ELSEVIER

S0032-3861(96)00238-8

Polymer Vol. 37 No. 18, pp. 4025–4032, 1996

0032-3861/96/\$15.00+0.00

A polymer network of unsaturated polyester and bismaleimide resins: 1. Kinetics, mechanism and molecular structure

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(Received 22 December 1994)

An unsaturated polyester resin has been modified by adding a thermosetting bismaleimide as a second co-reactive monomer. The bismaleimide resin was readily dissolved in the uncured polyester matrix up to a concentration of about 20 wt%. Fourier transform infra-red (*FT*i.r.) spectroscopy was employed to monitor the cure kinetics of this complex system. The available spectroscopic evidence indicated that both the mechanism and the kinetics of the crosslinking process were strongly affected by the presence of the bismaleimide in the system. The molecular structure of this intercrosslinked network is discussed. The dynamic mechanical behaviour of a typical blend composition was found to be in agreement with the proposed molecular structure. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyester; bismaleimide resin; *FT*i.r. spectroscopy)

INTRODUCTION

Unsaturated polyester (UP) resins are among the most widely used thermosetting materials since they are relatively inexpensive and offer advantages such as being light in weight and possessing reasonably good mechanical properties[1]. They are largely employed as matrices for composites, e.g. in automotive applications. However, as generally found for thermosetting materials, these matrices are very brittle and susceptible to catastrophic failure. Moreover, the shrinkage of the polyester resin during crosslinking with the reactive styrene (S) solvent leads to warpage and cracking. Usually these problems can be solved by blending the UP resins with suitable polymeric or non-polymeric additives. For example, the fracture properties of these materials can be improved by blending with reactive liquid rubbers[2–4], while thermoplastic additives such as poly(methyl methacrylate) or poly(vinyl acetate) are used to achieve 'low profile' or 'low shrinkage' behaviour[5,6]. A further deficiency, which is due to the molecular structure developed upon curing, is an extremely broad glass transition region with a main relaxation process starting just above room temperature and extending for over 100°C[7,8]. Thus, the mechanical properties and particularly the elastic modulus, rapidly deteriorate above room temperature. A recently developed approach to overcome this limitation is the modification of UP resins by a co-reactive second component. In this present contribution the system consisting of a UP and a thermosetting bismaleimide resin (BMI) is investigated. The choice of the bismaleimide as the reactive second component is due to its very high rigidity and glass transition temperature which would give, in principle, an increase in the stiffness of the UP matrix over a wide range of temperatures. In the first part of this present work, Fourier transform infra-red (*FT*i.r.) spectroscopy is used to investigate the effect of the BMI on the mechanism and kinetics of the curing process. The complex molecular structure which is realized upon curing is also discussed on the basis of the available spectroscopic evidence.

In the second part of the work, the yield behaviour of this material is investigated over a wide range of temperatures and strain rates. The results are analysed in terms of the molecular theories of yielding which were originally developed for glassy thermoplastic polymers.

EXPERIMENTAL

Materials

The UP resin used in this work was an uncured, unsaturated polyester which was kindly supplied by Alusuisse Italia SpA. The resin was available either as a solution containing 35% of styrene, or in the form of the pure prepolymer. The acid number of the prepolymer, defined as the number of mg of KOH required for the titration of 1 g of prepolymer was 19.2. The OH number, obtained by titration of the excess acetic anhidryde needed to fully esterify the hydroxyl groups, was 53.4. This corresponded to 0.34 mmol of COOH groups and 0.95 mmol of OH groups per g of resin. In the UP formulation, 0.1 wt% of hydroquinone was employed as an inhibitor to prevent premature curing. Benzoyl

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Table 1 Compositions of the UP/BMI blends used in this work

Code	UP (wt%)	BMI (wt%)
B0	100	
B5	95	5
B10	90	10
B15	85	15
B18	82	18

peroxide (BP) was used as the radical initiator and was recrystallized twice from absolute ethanol before use. The bismaleimide resin (BMI) used was 1,1′-(methylenedi-4,1-phenylene)bismaleimide, from Aldrich.

Preparation procedure and curing conditions

A typical blend (B10 composition) was prepared as follows: 7.0 g of BMI were dissolved in 63 g of the UP resin at 100°C. The temperature was lowered to 25°C and 1.9 g of the radical initiator, BP, were added with vigorous mechanical stirring. The reactive mixture was degassed for 5 min under vacuum and then poured in to a glass mould which was immediately immersed in a thermostatic bath kept at 55°C. The cure was carried out at this temperature for 2 h and then for an additional 12 h at 70°C. A postcuring step was performed in an oven at 100°C for 2 h. The same curing protocol was applied to the neat UP resin, which was used as a reference material throughout this work. The investigated blend compositions, along with their code numbers are presented in *Table 1*.

Techniques

*FT*i.r. spectra were collected on thin films of the uncured blends, which were obtained by sandwiching a drop of the reactive mixture between two KBr windows. The spectra were obtained at a resolution of 2 cm^{-1} using a Nicolet 5DXB spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a germanium/KBr beam splitter. The isothermal kinetic measurements were performed in a SPECAC temperature cell directly mounted in the spectrometer. This unit was driven by an Eurotherm 071 temperature controller to an accuracy of ±1°C.

RESULT AND DISCUSSION

Kinetic analysis of the curing process

In a UP/BMI blend three different reactive unsaturations are present, i.e. fumarate double bonds on the polyester prepolymer, styrene double bonds and maleimide unsaturations. All of these have to be individually monitored in order to completely characterize the kinetic behaviour of the system. To this end, we have compared the *FT*i.r. spectra of the polyester prepolymer (*Figure 1A*), the uncured UP resin (polyester prepolymer plus styrene) (*Figure 1B*) and that of a UP/BMI (85/15 (wt/wt)) blend (*Figure 1C*).

The fumarate double bonds exhibit two sufficiently well-resolved peaks at 1645 cm^{-1} (C=C stretching) and at 982 cm^{-1} (*trans*- –HC=CH–wagging). However, when styrene is present, a further absorption is detected at 1630 cm^{-1} (styrene C=C stretching) which is only partially resolved from the fumarate absorption at 1645 cm^{-1}. It should be noted that this doublet is relatively weak. The styrene unsaturation presents two characteristic modes in the =C–H wagging region. One is found at 992 cm^{-1} and is due to a *trans*- –HC=CH– wagging, while the other, at 912 cm^{-1}, arises from a vinyl =CH$_2$ wagging[9,10].

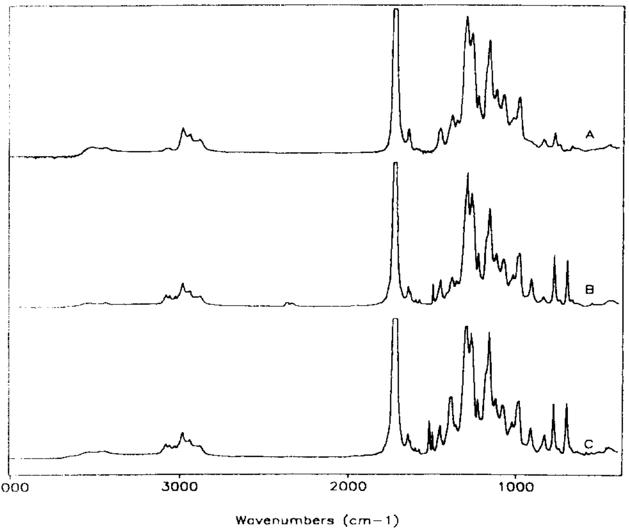


Figure 1 *FT*i.r. transmission spectra in the frequency range 4000–450 cm^{-1} of: (A) polyester prepolymer; (B) UP resin (polyester/styrene mixture); (C) UP/BMI(85/15(wt/wt)) blend

Both of these peaks have medium intensity but the former is completely overlapped with the already mentioned fumarate absorption at 982 cm^{-1}, while the latter is completely free from any interfering absorption. Several methods have been proposed in the literature to resolve the two-component profile at 992 and 982 cm^{-1}, so as to provide, based on a series of simplifying assumptions, quantitative kinetic information[11,12]. However, due to the high degree of overlapping and particularly to the difficulty in defining a reasonable baseline, we preferred to turn our attention to the better-resolved region between 1700 and 1600 cm^{-1}.

Our experimental data were analysed by the following two-step procedure. First, a pseudo-baseline was found in the region of interest by using a fourth-order polynomial regression (see *Figure 2A*). After subtraction of this baseline, the resulting spectral profile was separated into the individual components by applying an iterative curve-fitting algorithm based on a least-squares refinement procedure[13]. To insure the uniqueness of the results, the peak shape (Gaussian), the number and the position of the peaks (as evaluated by second-derivative analysis) and the baseline were kept fixed, while the program was allowed to calculate the height and the full-width-at-half-height (FWHH) of the components. Typical results of such an analysis are presented in *Figure 2B*; note the presence of two unidentified low-intensity absorptions along the wings of the two main components. The relative conversion of polyester and S unsaturations, α, defined as:

$$\alpha = \frac{C_0 - C_t}{C_0} = 1 - \frac{C_t}{C_0} \qquad (1)$$

and, for the Beer–Lambert law:

$$\alpha = 1 - \frac{A_t}{A_0} \qquad (2)$$

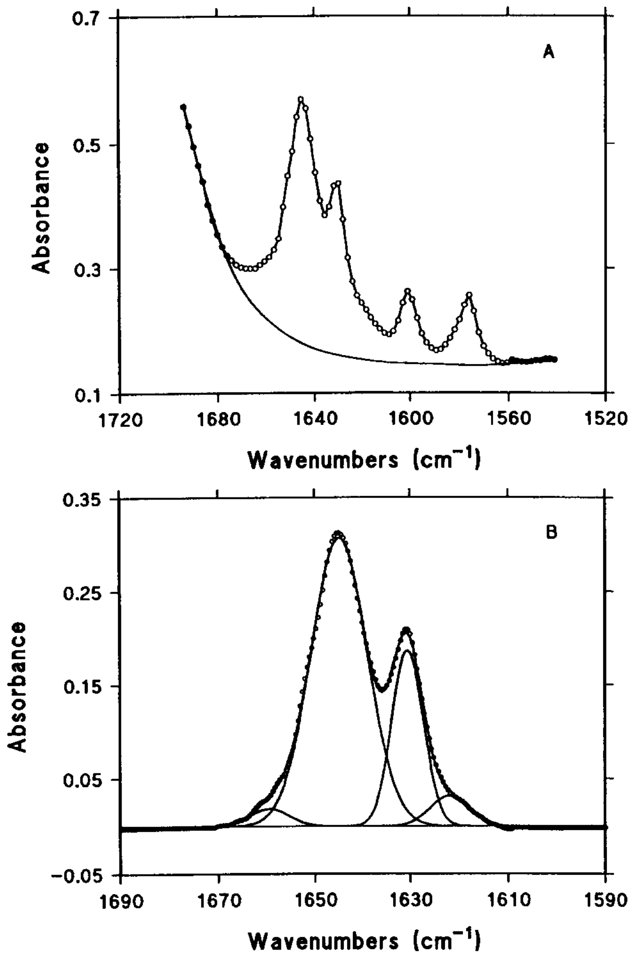


Figure 2 Curve-fitting analysis in the 1700–1600 cm^{-1} region: (A) experimental spectral profile with the evaluated pseudo-baseline, where the solid circles represent the data points used to calculate the fourth-order polynomial fit; (B) the four Gaussian components obtained by a best-fit of the experimental data points

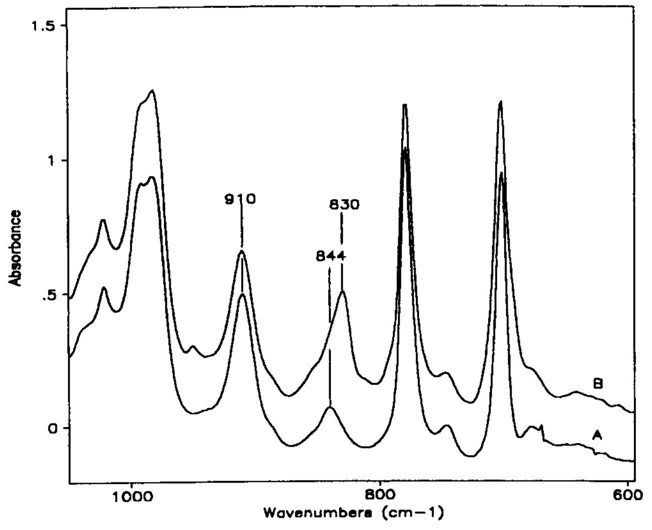


Figure 3 *FT*i.r. spectra in the frequency range 1000–650 cm^{-1} for the neat UP resin (A) and the B15 blend (B)

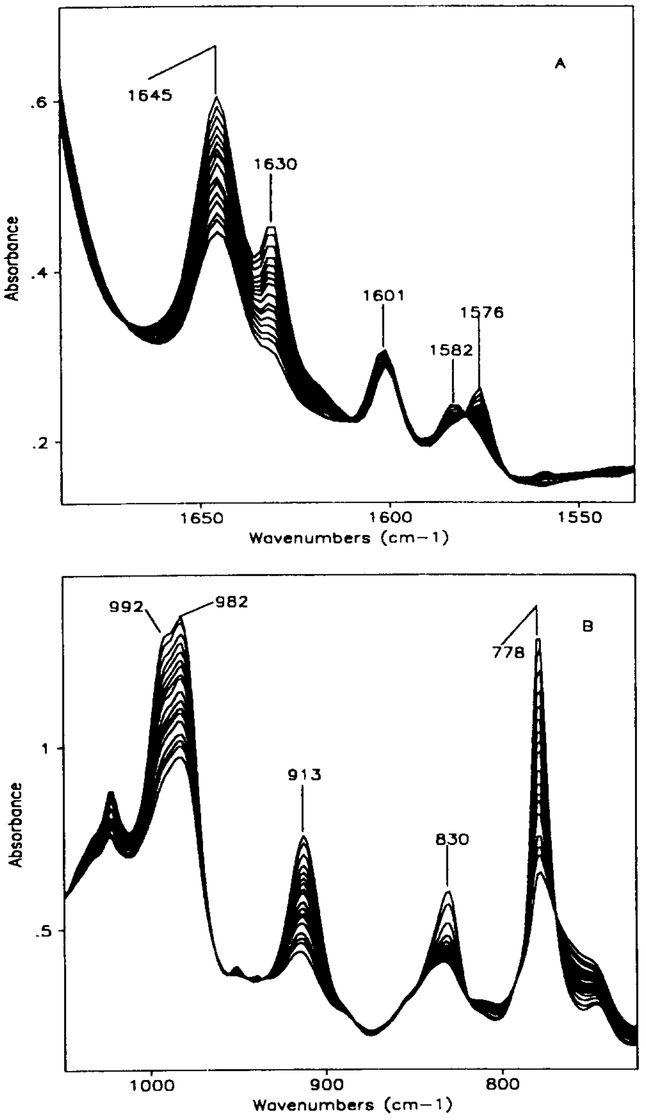


Figure 4 Real-time spectroscopic monitoring of the curing reaction. The spectra were collected at different reaction times at 55°C for the B15 UP/BMI blend. The two figures show the analytical frequency ranges: (A) 1700–1500; (B) 1100–600 cm^{-1}

can now be followed as a function of the reaction time.

In particular, α_S can be evaluated from both the component at 1630 cm^{-1} and the peak at 912 cm^{-1}. As already noted, the 912 cm^{-1} peak is free from any interfering absorption and yields 'true' α_S values, while the α_S values from the 1630 cm^{-1} component can be used to cross-check the correctness of the curve-fitting analysis; coincident results were obtained over the whole time range.

Following the BMI double bonds' conversion was less straightforward: the maleimides present a typical absorption at 3100 cm^{-1}, which is generally employed to monitor the progress of the curing reaction[14,15]. Unfortunately, this peak has a relatively low intensity and, due to the low BMI content in the blend, goes completely undetected. However, a peak at ca. 830 cm^{-1} has been reported for several maleimides, and this has been assigned to an out-of-plane blending of the =C–H group[16]. This absorption is clearly detected in the spectrum of the B15 blend, superimposed on a rather broad absorption of the polyester at 844 cm^{-1} (compare the spectra shown in *Figure 3*). The 830 cm^{-1} peak gradually and continuously decreases in intensity while the blend is being cured, thus confirming the assignment and indicating consumption of the BMI unsaturations

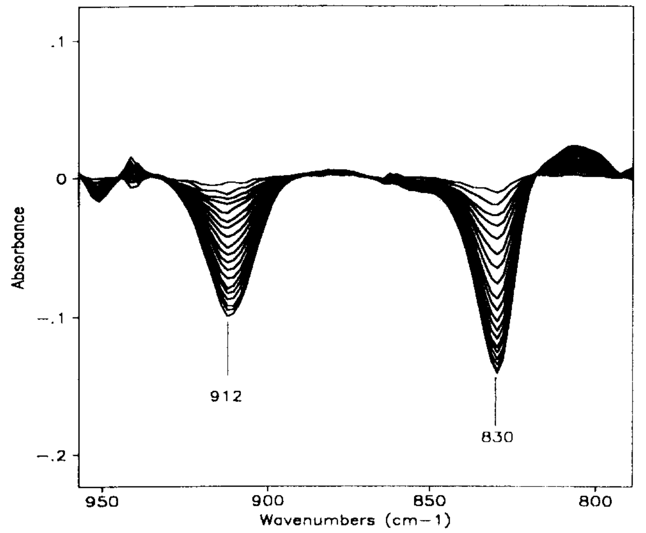


Figure 5 Difference spectra collected in the early stages of the curing reaction for the B15 blend in the frequency range 950–800 cm^{-1} (see text for details)

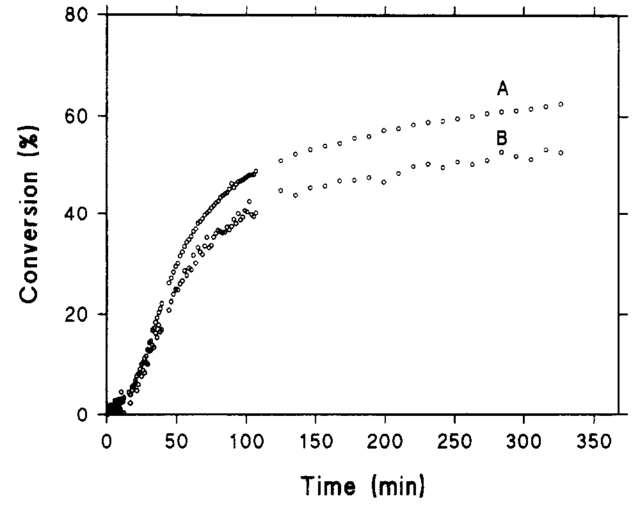


Figure 6 The conversion of styrene double bonds (curve A) and of the polyester unsaturations (curve B) as a function of the reaction time for the neat UP resin from isothermal measurements carried out at 70°C

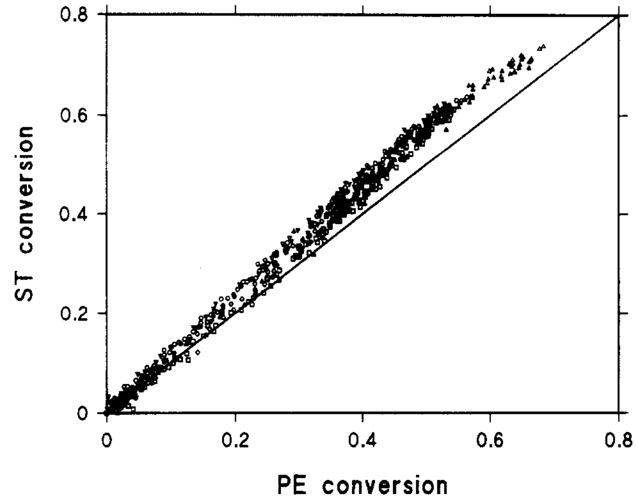


Figure 7 The conversion of styrene double bonds *versus* the conversion of polyester double bonds in the neat UP resin at reaction temperature of 63 (○), 70 (▽), 75 (○), 80 (□) and 90°C (△)

during curing (see *Figure 4B*). This peak can be suitably used to monitor the BMI conversion provided that the interference of the 844 cm^{-1} background absorption is eliminated. To this end, spectral subtraction was employed[17], which is based on the following relationship:

$$A_s = A_t - SF\,A_0 \qquad (3)$$

where the subscripts, s, t, and 0 denote the absorbance of the subtraction spectrum, of the spectrum collected at time *t*, and of the spectrum collected at zero time, respectively. The subtraction factor, *SF*, allows us to compensate for differences in thickness between the spectra collected at zero time and at time *t*. Its value is obtained by zeroing an internal thickness band, which, in the present case is the 1601 cm^{-1} peak. It has been found that the change in thickness which occurs during the process is very limited, so that the *SF* is always close to one. The relevant advantage in using spectral subtraction in kinetic studies relies on the fact that peaks not affected during the experiment (the peak at 844 cm^{-1} in this present case) are compensated and thus completely removed in the subtraction spectrum. It is clear that positive absorbances from the zero baseline reflect structures that are formed during the process, while negative absorbances reflect structures that are lost. The subtraction spectra reported in *Figure 5* in the frequency range 950–800 cm^{-1} show the gradual development of the completely resolved BMI peak at 830 cm^{-1}, for which a linear and consistent baseline can be identified. These absorbance values can be directly used to evaluate the BMI conversion as a function of the reaction time.

Typical conversion *versus* time curves of the S and polyester unsaturations in the neat UP resin are reported in *Figure 6*. The isothermal measurements reported in this figure have been carried out at 70°C, a typical curing temperature for a benzoyl-peroxide-initiated process. It is observed that the two conversion curves are coincident in the early stages of the process, while starting from ca. 40 min the styrene conversion gradually exceeds the polyester conversion. For the neat UP resin the above kinetic analysis has been performed over a wide range of temperatures and will be discussed in detail in a separate publication. However, for the whole temperature range investigated in the latter work, a kinetic behaviour analogous to that found at 70°C was observed.

Another way of plotting the kinetic data for this system is a conversion–conversion plot, as shown in *Figure 7*. In this representation, at 45° line characterizes the near-azeotropic behaviour of the system in which styrene and polyester unsaturations are incorporated into the network in the same ratio as the initial composition of the reaction mixture, regardless of the conversion. In *Figure 7* the kinetic data relative to the various investigated temperatures are collectively reported. It is found that all of the experimental data fall, within experimental uncertainty, on a common master-line which is close to the theoretical near-azeotropic copolymerization line. Only at higher polyester conversions (>0.5) do we observe a 'bending-up' of the experimental curve, thus indicating that the styrene conversion substantially exceeds that of the polyester.

This behaviour can be interpreted by assuming, for the whole range of temperatures investigated for most of the process where the near-azeotropic copolymerization

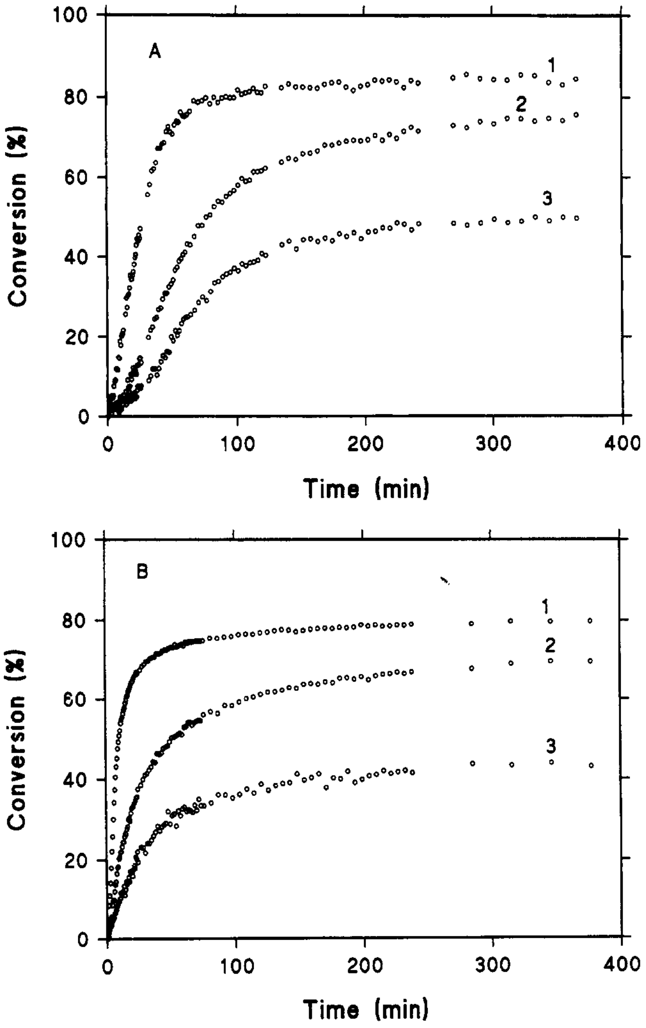


Figure 8 Conversion of the various reactive species at 55°C as a function of time in the B10 (A) and B15 (B) blends; in both cases curve 1 refers to the BMI double bonds, while curves 2 and 3 refer to the styrene and polyester unsaturations, respectively

behaviour dominates, that the crosslinking density of the system is not sufficient to influence the propagation mechanism of the styrene and polyester molecules. However, towards the end of the reaction the crosslinking density increases substantially, thus lowering appreciably the mobility of the vinyl groups in the large polyester molecules, while the styrene monomer is less affected. Consequently, styrene self-propagation is favoured, causing a higher conversion of styrene with respect to the polyester[12].

Attempts to follow the kinetic behaviour of the UP/BMI blends in the above temperature range were unsuccessful because the process was too fast, with the conversion of the reactants already being high when the spectrum at zero time was collected. To circumvent this problem the kinetic analysis was performed at 55°C for both a B10 and a B15 blend. The results are reported in *Figures 8A* and *8B*, respectively.

It is observed in both of the blends that the BMI conversion is fast and almost quantitative. A conversion of ca. 80% is reached in 100 and in 50 min for the B10 and B15 blends, respectively. In addition, both the styrene and polyester unsaturations are involved in the crosslinking process, but with lower initial rates and lower values of conversion at the end of the process.

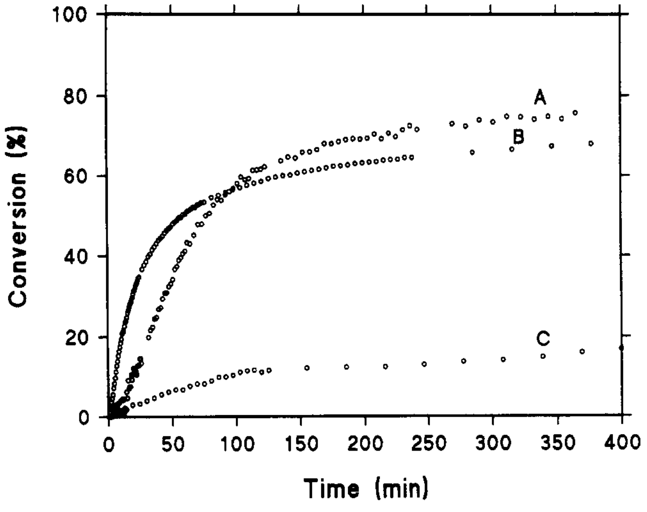


Figure 9 Styrene double-bond conversion at 55°C as a function of the reaction time for the B10 blend (curve A), the B15 blend (curve B), and the neat UP resin (curve C)

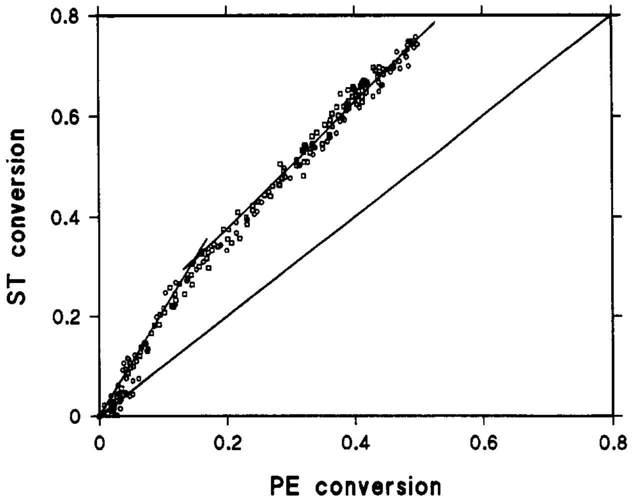


Figure 10 The conversion of styrene double bonds *versus* the conversion of polyester double bonds at 55°C for the B10 blend (○) and B15 (□) blends

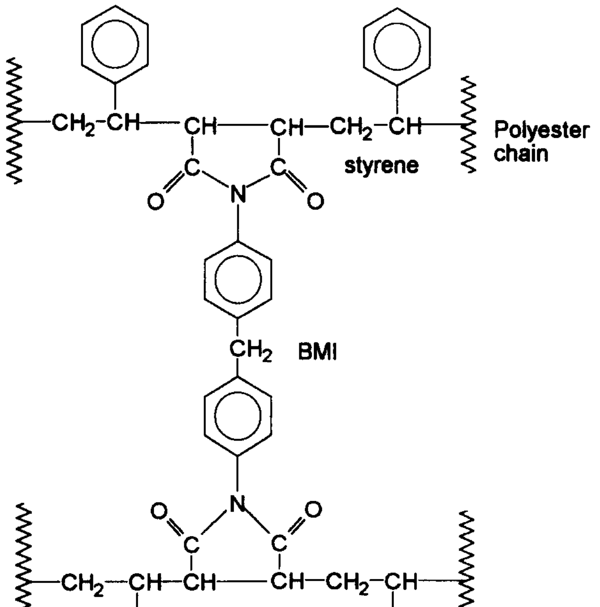
Figure 9 compares the styrene conversion at 55°C for the B10 blend (curve A), the B15 blend (curve B) and for the neat UP resin (curve C). Such a comparison provides evidence that at this temperature the neat resin reacts very slowly and to a very limited extent, while the process is substantially accelerated in the presence of the BMI. Moreover, increasing the BMI content in the blend considerably increases the rate of the individual reactions involved in the complex crosslinking process. The above results indicate that BMI radicals are formed very easily in the system and are highly reactive. They may interact with the other unsaturations present in the system, thus causing the reactive mixture to undergo crosslinking even if the conditions are not suitable for polymerization to take place in the neat UP resin.

Further details concerning the role played by the BMI in the crosslinking process can be gained by plotting the kinetic data on a S–Pe conversion–conversion diagram (see *Figure 10*). If the BMI does not interact chemically with the styrene and polyester unsaturations, a linear behaviour close to the 45°C line would be found, in analogy to that which occurs in the neat UP resin.

Figure 10 provides clear evidence that the two data sets relative to the B10 and B15 blends fall on a common master-curve which strongly deviates from the 45°C line. In particular, all of the data points are located well above the reference line and the whole master-curve can be suitably approximated by two linear portions which have considerably different slopes. By comparing *Figure 10* with *Figure 8* it appears that the change in slope occurs at a point where the BMI conversion is almost complete. Thus two different regimes can be distinguished: the first where the BMI actively participates in the crosslinking process, and the second where only the styrene and polyester unsaturations react. In the first regime, the slope is twice that of the reference line, thus indicating a much higher conversion of styrene with respect to the polyester. This suggests that BMI preferentially reacts with the styrene unsaturations, in agreement with literature data[18] which indicate that, in solution, BMI and styrene copolymerize through an alternating mechanism. On the other hand, styrene interacts with both BMI and the polyester unsaturations, thus resulting in a network structure. As the BMI is fully consumed, the copolymerization process proceeds with a mechanism which is analogous to that observed for the neat UP resin. In fact, the slope of the master-curve in the second regime of *Figure 10* is very close to the value found for the UP resin over a wide temperature range.

In the light of the above findings it may be reasonably assumed that the molecular structure realized during the polymerization of this system is as follows: the polyester chains are linked either intramolecularly or intermolecularly by short sequences of a BMI/styrene alternating copolymer which is formed in the early stages of the process, and by styrene sequences which are formed at a later stage when all of the BMI has been consumed.

The molecular structure of a typical BMI/styrene bridge can be represented as follows:



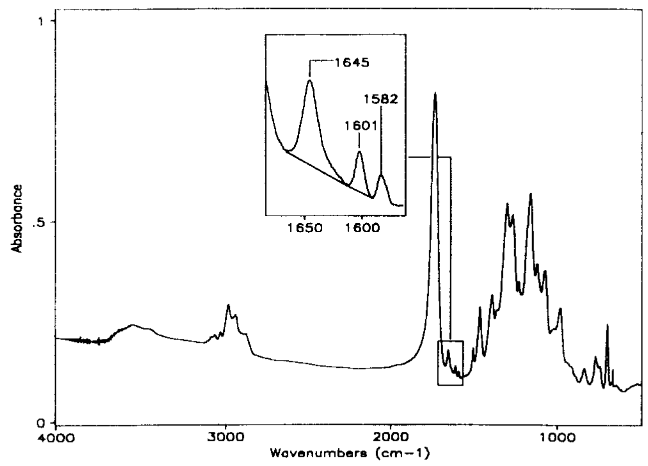


Figure 11 *FT*i.r. powder spectrum of the neat UP resin in the frequency range 4000–400 cm^{-1} after the curing protocol at 70°C; the inset indicates the analytical frequency range

The presence of the BMI monomer within this network structure has two effects:

1. It increases the crosslinking density, since the BMI is tetrafunctional, while styrene is bifunctional. In fact, as can be seen from the above molecular structure, a single BMI unit can link four polyester chains, while a styrene unit can link only two.
2. It increases the overall rigidity of the network, since the BMI unit is considerably stiffer than the styrene unit.

Both of these effects influence the dynamic mechanical response as well as the low-strain mechanical properties of the blend system, as will be shown in the following sections.

Spectroscopic analysis of the cured samples

In order to carry out a mechanical characterization of this blend system, sheets of 4 mm thickness were cured according to a protocol developed in the light of the above kinetic findings (see Experimental section). From these sheets, fine powders were obtained and these were then analysed by *FT*i.r. spectroscopy using the KBr pellet technique. *Figure 11* shows the *FT*i.r. powder spectrum of the neat UP resin after the curing step at 70°C in the frequency range 4000–400 cm^{-1}. It is noted that the peaks characteristic of styrene double bonds are absent, while the double-bond stretching of residual fumarate is detected at 1645 cm^{-1}, thus indicating incomplete polyester conversion. The amount of residual polyester unsaturations can be estimated from the area of the 1645 cm^{-1} peak, which is normalized for thickness by using the 1601 cm^{-1} reference band (see inset of *Figure 11*).

The residual fumarate content, R, can be expressed as follows:

$$R = \frac{\bar{A}_{1645}}{\bar{A}^{0}_{1645}} 100 \qquad (4)$$

where $\bar{A}_{1645}$ is A_{1645}/A_{1601} in the sample and $\bar{A}^{0}_{1645}$ is the same absorbance ratio calculated for a thin film of the reactive mixture prior to the curing process.

In *Figure 12* the R parameter is reported as a function of the BMI content in the blend for samples cured at

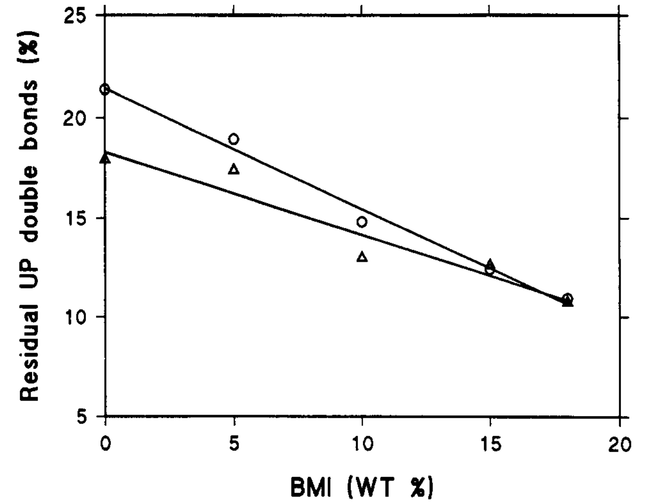


Figure 12 The residual fumarate content, *R*, as a function of the BMI content in the blend: (○) samples cured at 70°C; (△) samples postcured at 100°C

70°C (curve A) and for those postcured at 100°C (curve B). The neat UP resin shows a residual unsaturation content exceeding 20%, which gradually decreases as the BMI content in the blend is enhanced. The postcuring step decreases the residual unsaturations of the matrix by ca. 5%, while a less pronounced effect is found for all of the investigated blend compositions. Moreover, it was found that the styrene and BMI conversions were both already complete after the 70°C treatment at all compositions. These results provide evidence that a further effect of the BMI is to facilitate polyester–polyester interactions by altering the system microstructure. It is likely, during the early stages of the curing process (55°C), that dense microgel structures are present in the blends, with these containing mostly unreacted polyester chains with a low amount of styrene monomer. These structures may further react at 70°C owing to the presence of some unreacted radical initiator in the system. Thus the final polyester conversion and the local crosslinking density are increased with respect to the neat resin. A full morphological analysis is currently underway in order to obtain further details of the complex microstructure of this blend system.

Dynamic mechanical properties of the cured samples

The storage modulus (E') and the loss tangent ($\tan\delta$) curves as a function of temperature for the neat UP resin and for a B15 blend are reported in *Figures 13A* and *13B*, respectively. Over the temperature range investigated the storage modulus of the UP resin shows a gradual and continuous decrease in the range from −75 to 30°C. At this point, a sudden drop is observed, corresponding to the onset of large-scale molecular mobility. A similar trend is found for the B15 blend, with the only difference being that the E' values are slightly higher in the blend, with E' starting to drop at a slightly higher temperature. More information is gained by inspection of the $\tan\delta$ curves: two loss peaks are observed in the transition region of the neat resin, indicating the existence of two distinct relaxation processes, which are referred to as β and α (in order of increasing temperature). In the literature, a further relaxation peak has been reported below −75°C[19]. The β-transition appears as a shoulder of the main α-peak and is located at 98°C, while the α-peak is centered at 175°C. There have been some attempts to relate the chemical structure of the UP networks to their dynamic mechanical response. According to Tanaka[20] and to Cook and Delatyki[21–23], the α-transition corresponds to the activation of long-range motions of the polyester main chain, which are involved in the glass transition phenomena. There is some controversy, however, concerning the origin of the β-transition. Lenk and Padget[19] proposed that it was related to the relaxation of styrene-based bridges. More recently, Melot *et al.*[24] suggested that the β-transition is due to the motion of molecular groups in the vicinity of the residual fumaric double bonds (network defects). They showed, by decreasing the amount of residual double bonds, that the β-transition is shifted towards higher temperatures. The $\tan\delta$ relaxation spectrum of the B15 blend shows that the β-transition is shifted towards higher temperature by ca. 10°C, while the α-transition remains unaffected. Assuming that the β-relaxation is due to the bridging units, and in the light of the molecular structure of the network proposed above, the shift can be associated with an increased rigidity of the styrene/BMI structures bridging the polyester molecules in the blend, with respect to the styrene units in the neat UP resin. On the other hand the shift of the β-transition could also be due to a reduction of the 'network defects' which is brought about by the presence of BMI. In fact, we have shown that the amount of

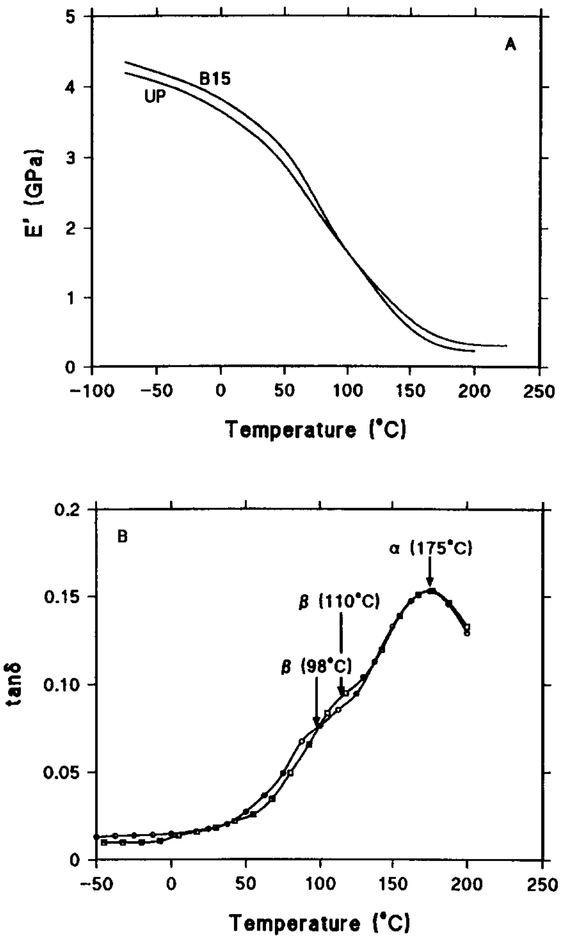


Figure 13 The storage modulus (A) and the loss tangent (B) as a function of temperature for the neat UP resin (○) and B15 blend (□)

residual unreacted double bonds decreases by increasing the BMI content in the blend. The mechanical and fracture properties of this blend system will be discussed in detail in a further publication.

CONCLUSIONS

In this present contribution we have reported on an intercrosslinked polymer network which is obtained by the simultaneous curing of an unsaturated polyester and a thermosetting bismaleimide resin. Information concerning the kinetics and the mechanism of the curing process was obtained by isothermal *FT*i.r. spectroscopic measurements. It was shown that BMI strongly accelerates the curing reactions of the UP matrix, thus causing the system to crosslink even at temperatures which are not suitable for obtaining polymerization in the neat UP resin. The available spectroscopic evidence also indicated that BMI interacts preferentially with the styrene unsaturations, in agreement with literature reports on BMI/styrene solution copolymerization. Moreover, the spectroscopic analysis allowed us to propose a likely molecular structure for this complex intercrosslinked network.

Powder *FT*i.r. spectra provided evidence that the residual amount of unreacted fumarate double bonds in the UP matrix (network defects) decreased on increasing the BMI content in the blend. In addition, the dynamic mechanical behaviour of a typical blend composition was found to be consistent with the proposed molecular structure of the network.

ACKNOWLEDGEMENTS

This work has been partially supported by the Progetto Finalizzato Chimica Fine II. Thanks are due to Mr V. Di Liello and Mr A. Lahoz for their skilled technical assistance.

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