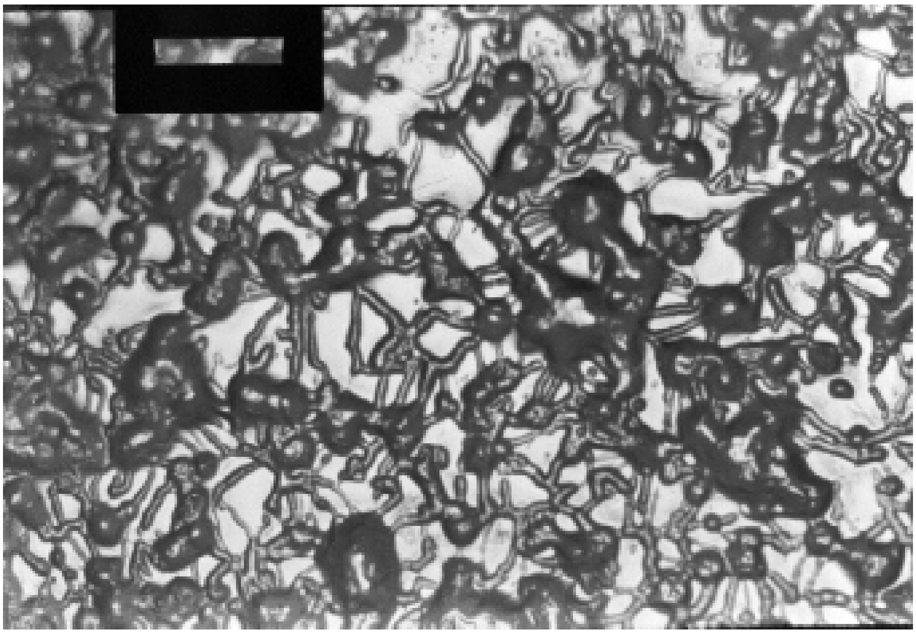

Figure 1. Optical micrograph (reflected light) of the surface of a cured unsaturated polyester containing paraffin preventing styrene emission. The wax covers approximately 50 % of the surface. The length of the marker is 200 µm. **[4]**

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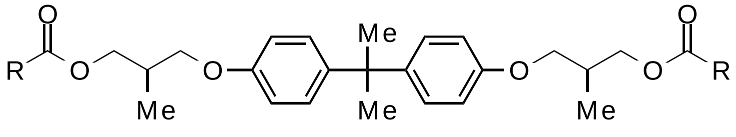
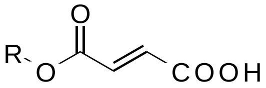
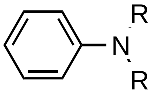
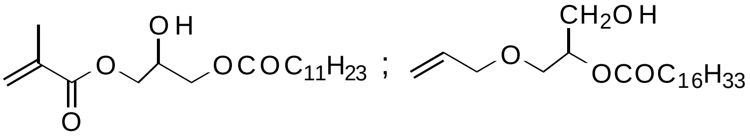
[*] Vinyltoluene is an isomer mixture composed of 67 % *o*-methylstyrene and 33 % *p*-methylstyrene.

High-solids resins

The average styrene content in conventional resins ranges between 38 - 45 wt %, and one approach for LSE resins is a reduction of the styrene content, preferably below 35 wt %. The viscosity of the resin will then increase drastically, and the processing by vacuum injection or spraying will be impossible. The high viscosity can be compensated with a reduced molecular weight of the polyester prepolymer, but then the mechanical properties of the cured resin will be poor.

Table II. Adhesion promoters for wax containing LSE resins. [20]

Adhesion promoter
corn oil, epoxidized soybean oil
poly(butyl acrylate)
 R = C5-C30
linseed oil
sunflower oil
 R = C6-C24
stearyl methacrylate, vinyl decanoate, lauryl methacrylate, n-octane
C18-C40 olefine
 R = Me, Et
2-ethylhexanol, n-nonanol, n-dodecyl benzene
alkyd resin
mixture of C5-C7 n-alkane and C5-C7 isoalkane
lanolin


3.5 Delamination in unsaturated polyester laminates

Delamination is a serious failure mechanism in unsaturated polyester resin laminates, and it can be the reason for complete break-down of a composite structure during use. [21] Delamination occurs if the interfacial bonding [†] between the layers of a laminate is not strong enough. This can be due to internal defects or voids in the matrix, which are a result of processing defects, high external impacts, or excessive loading levels.

Modes for delamination

Three basic modes for delamination can be defined, see Figure 2. Mode I represents the opening or peel by a tensile force normal to the plane of crack propagation, Mode II represents the sliding in the direction of crack propagation, and Mode III represents the tearing parallel to the propagating debond front. Of these modes of delamination, Mode I requires the least amount of energy to propagate a crack, and is therefore the most common to study. [22]

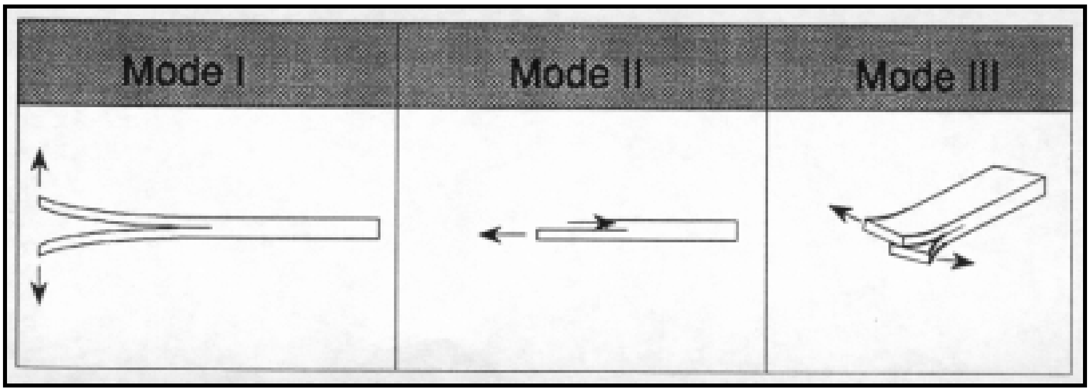


Figure 2. Three modes have been defined for delamination. Mode I represents a tensile opening perpendicular to the crack propagation, Mode II represents a sliding opening in the direction of the crack propagation, and Mode III represents a tearing opening mode parallel to the propagating debond front. [22]

[†] The term secondary bonding is also used.

Delamination in LSE resins

Normally the interfacial bonding is very good between successive layers in a laminate made from unsaturated polyesters. Atmospheric oxygen inhibits the free radical crosslinking reaction at the surface of the lower layer, thus giving a tacky surface with unreacted polyester and styrene monomers. [4] When applying a new layer upon the under-cured surface, styrene will diffuse into the under-cured layer, and an efficient interfacial bond will be formed. This can be seen by studying cross-sections of unsaturated polyester laminates under polarized light, see Figure 3.

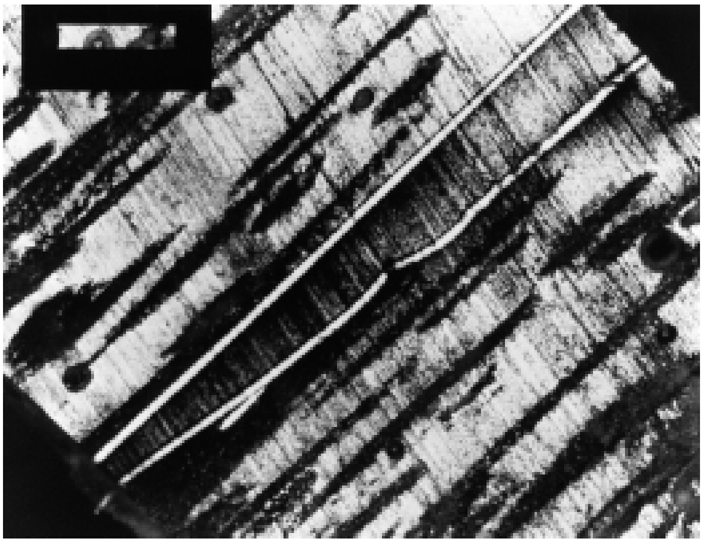


Figure 3. Optical micrograph in polarized light of a laminate made from a standard unsaturated polyester. The curved birefringent line is the surface of the under-cured layer. A resin-rich layer can be seen between the curved and the straight birefringent lines. Fiber bundles (dark areas) and resin regions (light areas) can be identified. The length of the marker is 500 µm, and the specimen thickness is 100 µm. [4]

The birefrigent lines are due to compressive stresses generated by the polymerisation of the styrene. In LSE resins containing film forming wax additives this is not the case. The additives will not only prevent the styrene emission by forming a thin wax film on the laminate surface, they will also prevent the oxygen inhibition effect. This gives a dry, cured surface, and a good interfacial bond cannot be formed. The delamination risk for LSE resins is particularly large if there are long delays between the lamination of consecutive layers. Delamination can also occur if too much initiator than recommended has been used, or if the surface is contaminated by dust, or by resin excess. [23]

Methods for interfacial bonding measurement

There are several methods available to measure interfacial bonding in composite laminates.

Fibre pullout test

For quality control purposes the fibre pullout test has been a common method for the industry to measure delamination and interfacial bonding. There are various variations of this method. [24,25,26,27]

In a typical procedure a two-layer laminate is prepared with an excess of resin applied on the first layer. The second layer is laminated after a time delay, typically between 24 and 72 hours. The excess resin and the time delay enhance the tendency for delamination, and simulate therefore lamination under severe conditions. Before the second layer is laminated, a strip of PET-film is placed along the edge of the laminate. This makes it possible to peel the layers apart by hand or forcing a wedge into the laminate. The surfaces are finally inspected qualitatively, and the laminate is considered delaminated if large areas of either halves show no fibre pullout. An example is shown in Figure 4, where the clear differences in fibre pullout between the laminates can be seen. This method is rather simple and straightforward, and gives reliable results if the delamination is severe. It is not suitable if quantitative delamination data is wanted, especially if small differences exist between studied laminates.

Wedge opening

To be able to study laminates with smaller differences in interfacial bonding a more reliable method has been developed. [2] The laminate is prepared in the same way as in the fibre pullout test, but the opening is done in a tensile testing machine. A designed wedge is attached to the upper load frame, and the laminate is clamped in a support, attached to the lower load frame. A typical set-up is shown in Figure 5. The wedge is then forced into the laminate at a constant cross-head speed, and the load is measured with a load cell. The laminate is considered to be delaminated if the load at break is below 400 N, if the load is between 400 and 800 N the delamination is partial, and if the load is above 800 N the laminate is not delaminated.

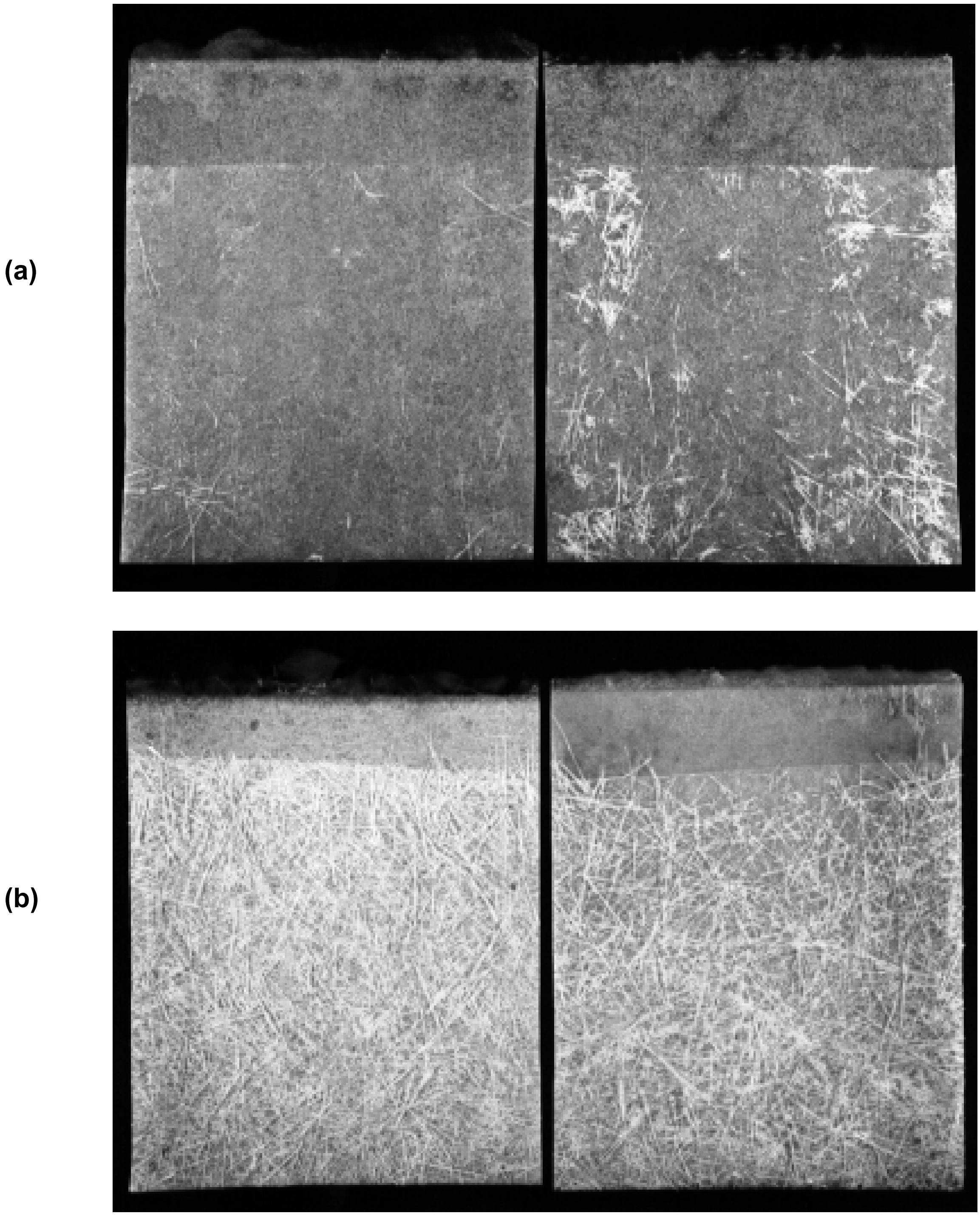


Figure 4. Surfaces of wedge-opened laminates (200 mm x 300 mm) showing distinct patterns of fibre-pullout. (a) A delaminated laminate. (b) A laminate with good interfacial bonding.

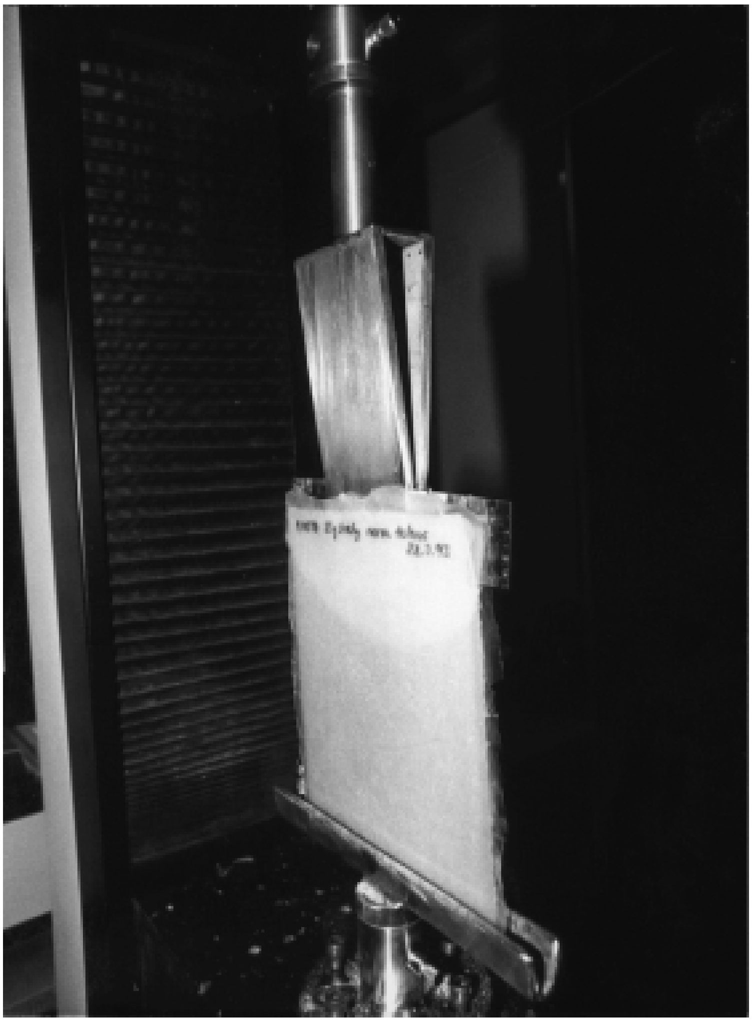


Figure 5. Wedge-opening of a laminate (200 mm x 300 mm) in a Instron 1175 tensile strength testing machine. [3] The laminate is clamped in the lower support, and the wedge is driven into the starter crack created by a PET film. The cross-head speed is 50 mm/min, and the load is measured with a 5 kN load cell.

Double cantilever beam test

The double cantilever beam (DCB) technique is a well-established method that uses fracture-mechanics to determine the toughness of a laminate interface, and can be used to determine the interfacial bonding in a laminate [3,22]. In the DCB test a linear elastic fracture mechanics methodology is used, and the mode I strain energy release rate, G_{IC}, can be calculated. The test consists of peeling apart the upper and lower halves of a beam specimen in a Instron testing machine. The dimensions and variables of the test specimen are shown in Figure 6.

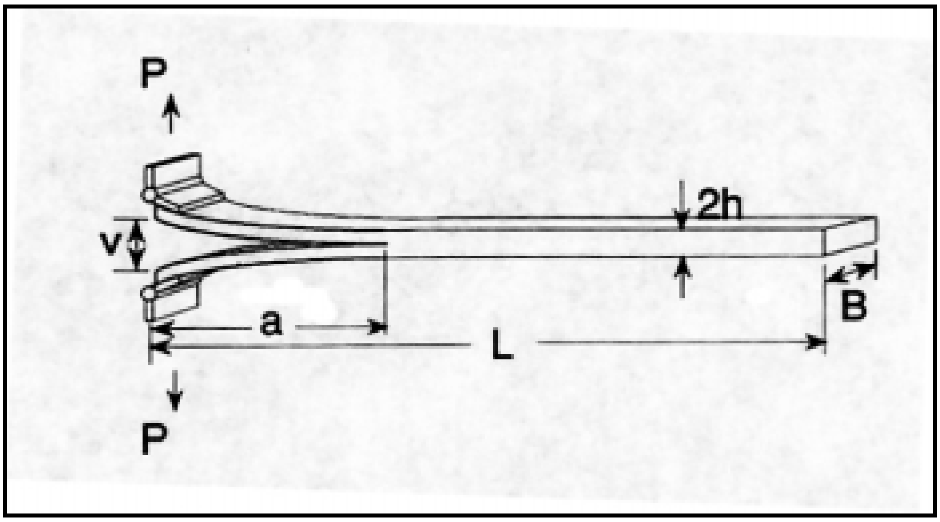


Figure 6. Specimen dimensions and variables for the DCB test. Typical dimensions are: L = 125 mm, B = 14 mm, 2h = 5 mm, a = 50 mm. [22]

The opening is done typically with a constant displacement speed of 1 – 5 mm/min. A slow opening allows easy following and recording of the crack propagation, which is done optically with a moving microscope, or by applying UV sensitive dye-penetrants, or by coating with a white marker. The strain energy release rate is then calculated from the load, the displacement, and the crack length using the equation:

$$G_{Ic} = \frac{3Pv}{2Ba} \quad (1)$$

Here is **P** the applied load, **v** the load-point displacement, **B** the specimen width, and **a** the cracklength.

4 STRATEGIES FOR TAILORING OF UNSATURATED POLYESTERS

The most common method to tailor the properties of unsaturated polyester resins to use modifying additives or polymers in the resin formulation. Flame retardance, impact strength, UV-stability and flow properties of commercial resins are regulated by additives. The blending of hyperbranched polyesters into the unsaturated polyester resin is a new concept to obtain enhanced properties. Reduced styrene emission, lower viscosity and improved toughness are achieved. [282930] Interpenetrating polymer network materials with improved toughness based on unsaturated polyesters and epoxy resins have also been reported. [31]. Synthetic modifications of unsaturated polyesters involve the introduction of flexibilising long chain aliphatic segments, and the introduction of rigid-rod segments into the unsaturated polyester backbone.

4.1 Unsaturated polyesters with rigid segments

Liquid crystalline polymers (LCP) are a well known class of materials with unique properties, due to the orientation of the individual polymer chains. Excellent mechanical properties in the orientation direction of the polymer chains, low coefficient of thermal expansion, low melt viscosity and high chemical and thermal resistance are typical for them. [32] In liquid crystalline thermosets (LCT) the properties of LCPs are combined with the properties of conventional thermosets. They are based on rigid-rod or extended-chain segments which are cross-linked into a three dimensional network. The main part of the reported LCTs are thermotropic, these are liquid crystalline oligomers or polymers, which are crosslinked within the nematic melt, resulting in either isotropic or anisotropic network structures, see Figure 7 a. [7,33,34] In a lyotropic LCTs the crosslinking occurs in the lyotropic solution, between the rod-like polymer, and a monomer, see Figure 7 b.

It was already in 1975 shown by Verbit and Tuggey [35,36] that diesters of fumaric acid and n-alkoxyphenols were liquid crystalline, due to the rigid-rod character of the fumaroyl segment. Several authors have reported unsaturated polyesters with mesogenic segments since that. Bilibin et al. [37,] reported semi-flexible unsaturated polyesters containing fumaroyl units within the mesogenic unit, see Figure 8. Rätzsch et al. [38,39] reported polyesters of similar structure with the double bond in the flexible part of the polymer,see Figure 9. The reason for the introduction of the fumaroyl unit in the flexible spacer was to avoid a destruction of the liquid crystalline state when the double bond reacts in the crosslinking reaction. These polyesters could be crosslinked in the liquid-crystalline state with styrene, and the crosslinking increased the isotropization temperature and extended the mesophase range. It was also reported that the crosslinking improved the physical and the mechanical properties above the glass transition temperature.

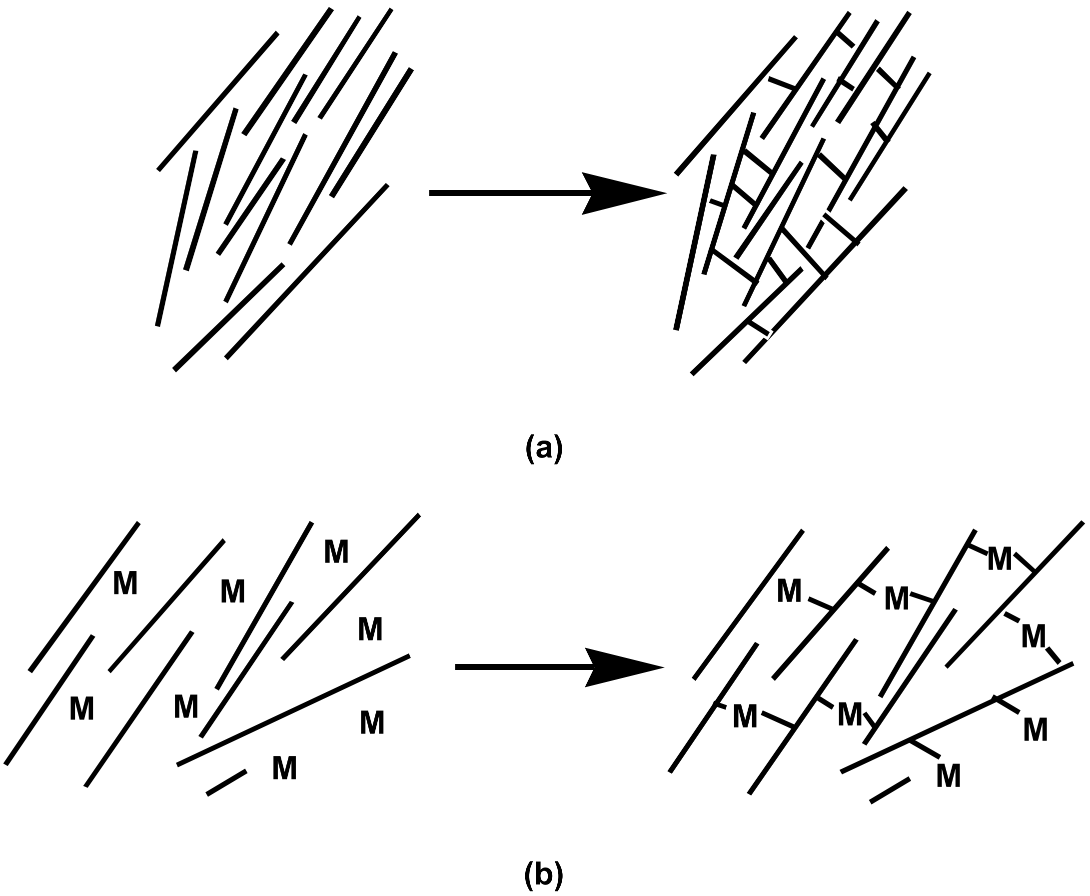


Figure 7. Thermotropic (a) and lyotropic (b) liquid crystalline thermosets. In a thermotropic LCT the crosslinking occurs in the thermotropic mesophase, while the crossinking occurs in a lyotropic LCT in a lyotropoic solution.

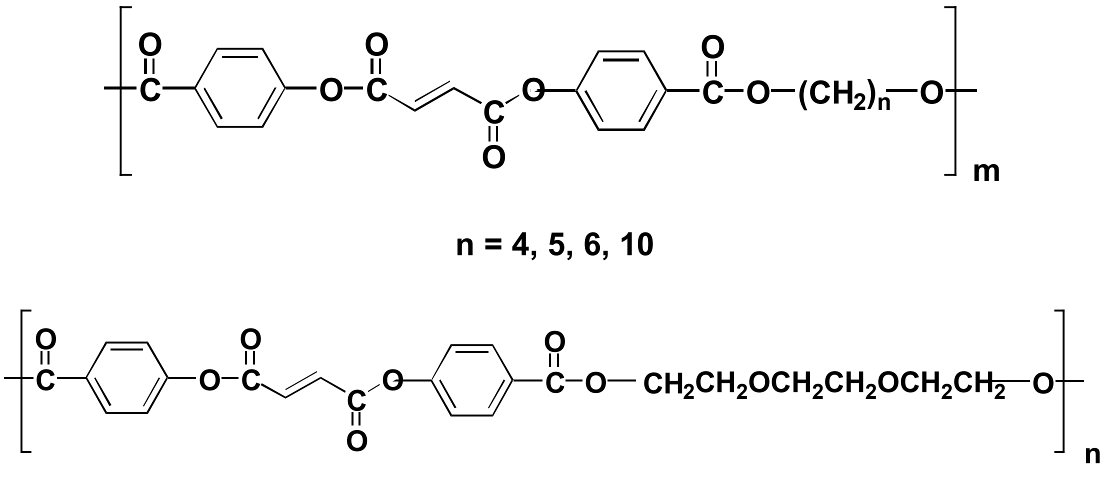


Figure 8. Thermotropic unsaturated polyesters containing fumaroyl units within the mesogen. [37]

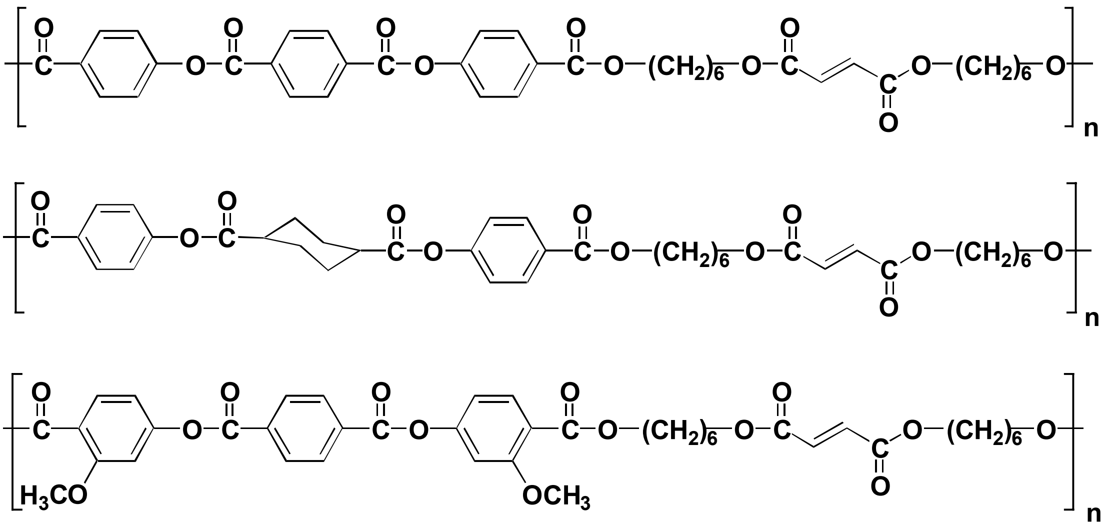


Figure 9. Thermotropic unsaturated polyesters containing fumaroyl units in a flexible spacer. [38,39]

Thermotropic unsaturated block co-polyesters were also described by Galcera et al. [40,41], see Figure 10. Block copolymers with a rigid block content of 75 % or above exhibited a nematic mesophase after melting. The copolymers could be crosslinked thermally in the nematic state, both in the presence or in the absence of *t*-butyl hydroperoxide as a radical initiator. The nematic state was retained after crosslinking.

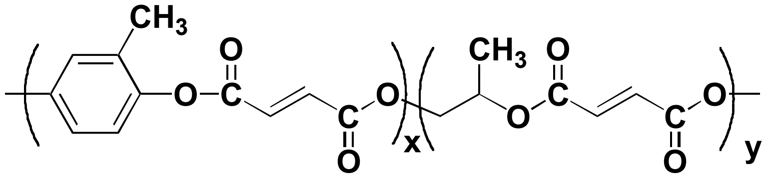
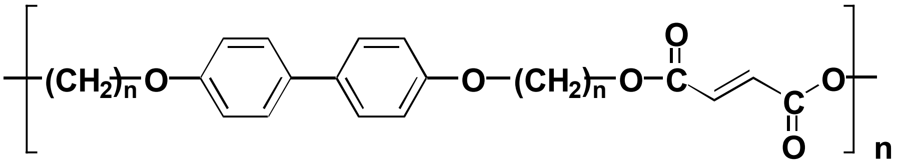


Figure 10. Thermotropic block copolyesters containing fumaroyl units in the rigid block. [40,41]

Thermal and photochemical crosslinking has also been observed for a series of thermotropic polyetheresters and copolyetheresters, see Figure 11. These polymers could also be crosslinked by copolymerisation with vinyl monomers, such as styrene and methyl methacrylate. [42] The crosslinked polymers exhibited a liquid crystalline behaviour.



n = 3, 4, 6

Figure 11. Thermotropic polyetheresters. [42]

4.2 Unsaturated polyesters with flexible segments.

In the development of unsaturated polyesters for high performance composites much attention has been paid on the improvement of fracture toughness and impact resistance. The most common way is to add dispersed elastomers such as butadiene-acrylonitrile rubbers into the unsaturated polyester, where they form phase-separated domains. [43]

Chemical modification can be done by incorporation of aliphatic diols or dicarboxylic acids into the polyester chain during the polycondensation reaction. A disadvantage is that a large amount of these reactants must be used in order to achieve sufficient toughness, which results in sacrifice of other properties. Another possibility for chemical modification is copolymerisation of poly(ethylene glycol)s into the polyester chain.

Tong et al. [44,45] have studied the mechanical properties of random block copolymers of unsaturated polyesters and poly(ethylene glycol)s with number-average molecular weights ranging from 6000 to 10000 g/mol. Tensile and flexural properties decreased with increasing molecular weight of the poly(ethylene glycol) segment, while the impact strength and elongation was improved. A one stage batch polycondensation of poly(ethylene glycol)s with an unsaturated polyester is however not easy. The rate of polycondensation decreases with increasing molecular weight of the poly(ethylene glycol), and the C – 0 bond can break down with the formation of oligomeric compounds. These will participate in the polycondensation, which will lead to side reactions. [46]

5 SUMMARY OF PAPERS I - VI

5.1 *PAPER I: Unsaturated para-linked aromatic LC-polyesters: Thermotropic and lyotropic systems*

This paper reports the synthesis and characterisation of thermotropic and lyotropic liquid crystalline unsaturated polyesters.

Synthesis

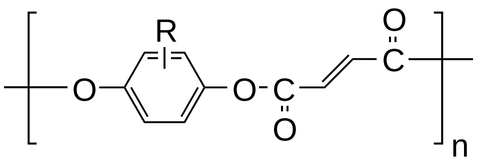
A series of unsaturated polyesters **(1 – 6)** were synthesised from fumaroyl chloride and t-butyl-, phenyl-, 2-phenethylhydroquinone and 2,2'-dimethyl-biphenyl-4,4'-diol respectively, in order to get the necessary extended, rigid-rod structures. The structures of the synthesised polyesters are shown in Figure 12. To achieve sufficient solubility of the polyesters, to lower the melting temperature, and to decrease the crystallinity, aromatic diols with bulky lateral substituents or a noncoplanar conformation were selected. A copolyester **(5)** from *t*-butylhydroquinone and phenylhydroquinone was also synthesised. The properties of these polyesters were compared to a polyester based on hydroquinone. The polymerisation was done by interfacial polycondensation. This method was selected to avoid degradation and side reactions of the unsaturated bond, which can occur if melt polycondensation is used.

Thermal properties

The polyesters were characterised by differential scanning calorimetry, see Figure 13. Depending on the substitution, glass transition temperatures between 40 °C to 115 °C were detected. The polyester with the more rigid *t*-butyl substituent **(2)**, had a clearly higher glass transition temperature compared to the polyester with the 2-phenethyl substituent **(4)**, which acts as an internal plasticiser. This was in accordance with the literature. [47] The copolyester **(5)** showed a glass transition temperature at 90 °C, which was between the glass transition temperatures for the corresponding homopolyesters.

Liquid crystalline properties

The polyesters were thermotropic liquid crystalline above their glass transition temperatures, as nematic textures were observed by polarisation microscopy. The phenylsubstituted unsaturated polyester **(3)** with a glass transition temperature at 85 °C had a different thermal behaviour. It exhibited a broad melting transition from 180 to 240 °C, above which this polyester also was liquid crystalline. All nematic polyesters showed broad clearing temperature ranges, in the range of 255 to 275 °C, during which simultaneous decomposition and cross-linking occurred. The unsubstituted polyester containing hydroquinone **(1)**, and the polyester containing the noncoplanar biphenyl unit **(6)** did not melt before the decomposition started.



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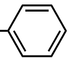
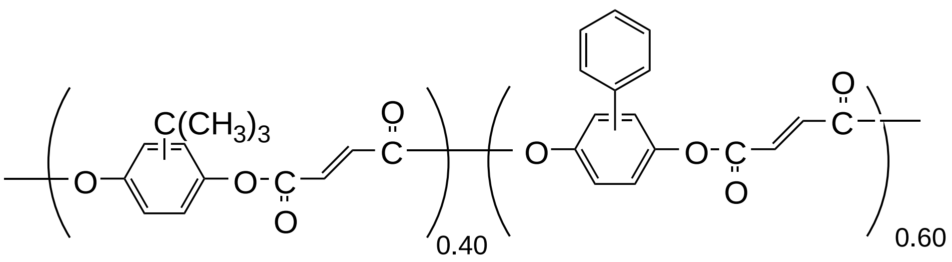
No.	**1**	**2a, 2b**	**3**	**4**
R	H	$C(CH_3)_3$		CH_2CH_2– 



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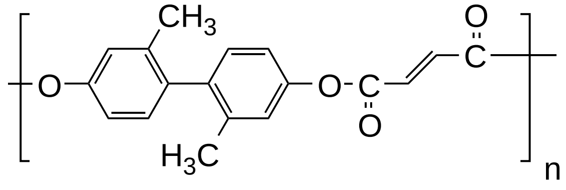

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Figure 12. Chemical structure of synthesised fumaroyl-based aromatic polyesters. (Paper I)

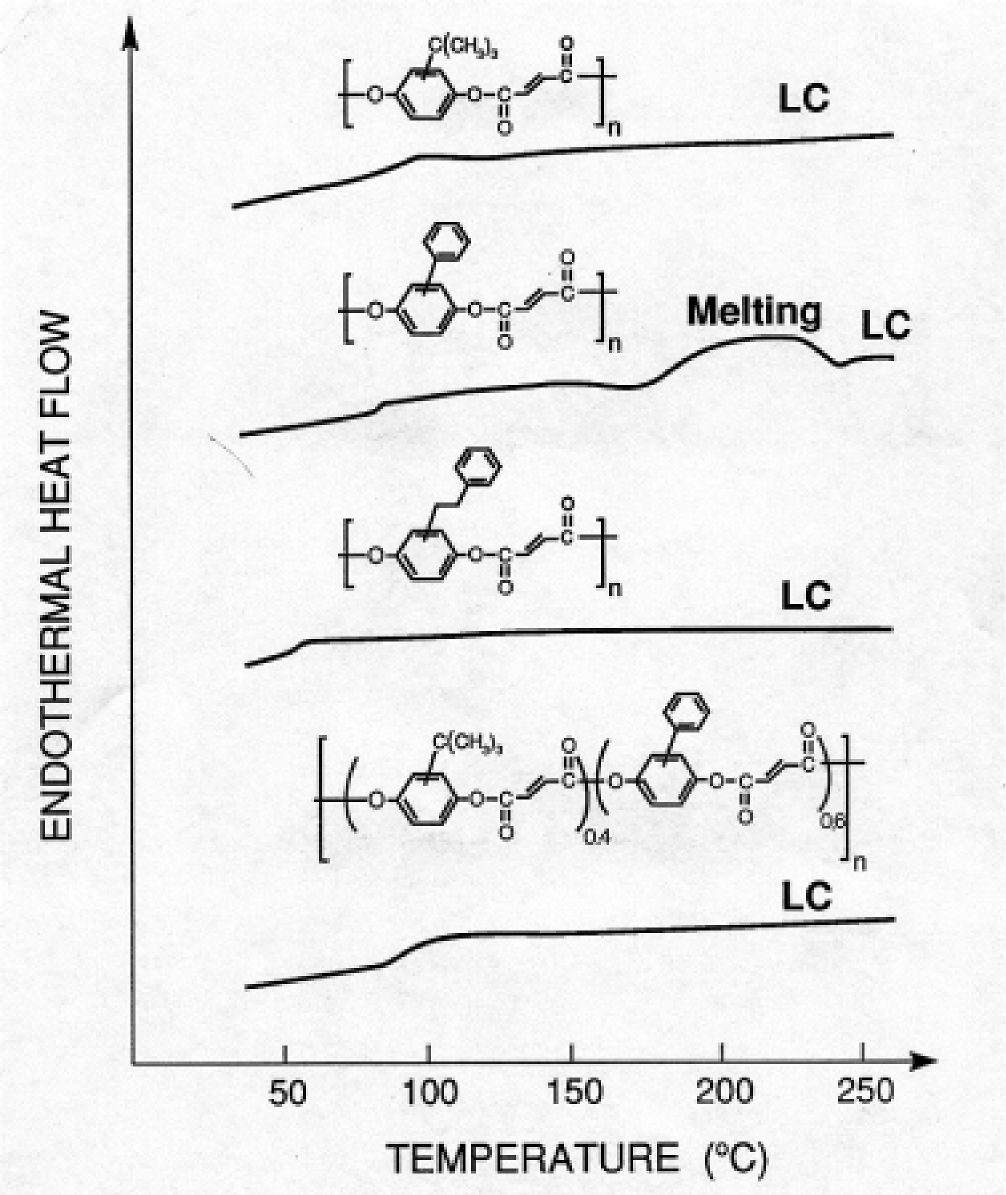


Figure 13. DSC heating curves of synthesised fumaroyl-based aromatic polyesters. Data from the second heating run, heating rate 10 °C/min, nitrogen atmosphere. (Paper I)

Preparation of lyotropic solutions

The first part of the paper showed that thermotropic unsaturated polyesters indeed can be synthesised. The next question was to investigate if lyotropic systems in styrene could be achieved. Styrene is the most common monomer for unsaturated polyester resins, and it was found that the *t*-butyl substituted unsaturated polyester dissolved quite well in styrene. Therefore a larger batch of this polyester was synthesised by melt condensation. This was possible, as the results from the interfacial polycondensation had shown that the polyester is thermally stable at the melt condensation temperature, 170 °C. Preparation of lyotropic solutions is usually a cumbersome procedure which requires long stabilisation and equilibrium times. Totally a series of 8 polyester-styrene solutions was prepared, with a concentration of 5 to 95 wt % polyester in styrene. To promote homogeneous conditions, a small amount of a co-solvent, methylene chloride, was used together with the polyester and styrene. The solutions were incubated at 50 °C, until the added methylene chloride had evaporated. The evaporation was followed by weighing the samples, until constant weight was achieved. This methodology was based on the assumption that methylene chloride will evaporate more easily than styrene, due to lower vapour pressure. The final composition and styrene content was then determined by thermogravimetry, as shown in Figure 14.

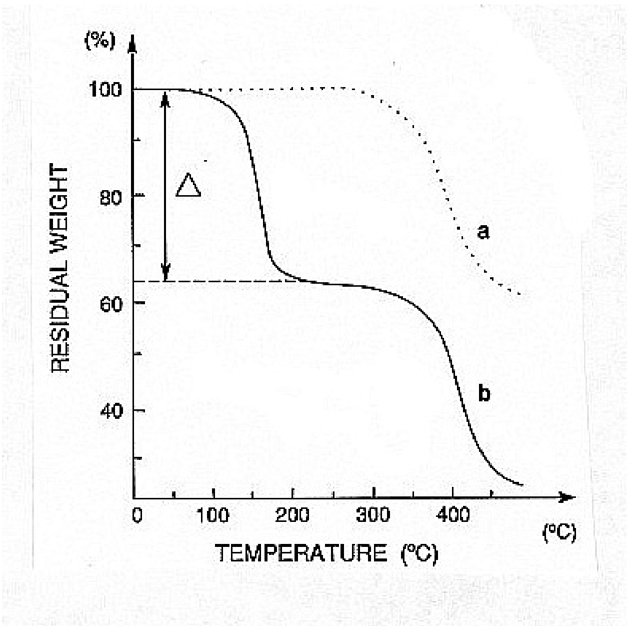


Figure 14. Thermogravimetric determination of the styrene content in polyester-styrene blends. (a) TGA scan of neat polyester. (b) TGA scan of a polyester-styrene blend containing 37 wt % styrene. Δ = determined styrene content. Heating rate 10 °C/min, nitrogen atmosphere. (Paper I)

The mixtures were studied by polarisation microscopy, and both anisotropic and isotropic gels could be seen. At polyester concentrations below 50 wt %, and at room temperature, the samples formed an isotropic gel, which melted into an isotropic liquid upon increasing the temperature. At higher polyester concentrations, the samples were birefringent gels at room temperature. With increasing temperature, the gels transformed into lyotropic liquid crystalline solutions. At a polyester content of 90 wt % the softening point was around 90 °C, which is lower than the glass transition temperature for the pure polyester. The lyotropic behaviour of the samples could be detected as nematic textures, and by the very low viscosity compared to the same thermotropic polyester. The lyotropic solutions could further be cross-linked into thin films, by rapid heating at 100 °C, and using benzoyl peroxide as an initiator.

5.2 PAPER II: Thermal and liquid crystalline properties of unsaturated polyesters containing rigid segments

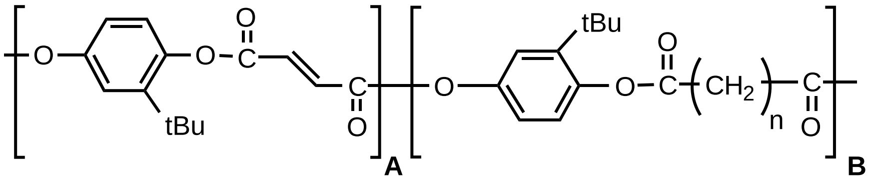
This paper continues the work in Paper I, and describes the influence of aliphatic and aromatic comonomers on the thermal and liquid crystalline properties of an unsaturated polyester based on fumaroyl chloride and t-butylhydroquinone. In order to achieve processability near room temperature, it is necessary to lower the transition temperatures. Introduction of aliphatic comonomers will affect the molecular packing of the polymer, which will in turn affect the properties compared to a fully aromatic polymer, where the mesogenic groups are closely packed. [48] By using diacid comonomers it is also possible to vary the molar amount of the unsaturated fumaroyl unit in the polyester, in this way the reactivity can be tailored, as discussed in Chapter 3.1. The density and structure of the network will depend therefore on the amount and distribution of the fumaroyl units in the polyester.

Synthesis

Four different modifications were introduced into unsaturated polyesters based on fumaroyl chloride and t-butyl hydroquinone, see Figure 15. Succinoyl chloride and/or adipoyl chloride were used to decrease the transition temperatures, terephthaloyl chloride was used to reduce the amount of fumaroyl units, and bisphenol A was introduced to reduce thermal transitions but keeping the amount of fumaroyl units constant. The polymerisations were done by interfacial polycondensation, and the thermal and liquid crystalline properties were investigated.

Properties

The results showed that up to 50 molar % of a flexible comonomer could be introduced without destruction of the thermotropic phase, higher amounts destroyed the liquid crystallinity, which was in accordance with results reported in the literature. Terephthaloyl chloride gave a thermotropic polyester, as expected, but large amounts will turn the polyester into an intractable polymer. Bisphenol A destroyed the liquid crystallinity in all cases, which is due to the kinked conformation of the monomer.



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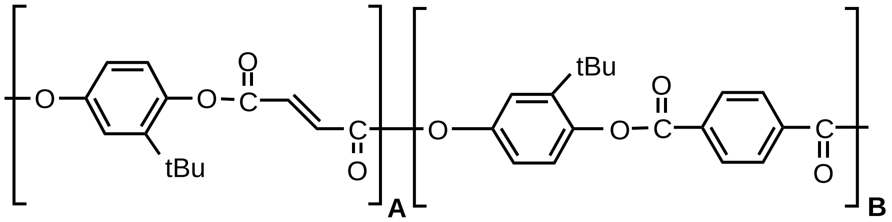

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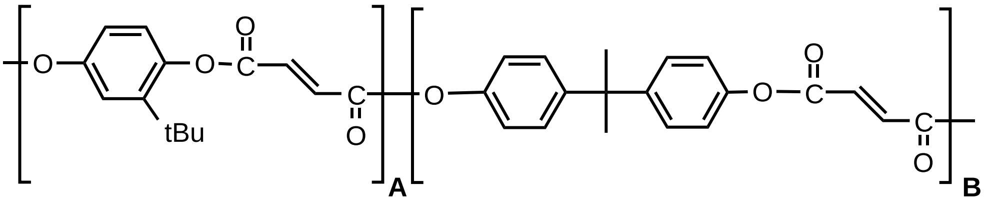

8 - 11

Figure 15. Chemical structures of synthesised fumaroyl based co-polyesters. (Paper II)

5.3 *PAPER III: Modification of unsaturated polyesters by poly(ethylene glycol) end groups*

Another way of tailoring unsaturated polyesters is described in this paper. From the literature it is known that poly(ethylene glycol) segments can be introduced in unsaturated polyesters, in order to reduce the brittleness which is often a problem in composite applications. [44] In the present paper poly(ethylene glycol) endgroups were used to tailor the styrene-solubility behaviour, and the mechanical properties of the cured resin. This was done by a coupling reaction between a separately synthesised carboxyl-terminated unsaturated polyester and poly(ethylene glycol) mono-methyl ethers of various molecular weights, see Figure 16. The result is a type of AB block copolymer, which was expected to have higher flexibility, lower viscosity and better styrene compatibility.

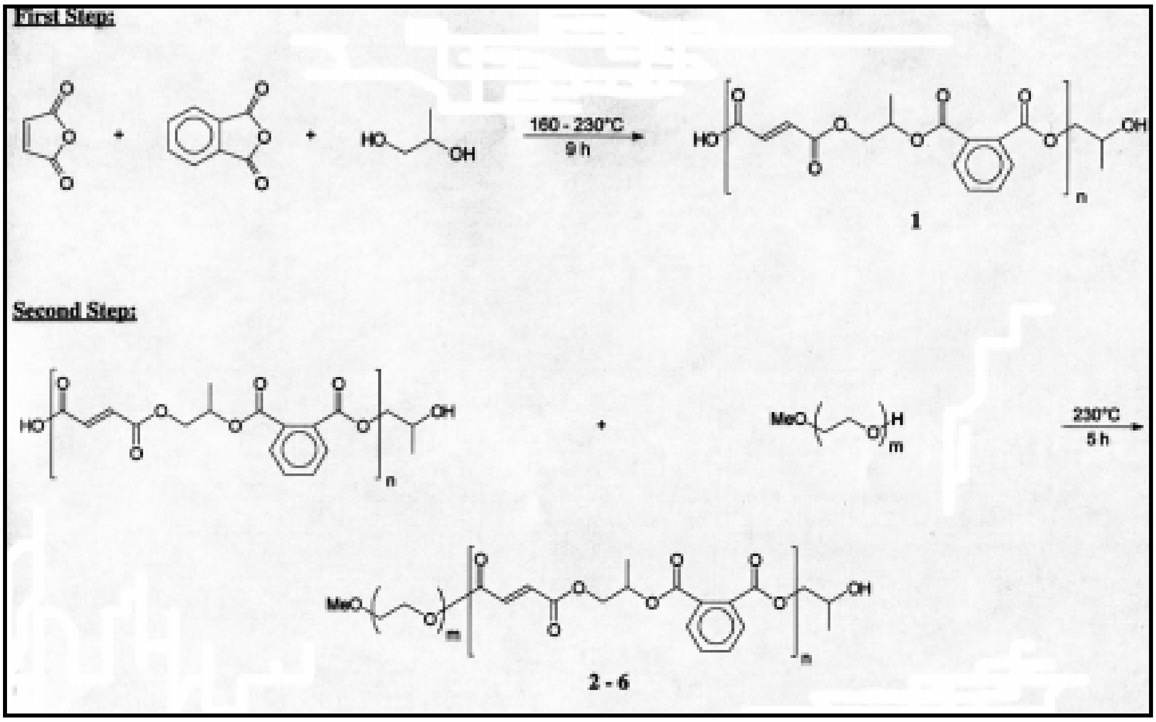

Figure 16. Two-step synthesis of unsaturated polyester with poly(ethylene glycol) end groups. (Paper III)

Synthesis

The carboxyl-terminated unsaturated polyester was synthesised from maleic anhydride, 1.2-propanediol and o-phthalic anhydride. The molar ratios were selected so that approximately every third acid component was unsaturated. An excess of 1.2-propanediol was used in order to get a number average molecular mass around 1400 to 1600 g/mol, which is typical for unsaturated polyester prepolymers. The synthesis was done by the melt polycondensation method, which involved 9 h heating using a temperature gradient from 160 to 230 °C. The amount of unreacted carboxylic groups in the prepolymers were then determined by acid number titration with 0.1 N KOH. The equivalent amount of the poly(ethylene glycol) monomethyl ether was then added. For the modification four different poly(ethylene glycol) monomethyl ethers with the molecular weights 350, 550, 750 and 2000 g/mol were used. The coupling reaction was continued for 5h at 230 °C, and the completion was verified by GPC analysis. The AB block copolyesters where then diluted into styrene, so that resins with 30 wt % styrene content were achieved. One of the polyester prepolymers was also diluted to 20 and 40 wt % styrene content. The unmodified polyester was also diluted in styrene, this resin was used a reference.

Characterisation

The unmodified polyester was characterised by GPC and by ^{1}H-NMR spectroscopy. The GPC results were in good agreement with the number average molecular weights calculated from the acid number titrations. GPC showed also that the desired molecular size is achieved after the 9 h reaction. The structures were finally verified by ^{1}H-NMR. The effectiveness of the coupling reaction between the poly(ethylene glycol) monomethyl ether and the unsaturated polyester was confirmed by GPC, IR, ^{1}H-NMR and ^{13}C-NMR. The GPC showed that there is no substantial amount of unreacted poly(ethylene glycol) monomethyl ether left, this could easily be verified by comparing the GPC diagram of the block copolymer with the GPC diagram of the pure poly(ethylene glycol) monomethyl ether. The spectroscopic analysis finally confirmed the structures.

Crosslinking

The curing behaviour of the block copolyesters diluted in styrene was investigated using a thermal scanning rheometer. This instrument detects changes in viscosity by moving a probe up and down into the sample. The gel time can be seen as a very rapid increase in the storage dynamic viscosity as shown in Figure 17. The molecular weight of the poly(ethylene glycol) monomethyl ether had an effect on the gel time, only those polyesters with the short segments, 350 and 550 g/mol, could be cured in a reasonably short time.

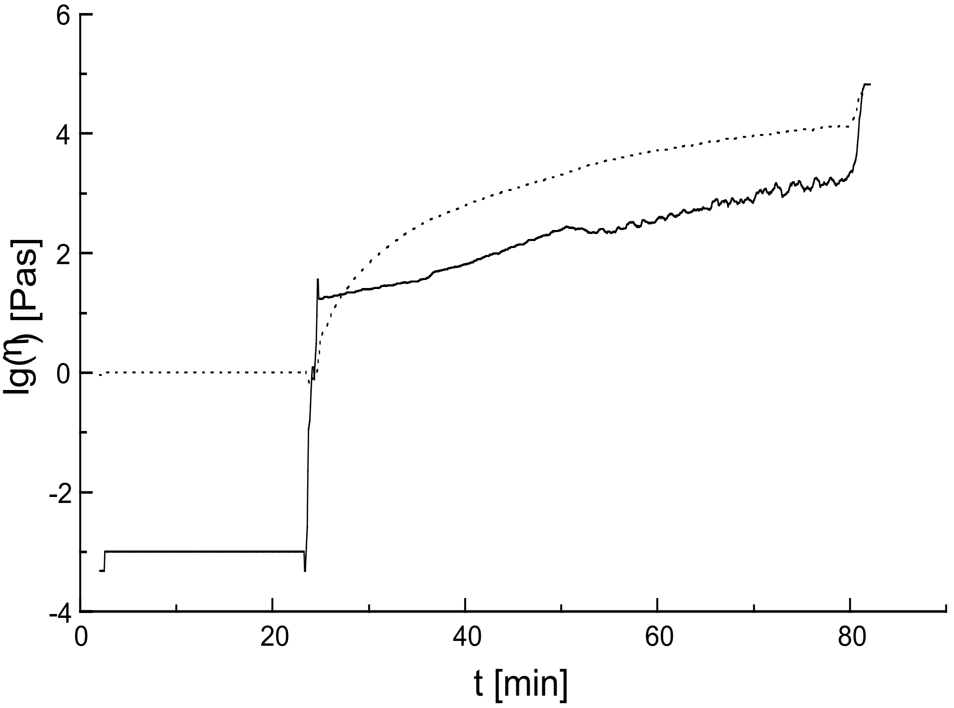

Figure 17. Determination of the gel time with a thermal scanning rheometer at 25 °C. The solid line is the storage dynamic viscosity, η', the dotted line is the loss dynamic viscosity, η''. The onset of the rapid increase in both viscosities was defined as the gel time. The sample contained 30 wt % styrene and was initiated with 1 wt % methyl ethyl ketone peroxide activated with 1 wt % cobalt octoate. (Paper III)

Thermal properties

The thermal properties were analysed by DSC to reveal if the poly(ethylene glycol) is phase separated or miscible in the cured resin, and to reveal if the cured resin contains still unreacted styrene monomer. Compared to the unmodified unsaturated polyester resin, which had a glass transition temperature around 55 °C, the glass transition temperatures for the modified polyesters were clearly lower, see Figure 18. The polyester modified with the poly(ethylene glycol) segment with the highest molecular weight, 2000 g/mol, was phase separated. This cured polyester showed an endothermic peak at 48 °C in the DSC scan. This is due to the melting of phase separated poly(ethylene glycol) segments. All other cured resins were miscible. The glass transition temperature decreased with increasing length of the poly(ethylene glycol) segment and only one glass transition was detectable by DSC in the miscible resins. From the DSC scan it could also be seen that the curing was almost complete for all polyesters except one. Unreacted styrene will crosslink thermally during the first heating run of the DSC experiment, which can be detected as an exothermic peak. Integration of this peak gives an enthalpy value, which is commonly named as the rest-reactivity of the resin.

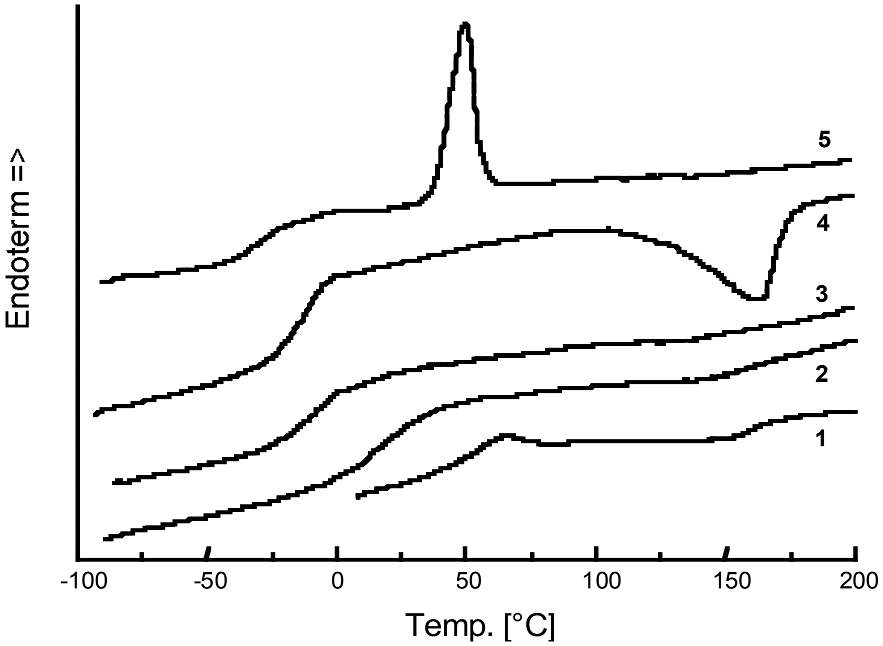

Figure 18. DSC curves for poly(ethylene glycol) end capped unsaturated polyesters. (1) reference with no modification, (2) end capped with 350 g/mol PEG, (3) end capped with 550 g/mol, (4) end capped with 750 g/mol PEG, (5) end capped with 2000 g/mol PEG. First heating scan, 10 °C/min heating rate, nitrogen atmosphere. (Paper III)

Mechanical properties

Mechanical properties were measured only for one of the cured resins. Modification with poly(ethylene glycol) end groups gave rather soft and flexible cured specimens, as the end groups acted as internal plasticisers. Tougher specimens were achieved by increasing the amount of double bonds in the polyester chain. This gives a more dense network, with reduced softness. For this purpose one unsaturated polyester resin was synthesised where two out of three acidic monomers were unsaturated. Modification was done with the 350 g/mol poly(ethylene glycol) mono methyl ether. The styrene content was also reduced, to additionally reduce flexibility. Unreinforced castings were then made and after post-curing, dumbbell shaped specimen bars were cut out of the castings. The results shown in Table III were as expected. Compared to conventional, unmodified unsaturated polyesters, both modulus and tensile strength were reduced, while the elongation was increased. This result is due to the plasticisation effect of the poly(ethylene glycol) end groups, which are freely dangling around in the crosslinked network.

Table III. Mechanical properties of three postcured (60 °C, 24 h) castings made from a unsaturated polyester end capped with a 350 g/mol PEG diluted in 20 wt % styrene.

Casting	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
reference [a]	3000	55	2.0
A	750	15.9	4.0
B	780	13.6	3.1
C	804	12.7	5.3

[a] Data from Neste Polyester, Finland

If the plasticisation effect can be controlled this would be an efficient way to tailor the brittleness and flexibility of unsaturated polyester resins. Currently this is done commercially by adding low profile additives, which typically are rubber particles heterogeneously blended with the unsaturated polyester. They will remain as domains dispersed in the resin network, and it is critical that a good interfacial attraction is achieved between the additive and the resin matrix. In reality this is however often a problem due to lack of compatibility. The interfacial interaction should be improved if the matrix resin is modified with poly(ethylene glycol) endgroups, which are compatible with the rubber particles.

5.4 PAPER IV: Crosslinking of unsaturated polyester resins studied by low-resolution ^{1}H-NMR spectroscopy

The cross-linking reaction between the unsaturated polyester prepolymer and styrene was studied by low-resolution pulsed NMR spectroscopy (LRP NMR). In this method, the free induction decay (FID) proton NMR signal, is monitored and characterised by the spin-spin relaxation time T_2, which further can be correlated to the molecular mobility of the components in the unsaturated polyester resin. T_2 is short for solid components, and long for liquid components. [49] As a comparison, the cross-linking was also estimated as the time for the temperature of the reaction to rise from 65 to 90 °C, according to the method by the Society of Plastic Industry. [50]

Sample preparation and measurements

Five unsaturated polyester prepolymers with different phthalic anhydride/maleic anhydride ratios were synthesised from maleic anhydride, phthalic anhydride and 1.2-propanediol by melt polycondensation. The prepolymers were dissolved in neat styrene to a styrene content between 43 and 49 wt %. The unsaturated polyesters were then cross-linked in NMR tubes inserted in the magnet of a 60 MHz NMR instrument. The temperature of the sample cavity in the magnet was 80 °C, and benzoyl peroxide was used as an initiator. The T_2 values were then measured and plotted as a function of the curing time. Short T_2 values were measured directly from the FID after a 2 µs 90 ° pulse, and long T_2 values were recorded using the Carr-Purcell-Meiboom-Gill pulse sequence. Populations of each component could also be calculated.

Proton mobilities

Three components with different proton mobility could be identified in the curing unsaturated polyester resins; very mobile, less mobile, and immobile ones, see Figure 19. The most mobile component with T_2 around 3 s corresponds to unpolymerized styrene, and the less mobile component with a T_2 around 150 ms corresponds to free polyester prepolymers. The mobility of these both components decreases during the cross-linking reaction, as the network is formed. The immobile component with T_2 around 0.04 ms corresponded to the cured resin polymer network. Both mobile components could be seen from the beginning of the cross-linking reaction, while the immobile component can be seen from the gel point. Before the gel point, there was an induction period where it was not possible to see any significant changes in relaxation times. This was obviously due to the inhibitors in the resin. At the end of the cross-linking reaction, the mobile components could still be seen.

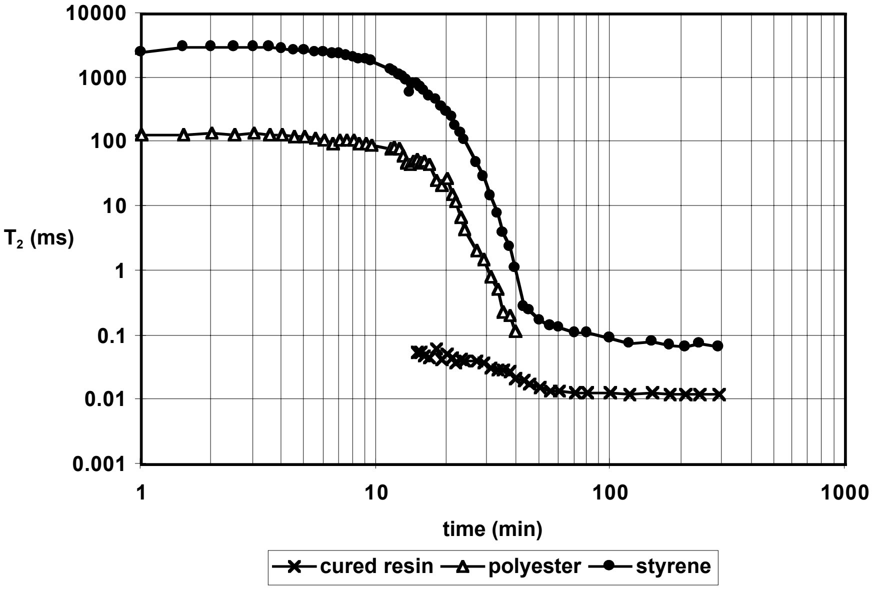

Figure 19. Spin-spin relaxation times of a unsaturated polyester. Three components can be detected: T_2 = 3 s corresponds to unpolymerised styrene, T_2 = 150 ms corresponds to free polyester polymers, and T_2 = 0.04 ms corresponds to cured resin. The resin was cured with 2 wt % benzoyl peroxide at 80 °C. (Paper IV)

Component populations

The same information was collected by the population measurements, although the immobile component was detected earlier, see Figure 20. Compared to the gel times measured according to the method by SPI, the LRP NMR results were in good agreement. For polyesters with different molar ratios it was seen that the mobile components started to loose their mobility earlier when the molar ratios of styrene to the double bonds in the polyester chain were lower. This correlated well with the gel time results. From the LRP NMR measurements it could also be seen that the proton populations for the cured resins are between 90 and 95 %, after a 100 min curing time. The rest is obviously unreacted styrene, which has been enclosed into the formed network.

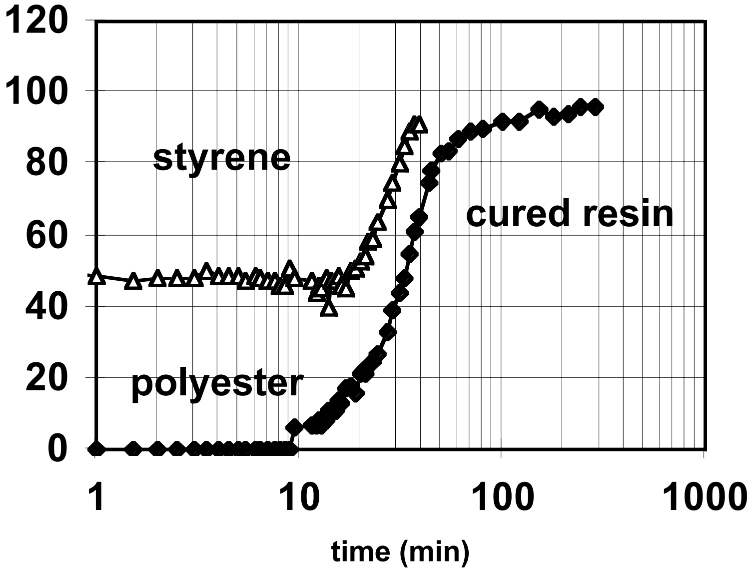

Figure 20. Differences in proton populations (Y axis) of the three components in a unsaturated polyester resin; unpolymerised styrene, free polyester prepolymer and cross-linked polyester. Unpolymerised styrene and free polyester prepolymer can be seen in the beginning of reaction. At the gel point, the formation of cured polyester resin can be seen. The resin was cured with 2 wt % benzoyl peroxide at 80 °C. (Paper IV)

5.5 PAPER V: Correlation of viscoelastic properties with low-resolution ^{1}H-NMR measurements of crosslinking unsaturated polyesters

This paper describes the continuation of the work described in the previous paper. Different unsaturated polyester resins were studied by LRP NMR spectroscopy, by rheological measurements, and by thermal analysis. The influence of the molar ratio (MR) of styrene to the double bonds in the polyester chain, molecular mass and mobility changes during the reaction on gel time were investigated.

Sample preparation

Four unsaturated polyester prepolymers with different phthalate/maleate molar ratios were synthesised from maleic anhydride, phthalic anhydride and 1.2-propanediol by melt polycondensation. Five commercial unsaturated polyesters where also included in the study. Of these three contained isophthalic anhydride.

Methods

The viscoelastic properties were studied using a cone and plate geometry. Measurements were done at 25 and 80 °C. The gel time was determined by both measuring steady shear flow properties and by measuring oscillatory shear flow properties. In the steady shear flow measurements, shear rates of 1.17 and 4.65 s^{-1} were used, and the gel time was determined by plotting the ratio of the initial viscosity (η_0) to the viscosity during cure (η_t) against time and extrapolating the ratio to zero. Oscillatory shear flow measurements were done with the frequencies 0.5, 1 and 5 Hz, and a 10 % strain amplitude. The gel time was determined as the cross-over point of G´ and G´´. The LRP NMR analysis was done at 80 °C in the same way as in Paper IV. Thermal analysis was done calorimetrically, by first measuring the reaction exotherms isothermally at 80 °C, and then re-heating them in the scanning mode from 80 to 250 °C with a rate of 10 °C/min, to get the residual reactivity from the isothermal reaction. From these values the degree of cure could be calculated. Two different curing systems were used; at 25 °C a redox system consisting of 2 wt % methyl ethyl ketone peroxide and 2 wt % cobalt octoate was used, at 80 °C the crosslinking was initiated by thermal decomposition of benzoyl peroxide.

Viscoelastic behaviour

The viscoelastic measurements showed that steady shear flow and oscillatory shear flow give similar values, for both curing systems. Comparable results were also achieved at the different frequencies and shear rates. The viscoelastic behaviour of the cross-linking resins followed the gelation model described by Yang and Suspene. [51] Three stages could be identified. In the first stage, the viscosity increases quickly, due to microgel formation. After that the viscosity remains almost constant, this corresponds to the transition stage. In the last stage before the gel point, the viscosity rises very rapidly, this is due to the formation of a macrogel.

Low-resolution NMR measurements

The LRP NMR measurements were only done at 80 °C, as measurements were not possible at 25 °C with the NMR spectrometer used. The results were similar as in Paper IV. Very mobile, less mobile and immobile components, which correspond to the unreacted styrene, to the unreacted polyester prepolymers and to the cured resin could be identified. Gel times were determined as the time when the immobile component could be seen. Compared to the gel times obtained by the rheological measurements, the LRP NMR results were clearly different for the commercial unsaturated polyesters. The immobile component appeared when the transition from the microgel formation stage to the transition stage occurred in the rheological measurements. The LRP NMR method is more sensitive for the changes in the molecular topological structure than the rheological measurements. These commercial unsaturated polyesters contained crosslinking inhibitors, and thixotropy inducing additives. These additives will affect the viscoelastic behaviour of the resins, and the differences between the two measurements could be due to this.

Thermal properties

The commercial unsaturated polyesters were further analysed by DSC. The isothermal and total reaction exotherms, the time to the maximum reaction exotherm, the degree of cure at the gel point, and the degree of cure of the isothermal reaction were determined. The time to the maximum reaction exotherm came around the average gel time measured by the rheological measurements. The gel times measured by LRP NMR came around the midpoint in the increase of the reaction exotherm. The influence of the molecular mass, the molar ratio of styrene to the double bonds in the polyester chain, and the type of aromatic acid used in the resin, on the crosslinking reaction were also studied. It could be concluded that the gel time and the degree of cure increased when the MR increases if the other structural parameters are equal. Higher molecular masses decreased the gel time. If isophthalic anhydride is used instead of phthalic anhydride, will this give a lower degree of cure.

5.6 *PAPER VI: A solid-state ^{13}C nuclear magnetic resonance study of cured, unsaturated polyester resins*

Empirically it is known that a rather large amount of the styrene and the double bonds in the polyester chain remain unreacted in the cured resin. This can be determined by DSC, as done in Paper V. The low-resolution NMR measurements in Paper V confirmed also that this is the case.

The aim with this work was to study the influence of styrene content on the length of styrene sequences in a cured unsaturated polyester resin, and to estimate the amount of unreacted double bonds in the cured polyester. The sequence lengths were determined by solid-state ^{13}C-NMR spectroscopy, in a rather straightforward way. The effect of styrene content on glass transition temperature and mechanical properties were also studied. These relationships are fundamentally important to understand if novel unsaturated polyester resins are developed.

Sample preparation

Five different unsaturated polyester prepolymers **(1 – 5)** with about the same phthalate/maleate ratios were synthesised by meltpolycondensation. 1.2-propanediol was used as the diol component in all but one, where 1.6-hexanedioll was used. One prepolymer without phthalic anhydride was additionally made. **(6)** The styrene content varied between 26 to 50 wt %.

Characterisation methods

The length of the styrene sequences and the amount of unreacted fumarate units were estimated by cross polarisation/magic angle spinning (CP/MAS) measurements using a 270 MHz NMR spectrometer. Interrupted decoupling measurements were used to detect the quaternary carbons in the crosslinked styrene. DSC was used to determine the glass transition temperature and the residual reactivity in the cured resins. The samples were heated from – 100 °C to 250 °C, with a heating rate of 10 °C/min and under a nitrogen atmosphere. Mechanical properties were determined from specimens made from the polyesters. Castings were cured with 1 wt % methyl ethyl ketone peroxide, and postcured at 50 °C for 24 h before cutting the specimens.

Effect of styrene content on thermal properties

The styrene content did not have a significant influence on the glass transition temperature when the polyester composition is the same, as shown in Table IV. Postcuring decreased the T_g, as well as the very flexible 1.6-hexanedioll component. It was not possible to detect a T_g for the unsaturated polyester made from only 1.2-propanediol and maleic anhydride. This is due to the high cross-linking density, which prevents the motions of the main chain. Postcuring decreases the residual reactivity (ΔH_{res}), and was highest for resin **6** made from only maleic anhydride and 1.2-propanediol.. The styrene content did not affect residual reactivity.

Table IV. Influence of styrene content on glass transition temperature of cured unsaturated polyester resins. Resins **1 – 4** were made from maleic anhydride, phtahlic anhydride and 1.2-propanediol (molar ratio 0.8:3:4), resin **5** was made from maleic anhydride, phthalic anhydride and 1.6-hexanediol (molar ratio (0.9:3:5.1) and resin **6** was made from maleic anhydride and 1.2-propanediol (molar ratio 1:1.7)

Cured Resin	**Styrene (wt %)**	**T_g (°C)**	**ΔH_{res} (J/g)**
1	26	47	22
2	30	46	30
3	36	45	47
4	40	46	33
4a	50	56	50
4b	50	51	28
5	40	- 9	29
6	40	ND	59

ND = not determined, **4a** = measured before post curing, 4b = measured after post curing

Solid-state NMR measurements

From the interrupted decoupling experiments the length of the styrene sequences between the polyester chains and the amount of unreacted fumarate units were estimated. The intensity of the proton bearing carbons is reduced in the interrrupted decoupling NMR spectra, compared to a normal CP-MAS spectra, and quaternary carbons can be more easily identified. The obtained spectra are shown in Figure 21 and Figure 22.

Three components in the 139 - 150 ppm region where identified by deconvolution, corresponding to the sequences styrene-styrene-styrene (SSS), fumarate-styrene-fumarate (FSF) and a combination of fumarate-styrene-styrene (FSS) and styrene-styrene-fumarate (SSF). These are illustrated in Figure 23. The 160 - 180 ppm region could be deconvoluted to peaks corresponding to unreacted and reacted fumarate units. Interpretation of the spectra is to some extent disturbed by the peaks originated from the other carbons in the styrene ring and in the phthalate rings, and from the phthalate carbonyls.

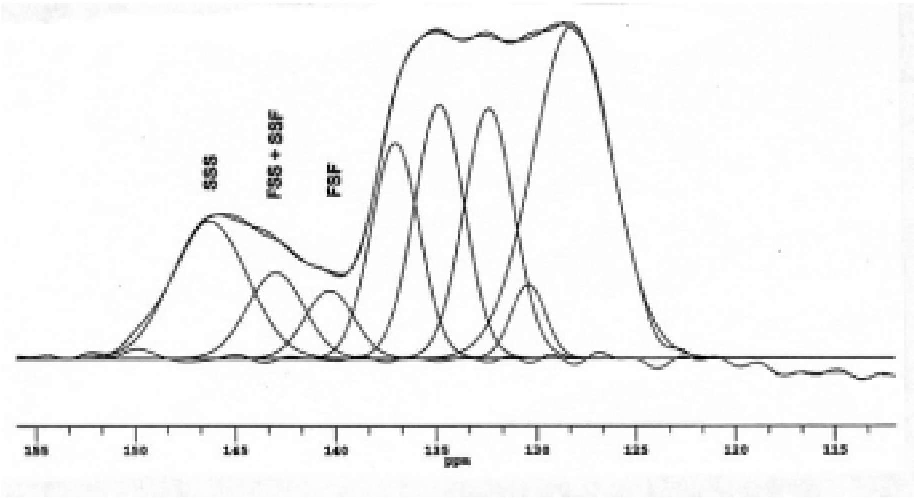

Figure 21. Deconvolution of the ^{13}C-NMR peaks in the 120 – 150 ppm area, corresponding to aromatic peaks from the crosslinked styrene monomer. Three components could be identified, styrene-styrene-styrene (SSS), fumarate-styrene-fumarate (FSF), and a combination of the sequences fumarate-styrene-styrene (FSS) and styrene-styrene-fumarate (SSF) in one component.

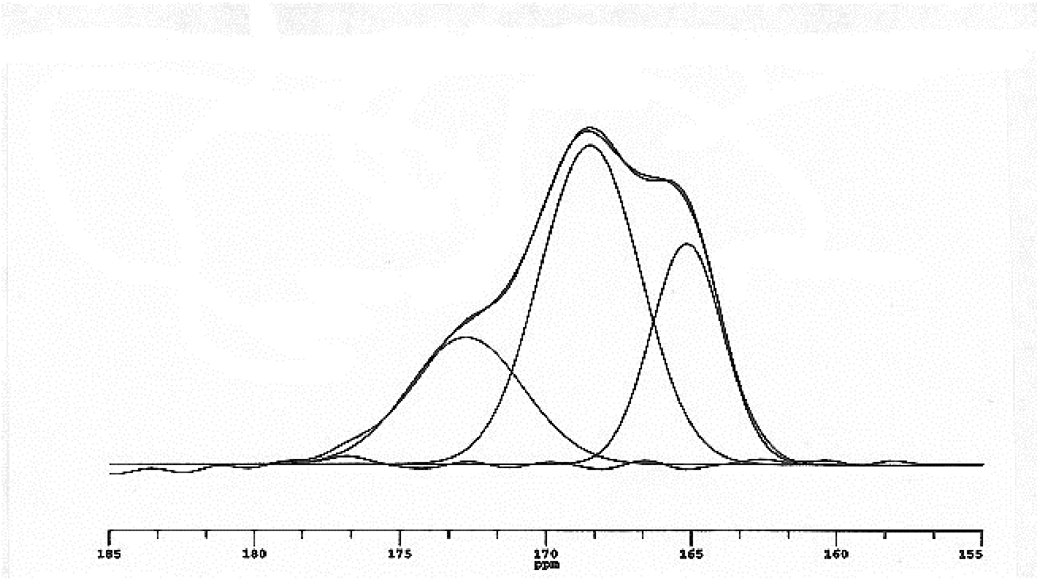

Figure 22. Deconvolution of reacted and unreacted fumarate units of a cured resin measured by solid-state, interrupted-decoupling ^{13}C-NMR. The reacted fumarate unit gives a carbonyl chemical shift around 173 ppm, while the unreacted fumarate unit gives a carbonyl chemical shift around 165 pp. The phthalate unit gives a partly overlapping carbonyl chemical shift around 168 ppm.

The results are summarised in Table V. The styrene sequence lengths increased with increasing styrene content and increasing styrene/maleic anhydride molar ratio. The amount of monad (FSF) distribution increased when the styrene content decreased. The diad (FSS) and n-ad (SSS) distributions increased with increasing styrene content. The amount of unreacted fumarate units was high, in the resins with styrene content less than 40 wt % not more than every second fumarate had reacted. Postcuring, which was done on one resin, did not have an effect on sequence distributions, but the amount of unreacted fumarate units decreased. Changing the diol from 1.2-propanediol to 1.6-hexanediol did not affect the sequence distributions. The resin made from only maleic anhydride and 1.2-propanediol had a very high content of monad sequences and a high cosslinking density compared to the others.

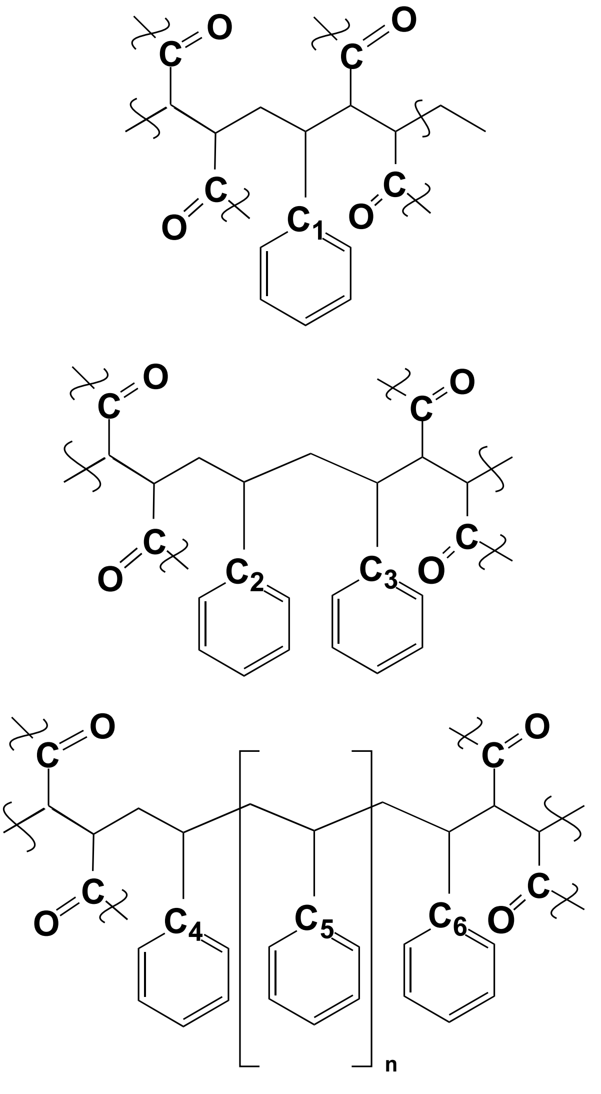

Figure 23. The different styrene sequences giving different resonances for the quaternary carbon in styrene in ^{13}C-NMR experiments. C_1 (FSF) = 140.4 ppm, C_2,C_4 (FSS) = 143.0 ppm, C_3,C_6 (SSF) = 143.0 ppm, C_5 (SSS) = 146.3 ppm. Peak assignments were made according to Birley et al.[52]

Table V. Styrene sequences in cured unsaturated polyester resins and the amount of reacted fumarate units. MR is the molar ratio of styrene and the double bonds in the polyester, and it was measured by ^{1}H-NMR.

No	Styrene (wt %)	MR	FSF (%)	FSS + SSF (%)	SSS (%)	Reacted Fumarate (%)
1	26	3.4	18	26	56	47
2	30	3.6	17	24	59	49
3	36	4.7	16	19	65	53
4	40	5.7	12	20	68	58
4a	50	ND	9	19	72	52
4b	50	ND	7	22	70	56
5	40	5.9	15	21	64	ND
6	40	1.4	30	34	36	69

ND = not determined, 4a = measured before post curing, 4b = measured after post curing

Mechanical properties

The mechanical properties were influenced quite much by the polyester composition, see Table VI. The flexible 1.6-hexanediol gave a very soft casting, and no specimens for testing could be made. The polyester **2** with 30 wt % styrene content gave a casting with poor mechanical properties, while the mechanical properties did not differ much for polyesters **3** and **4** with 35 and 40 wt % styrene content. The polyester **6** containing no phthalic anhydride gave a casting with higher elongation. When the mechanical properties are compared with the sequence distributions and the amount of unreacted fumarate units; it can be concluded that the mechanical properties are improved when the amount of reacted fumarate units increase, and at the same time, shorter lengths of styrene sequences give longer elongation at break.

Table VI. Mechanical properties of cured unsaturated polyester resins.

Resin	Tensile strength (MPa)	Youngs modulus (MPa)	Elongation at break (%)
2	13.8	5320	0.28
3	28.9	4260	0.71
4	24.9	4400	0.65
6	24.5	2800	0.97

This paper showed that solid-state ^{13}C-NMR spectroscopy gives good information about the structure of cured unsaturated polyesters. The cross-linking density and amount of reacted fumarate units can be determined. This information, in combination with thermal analysis and mechanical testing, is very important when developing new polyester resins.

6 CONCLUSIONS

Papers I and II demonstrated the synthesis of liquid crystalline unsaturated polyesters, and also that it is possible to prepare lyotropic solutions of unsaturated polyesters in styrene. So far there has not been any commercial developments based on these materials. High raw material prices will limit their use in high volume applications.

In paper III the modification of unsaturated polyesters with poly(ethylene glycol) segments was reported. The solubility of styrene in the unsaturated polyester prepolymer was enhanced, and it was possible to prepare room temperature processable and curable resins with a styrene content as low as 20 wt %. The mechanical properties of the cured samples varied from soft to hard, depending on the molar mass of the end group. Modification of unsaturated polyesters with poly(ethylene glycol) segments could be a possibility to get unsaturated polyester resins with lower shrinkage, reduced brittleness and increased flexibility.

Papers IV and V showed that low-resolution NMR spectroscopy can be used for cure monitoring of unsaturated polyesters. The results correlated well with results from DSC analysis and viscoelastic measurements. The method can be used to follow the cure kinetics and to determine residual monomer content in unsaturated polyesters.

Paper VI demonstrated the applicability of solid-state ^{13}C-NMR spectroscopy in studying the network structure of cured resins. It gives information about the cross-linking density and the amount of the double bonds that are involved in the free radical copolymerization reaction between styrene monomers and polyester double bonds. This is particularly useful when trying to understand structure-property relationships.

7 CONCLUDING REMARKS

Unsaturated polyester resins will still be important resins for composites. Their production is rather simple and straightforward, their structure and properties can be varied almost indefinitely, and most important of all, their prices will be low.

Until recently, the main application methods for unsaturated polyesters were hand and spray lay-up lamination in open moulds. New production methods are also being introduced. Resin transfer moulding (RTM) is one example. This technique is suitable for the production of smaller size products with more simple geometry in longer series. Vacuum infusion is another example. This technique is a combination of open mould lamination and RTM, and the resin is injected by vacuum into a mould filled with reinforcement covered with a flexible plastic film.

New reinforcement materials for unsaturated polyesters, such as carbon fibres and natural fibres, are also being introduced. Glass fibres have been the dominating reinforcement material, but increasing demands on mechanical properties, and on recycling have made other reinforcements interesting for unsaturated polyesters. These factors will lead to higher demands on the resin properties. Important properties are for example low viscosity, good wetting of the reinforcement, efficient mould filling, good surface quality, low shrinkage, adjustable curing behaviour and good adhesion to the reinforcement.

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