

Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties

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Abstract

Styrene is frequently used as comonomer for unsaturated polyester (UP) resins. Variations in the styrene content in the polyester affect the resulting properties. Dynamic mechanical tests show the phase separation in the cured resin with an increase of styrene concentration. The dependence of the glass transition temperature of the UP resin on the styrene content is complex and reflects a balance of elastic forces of the network and the immiscibility of polystyrene and UP. The thermal stability and the mechanical properties are governed by the phase behaviour of the mixture and therefore can be controlled by the styrene content. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is now great scientific and technological interest in the structure–property relationships in the field of thermosets used as composite matrices. Among the thermosetting resins, unsaturated polyesters, UP, are the most commonly used matrix materials for fiber-reinforced plastics [1].

Thermoset polyesters have many applications in automotive, aircraft, electrical, and appliance components as a substitute for traditional materials. The advantages of these resins besides their low cost and design flexibility is their thermal and dimensional stability, good electrical insulation, very good mechanical properties, good chemical resistance and low density.

However, several problems were related with the cure reaction and were not completely elucidated, which justifies the relative abundance of literature on all aspects of the cure and production of these resins.

Unsaturated polyesters become insoluble and infusible by crosslinking with a monomer, usually styrene (ST). The commercial resins contain about 30–40% by mass of styrene. The miscibility of the resin and the styrene depends on the resin composition.

The morphological state of a polymeric material may be highly affected by the interaction between the polymerisation

kinetics and the thermodynamics and kinetics of phase separation. This is especially relevant to the preparation of high-impact polystyrene from a styrene solution of an unsaturated rubber. An unsaturated polyester resin is analogous except that it consists of a relatively low-molecular-weight polymer dissolved in styrene. In this case, a distinct phase has not been observed but the development of a microstructure consisting of regions with a wide variation in the crosslinking density is generally becoming accepted [2].

However, some researchers accept that the copolymerisation of unsaturated polyester with styrene, UP/ST, results in the formation of a heterogeneous structure through strong intramolecular reactions and phase separation [3]. Zheng et al. studied the effects of the thermal treatment on the phase separation of UP/ST observing that samples cured at room temperature exhibit phase separation and that the final morphology can be modified by thermal treatment [4]. Abdel-Azim et al. evaluated the effect of the resin microstructure on its cure behaviour concluding that the maximum cure temperature is related to the molecular weight of the glycol segment incorporated in the resin [5]. Urban et al. demonstrated the homopolymerisation of styrene during the cure reaction of a UP/ST system by FTIR spectroscopy [6].

The influence of the molecular weight and the chain termination groups has been investigated. In general, an increase in molecular weight decreases the miscibility. Chain termination of UP resins consists in hydroxyl and

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Table 1
Characteristics of the styrene free unsaturated polyester resin

Composition ^a	Orthophthalic acid	57 wt.%
	Propylene glycol	12 wt.%
	Fumaric acid	23 wt.%
	Diethylene glycol	8 wt.%
Molecular weight ^b	M_n	3560 (mol g ⁻¹)
	M_w/M_n	1.3
Glass transition temperature ^c	T_g	22°C

^a Determined by ¹H NMR spectroscopy.

^b Determined by GPC.

^c Determined by DSC.

carboxyl groups whose polarity has an unfavourable effect on the UP/ST miscibility. Hydroxyl and carboxyl groups are always present. Consequently, the resin miscibility can only be changed by controlling the copolymer composition [7].

The effects of comonomer composition on the cure kinetics of unsaturated polyester resins at 70–90°C were studied by differential scanning calorimetry (DSC) and infrared spectroscopy over the whole conversion range by Huang and Chen [8]. Kinetic models have been reported for the cure of UP/ST and mechanisms have been proposed for the microstructure formation [9]. Ramis and Salla observed by gel permeation chromatography (GPC) that a fraction of the polyester and styrene, as well as low molecular weight oligomers of styrene and branch styrene on polyester molecules do not participate in the polymer network. From the GPC data, resin and styrene contents, and the total conversion can be determined. For all the resins studied, a dependence of the maximum conversion on the styrene percentage was observed. This maximum varies according to the type of resin [10].

Solubility studies of unsaturated polyesters in styrene have been widely reported. The influence of the styrene monomer concentration on the formation and on the

microstructure of the matrix is stronger than that of the different components of unsaturated polyester (acids, glycol, etc.) [11].

Cook and Delatycki showed the variation of the T_g with the styrene concentration in networks based on fumaric acid/propylene glycol/phthalic anhydride, using the method of freely oscillating torsion pendulum. The basic shape of the tan δ versus temperature curves is similar, exhibiting a maximum T_g around 40 wt.% styrene [12].

Eisenberg et al. [13] showed that the T_g of the cured resin shifts to a higher temperature with increasing styrene concentration approaching to the pure polystyrene value. However, there is no conclusive work on the phase behaviour and the dependence of T_g with styrene concentration.

The aim of the present study is to evaluate the influence of the styrene content on the miscibility, thermal and mechanical properties of an unsaturated polyester resin. Thermogravimetric, dynamic mechanical analyses and flexural tests were carried out to investigate these properties.

2. Experimental

The commercial unsaturated polyester resin containing 38 wt.% of styrene, RESAPOL 10-203, was used to prepare mixtures with different styrene concentrations by evaporation of the monomer under vacuum and by addition of monomer. Samples with 6, 7, 13, 18, 24, 38 and 58 wt.% of styrene were studied. The composition of the styrene-free unsaturated resin was determined by ¹H NMR spectroscopy, the glass transition temperature (T_g) by DSC and the molecular weight by GPC.

UP resin with different contents of styrene were cured in moulds (2 mm diameter cylinder) at room temperature for 24 h and post-cured at 60°C for 48 h. After this, the specimens were placed in a vacuum oven at 70°C for 2 h. In all cases, the resin was cured using 1 phr of methyl ethyl ketone peroxide solution as initiator and a 0.5 phr of cobalt octoate solution as catalyst.

Dynamic mechanical analysis was performed with a DMA 938 from TA Instruments. Specimens of 15 mm × 2 mm dimensions were submitted to sinusoidal deformation with 0.2 mm amplitude at a frequency of 1 Hz in the temperature range of –120–200°C. The heating rate was 5°C min⁻¹.

The T_g of styrene-free resin was determined with a DSC 2910 differential scanning calorimeter from TA Instruments, in the temperature range of –80–150°C in a nitrogen atmosphere, at a heating rate of 20°C min⁻¹.

The thermogravimetric analysis were performed using a Du Pont 951 thermogravimetric analyser in the temperature range of 25–1000°C, at a heating rate of 10°C min⁻¹ in argon atmosphere.

Flexural tests were carried out for specimens of 6, 24, 38 and 58 wt.% of styrene content in a MTS 810 testing machine according to ASTM D-790 procedures.

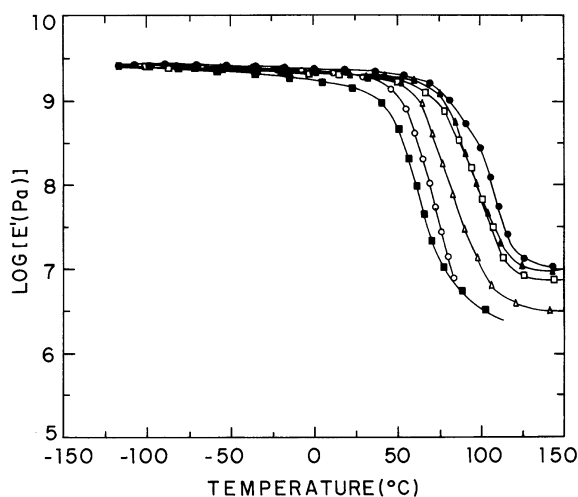


Fig. 1. Storage modulus E' as a function of temperature for UP resin with 6 (■), 7 (○), 18 (△), 24 (□), 38 (▲), and 58 wt.% of styrene (●).

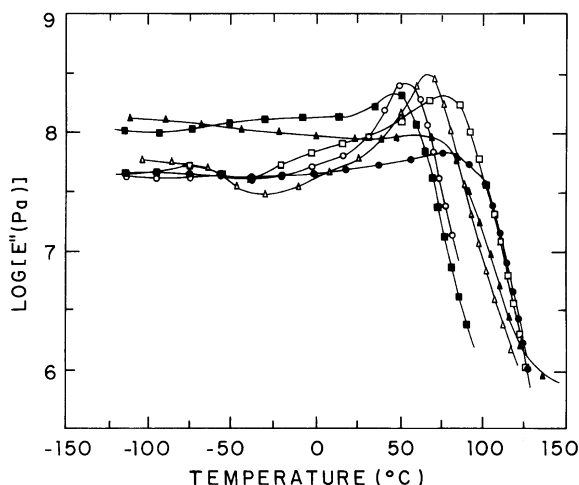


Fig. 2. Loss modulus E'' as a function of temperature for UP resin with 6 (■), 7 (○), 18 (△), 24 (□), 38 (▲), and 58 wt.% of styrene (●).

3. Results

The styrene-free UP resin characteristics are collected in Table 1.

The dynamic mechanical results expressed as storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) as a function of temperature and resin compositions are shown in Figs. 1–3, respectively.

The $\log E''$ versus T curves show peaks related to the transitions. The peaks at higher temperature are attributed to the glass transition of cured resin and the other peaks to the secondary relaxations. The T_g shifts to higher temperature with increasing styrene content, due to the introduction of the stiff polystyrene segments in the UP chain.

Structural relaxation in the glass transition (α -relaxation) region results from molecular segments of the polymer backbone chain. In contrast, the secondary (β) relaxations,

which occur at lower temperatures, are generally believed to involve much more localised molecular motions. These relaxations show characteristic behaviour which are quite distinct from that of the main glass transition and confer many interesting mechanical properties [14].

Melot et al. [15] combined dynamic mechanical spectroscopy with high-resolution solid-state ^{13}C NMR to characterise the molecular motions responsible for γ and β secondary relaxations in unsaturated polyester networks. The γ transition, which manifests itself at about -100°C at 1 Hz, may be related to some motion of the phenyl groups in the styrene sequences. The β transition originates mainly from local modes of polyester units remote from the styrene crosslinks. Cook and Delatycky reinforce this assumption [16–18]. The variation of the β peak area as a function of the crosslink content can be explained on the basis of the variation of the density of these mobile units. In that sense the β transition may be assigned to mobility of network defects.

The increase of styrene content in UP resins results in the broadening of the glass transition, which is associated with the development of the microenvironments with different compositions and crosslinking density. These microenvironments are formed during the resin cure as a consequence of the drop in the miscibility with the growth of the molecular chains. The network structure also contributes to the phase segregation because its swelling capacity decreases with the increase of the crosslinking density resulting in an exclusion of monomers, oligomers and polymers from it. The sample with 18 wt.% of styrene shows a shoulder at approximately 50°C and a maximum at 66°C , suggesting that the UP resin consists of at least two phases, a UP cross-linked phase and a polystyrene rich phase. Samples with 38 and 58% of styrene show a shoulder at 100°C , characteristic of a higher phase separation. In Table 2 are listed the glass transition temperature for UP resins containing different styrene concentrations. The glass transition temperature was assumed as the temperature corresponding to the maximum and to the shoulders of the peaks in the $\log E''$ versus T curves.

The phase behaviour as a function of the styrene content in UP resins can also be observed in the $\log \tan \delta$ versus T curves (Fig. 3), where the shoulders are more evident. The maximum of the $\log \tan \delta$ versus T curves exhibit an evident change to higher temperatures with the increase of the styrene content.

In Fig. 4 the dependence of T_g on the styrene concentration is shown. The increase of styrene concentration shifts the glass transition of different phases to higher temperatures. This means all phases become richer in polystyrene, despite the rising immiscibility. A possible explanation for these results is the competition between two antagonist effects. The increase of styrene concentration causes a drop in the crosslinking density, because the size of molecular segments between the crosslinking points is probably greater. As a consequence, the network has a greater

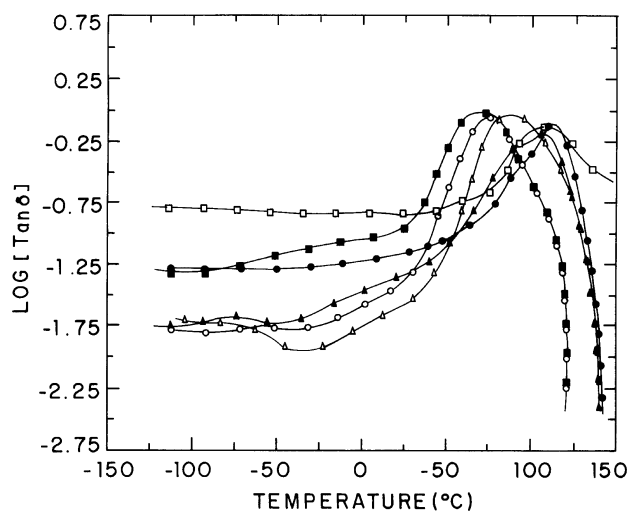


Fig. 3. Loss tangent ($\tan \delta$) as a function of temperature for UP resin with 6 (■), 7 (○), 18 (△), 24 (□), 38 (▲), and 58 wt.% of styrene (●).

Table 2
Glass transition temperature and maximum degradation temperature rates

Styrene (wt.%)	T_g (°C) ^a	TMD (°C) ^b
58	74; 100 (s) ^c	370
38	63; 100 (s) ^c	387
24	55(s) ^c ; 74	373
18	50 (s) ^c ; 66	369
7	54	367
6	47	350

^a Determined from E'' versus T curves.

^b Determined from the derivative of thermogravimetric curves.

^c (s): shoulder.

capacity to swell with styrene and its polymer. Conversely, a higher styrene concentration leads to higher concentrations and higher molecular weight of free polystyrene chains and therefore to immiscibility. The balance of these factors determines the phase behaviour of the UP resins.

In the $\log E'$ versus T curves the evolution of phase segregation with an increase of styrene concentration can also be observed. The modulus values at higher temperatures than T_g increase with the styrene content.

The thermogravimetric curves (Fig. 5) show only a single degradation process under argon atmosphere for all samples. In Table 2 the temperatures corresponding to the maximum of the derivative curve (dm/dT) are presented, i.e. the temperature corresponding to the maximum rate degradation (TMD). The TMD increases with the styrene content

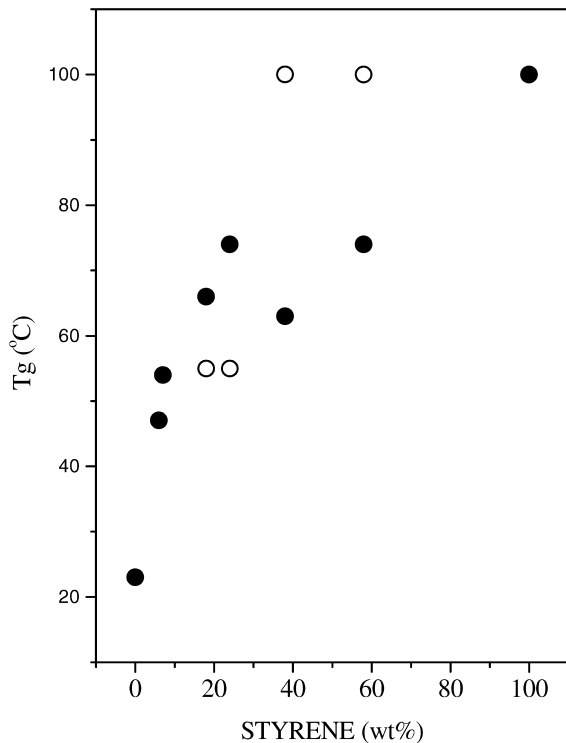


Fig. 4. Glass transition temperature of the UP resin as a function of the styrene content. (●) principal peak; (○) shoulder.

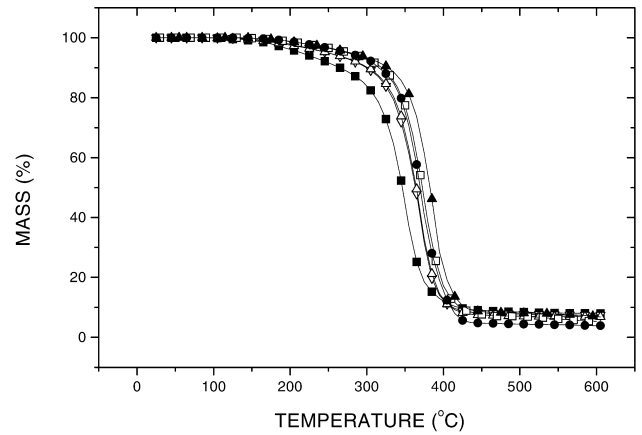


Fig. 5. Thermogravimetric curves of the resin UP with 6 (■), 13 (▽), 18 (△), 24 (□), 38 (▲), and 58 wt.% of styrene (●).

for specimens until 38 wt.% and after this composition, the TMD decreases. This behaviour is associated with the cross-linking density and the phase segregation in the different styrene content specimens. The highly cross-linked nature of the three-dimensional polymer network enhances the thermal resistance of the resin at high temperatures. The cross-linked resins, irrespective of the composition of polyester polymer, undergo spontaneous decomposition near 300°C, even in the absence of oxygen. This is a

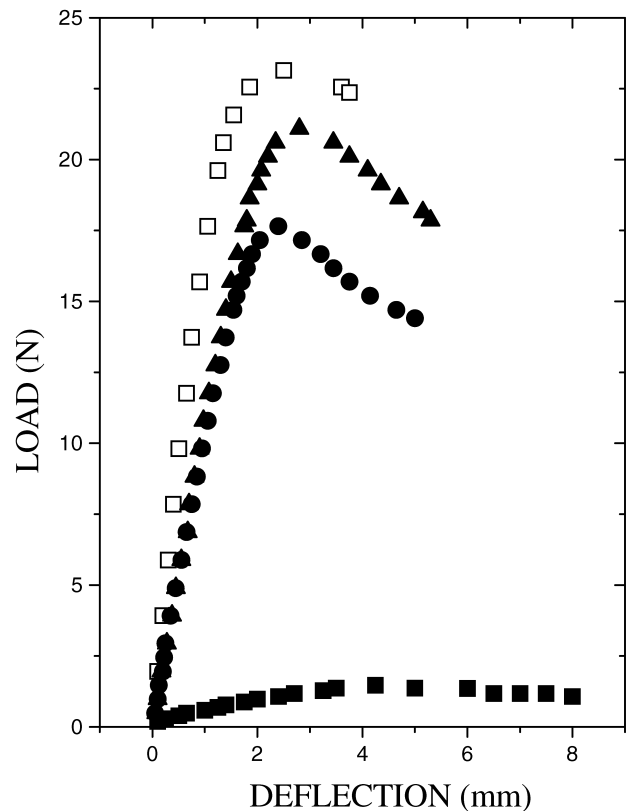


Fig. 6. Flexural behaviour of the UP resin with 6 (■), 24 (□), 38 (▲), and 58 wt.% of styrene (●).

characteristic of all vinyl copolymers which are degraded into monomeric units at high temperatures, unlike nonvinyl crosslinked thermosets, such as the phenolic and epoxy resins, which tend to carbonise [11].

Fig. 6 shows the mechanical behaviour of different UP resin compositions obtained by flexural tests. The 6 wt.% styrene content specimen does not fail and shows a ductile characteristic. The UP resins become stiffer, increasing the styrene content, and the maximum of stress is achieved by the resin with 24 wt.% of styrene. The mechanical performance must reflect the phase behaviour of the mixture.

4. Conclusions

The UP resins properties are very dependent on styrene content. The phase segregation is governed by the crosslink density and by the immiscibility of UP and polystyrene, which depend strongly on the styrene content in the resin. The thermal stability and the mechanical properties of the UP resin reflect the extension of phase segregation.

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