FTIR Spectroscopy and Microscopy on the Interfacial Reaction and Interdiffusion of Styrene/Maleic Anhydride Copolymer and Bis(amine)-Terminated Poly(tetrahydrofuran)

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ABSTRACT: The interfacial reaction of a random copolymer of styrene and maleic anhydride (SMA) with bis(amine)-terminated poly(tetrahydrofuran) (PTHF) is studied by FTIR spectroscopy and microscopy as a function of temperature and for two different PTHF molecular weights. The reaction rate constants in the range from 170 to 230 °C, obtained from the initial slope of conversion–time plots, give values between 3.6×10^{-5} and 2.5×10^{-4} s^{-1}. It can be shown that the diffusion of the PTHF into the SMA phase occurs prior to the imide formation. Thus the imide is formed in the SMA phase and can be estimated quantitatively by the appearance of the imide peak at 1702 cm^{-1} and the decrease of the out-of-phase carbonyl stretching vibration of the maleic anhydride at 1780 cm^{-1}. The concentration profiles near the interface of the used polymers and the formed imide are studied by FTIR microscopy.

Introduction

Nowadays polymer blends have become more and more important from an industrial as well as a scientific point of view. There are only a few miscible polymer blends with a commercial application. By far, most of the polymer blends used on an industrial scale are heterogeneous systems.[1] Thus, for completely immiscible systems the question of compatibilization arises. The main goal of compatibilization is a better interfacial adhesion, which can be achieved by adding preformed block copolymers[2–4] or by reactive blending.[5–9] Using preformed block copolymers has the disadvantage that micelles might be formed and only a small fraction of the block copolymer is actually situated in the interface.[10–12] During the reactive blending grafting reactions, block copolymer formation or network formation might occur directly in the interface.

This study is concerned with interfacial reaction and interdiffusion of poly(styrene-*co*-maleic anhydride) (abbreviated as SMA) with a bis(amine)-terminated poly(tetrahydrofuran) (PTHF). In order to have a suitable number of reactive groups, one relatively low molecular weight component, PTHF, is chosen. Thus, the kinetics of the imide formation can readily be studied by FTIR. Furthermore, it is possible to study interdiffusion and interfacial reaction phenomena in this system by FTIR microscopy. Therefore, two-layer specimens were prepared and microtomed perpendicular to the surface. Then the FTIR measurements are performed at different distances from the interface.

Experimental Section

Materials. The SMA had a maleic anhydride content of 16.0 wt %. The M_w value was determined by light scattering and is 145 000. The sample was supplied by Chemische Werke Buna. The PTHF samples had molecular weights of M_n = 1100 and 2100 and were supplied by BASF AG, Ludwigshafen. The samples will be called PTHF-1100 and PTHF-2100. The PTHF chains were functionalized at both ends with 3-aminopropyl groups.

Sample Preparation for FTIR Studies. A total 3 wt % of the respective pure polymers was dissolved in $CHCl_3$ and cast separately onto two different KBr plates. These samples were dried at 50 °C overnight. The thickness of the films was optimized in order to provide the best absorbance ratio. For kinetic measurements, both plates were put together.

For FTIR microscopy measurements, an SMA plate with a thickness of 2 mm was pressed in a hot melt at 170 °C for 1 min. On top of this sample, the PTHF-2100 was mounted at 30 °C. This sandwich was annealed for 23 h at 170 °C. Then the two-layer specimen was cut perpendicular to the surface at room temperature into two pieces. A thin film with a thickness of about 1 μm was then prepared with a cryomicrotom (Leitz) at −18 °C.

FTIR Spectroscopy. The FTIR spectra were obtained on a Bruker IFS 88. For every spectrum, 30 scans were accumulated and the measurements were repeated every 60 s in order to follow the imide formation. A DTGS detector was used with a resolution of 4 cm^{-1}. The peak integration program was included in the OPUS software, and a method with two baseline points was used. The limits of integration for the imide peak were 1715 and 1699 cm^{-1}. As an internal standard, the out-of-plane deformation vibration peak of the phenyl ring of styrene at 700 cm^{-1} was used. A heating cell with a temperature control of ±0.1 °C was used (Eurotherm). The heating cell reached the isothermal state after 2 min, and then the data were recorded.

FTIR Microscopy. For the FTIR microscopy, a spot size of approximately 25 μm and a step size of 5 μm were chosen. The aperture of 300 μm results in an apparent spot size of 20 μm in diameter by using a condenser magnification of 15×. Taking into consideration diffraction effects leads to an average spot size of 25 μm over the wavenumber range applied.[13] A very sensitive liquid-nitrogen-cooled MCT detector was used for all interdiffusion measurements. The optical interface can clearly be detected because the PTHF has a slightly yellow color after thermal annealing and thus is taken as a distance of 0.

The resolution function was measured by moving the sharp boundary polyethylene (LDPE)/air with a step size of 5 μm through the IR beam spot. The sharp polyethylene boundary was prepared by microtoming a thin polyethylene film. It was checked by atomic force microscopy that the roughness of the sharp boundary is in the nanometer range. The polyethylene peak at 2920 cm^{-1} was integrated as a function of distance.

DSC and Light Microscopy. The blends were prepared by dissolving the respective polymers in chloroform (3 wt % total). For light microscopy, a drop of the solution was cast onto a cover glass and the solvent was evaporated at room temperature. Then the sample was dried under vacuum and placed into a hot stage (Linkam THM600) and annealed at 200 °C for 5 min. For DSC, the thin films were removed from

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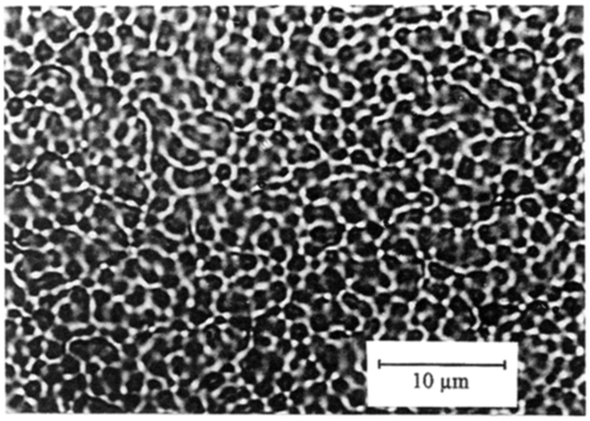

Figure 1. Optical micrograph of the phase-separated structures of SMA and PTHF-1100 after isothermal annealing at 230 °C for 5 min.

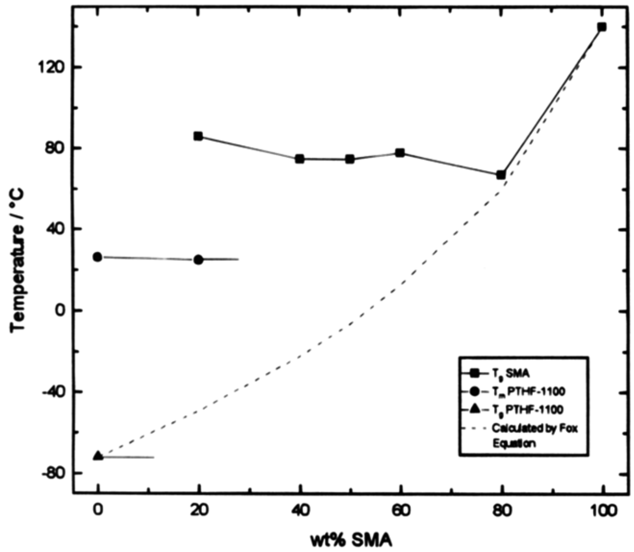

Figure 2. Glass transitions and melting points of the system PTHF-1100/SMA measured by DSC. The dashed line is calculated for the hypothetical T_g of miscible blends using the Fox equation.

the cover glass and placed into DSC pans (about 10 mg). The samples were first heated up to 150 °C at 10 K/min and then immediately cooled to room temperature. The samples were measured in the second run with a heating rate of 10 K/min. A Perkin-Elmer DSC-7 was used.

Results and Discussion

Figure 1 shows the morphology of an SMA/PTHF-1100 (50/50 wt %) blend prepared by casting from a common solvent and after isothermal annealing for 5 min at 230 °C. A clearly phase-separated structure can be seen. Thus the blend showed at all temperatures a two-phase morphology. A similar result can be obtained from DSC measurements. Figure 2 shows a plot of glass transition temperatures and melting points as a function of blend composition. It can be seen that the T_g of SMA is lowered by the addition of PTHF-1100. But the T_g values of the blends are far from the values expected for miscible blends as estimated, e.g., by the Fox equation. The T_g of the neat PTHF-1100 is −73 °C (Δc_p at T_g is only very small). The expected second T_g at lower temperatures for the blends could not be detected, probably because of the small Δc_p values. The melting point of the PTHF-1100 was only visible in the neat PTHF-1100 sample and in the blend with 20 wt % SMA. T_m is about 25 °C. It follows from light microscopy and DSC that the system is immiscible but not far from miscibility. The co-continuous structure usually occurs only in systems which are not too far from miscibility, i.e., not too far from critical temperature and critical composition.[14] Thus, assuming a UCST, it is also reasonable that the phases in equilibrium are not completely demixed but the composition of the two phases is determined by their phase boundary. In that way, the depression of the T_g of the SMA-rich phase might be understood.

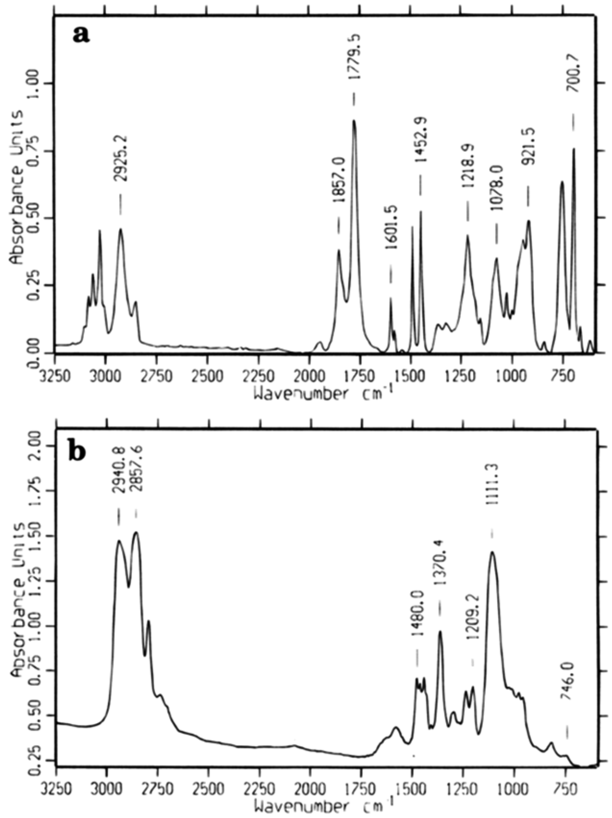

Figure 3. FTIR spectra of (a) pure SMA and (b) PTHF-1100 at 30 °C.

FTIR spectra of both pure polymers are shown in Figure 3. The SMA spectrum (Figure 3a) shows the two characteristic carbonyl peaks of the maleic anhydride at 1857 and 1780 cm^{-1} and the out-of-plane deformation vibration of the phenyl ring of styrene at 700 cm^{-1} which is taken as the internal standard. All peak integrals were related to the peak integral at 700 cm^{-1} in order to normalize the film thickness. The PTHF spectrum (Figure 3b) shows clearly the aliphatic CH_2 groups and the ether peak at 1111 cm^{-1}. There are no distinct amine peaks.

Figure 4 depicts two spectra after the two separate polymer films of SMA and PTHF-1100 on KBr plates were placed together. The spectrum at the bottom shows the initial spectrum before the imide formation occurred, and the upper spectrum is taken after 122 min. It can be seen that a peak at 1702 cm^{-1} starts to grow which can be assigned to the imide formation.[15] Thus, it is possible to follow the imide formation, whereas the intermediate product, the secondary amine salt, cannot be distinguished clearly from other peaks.

The growing imide peak can be seen as a function of time at 170 °C in Figure 5. The lower spectrum in this plot is obtained before the reaction started. The next spectra were taken always after 7 min; i.e., the lower curve is taken after 7 min and the upper curve after 98

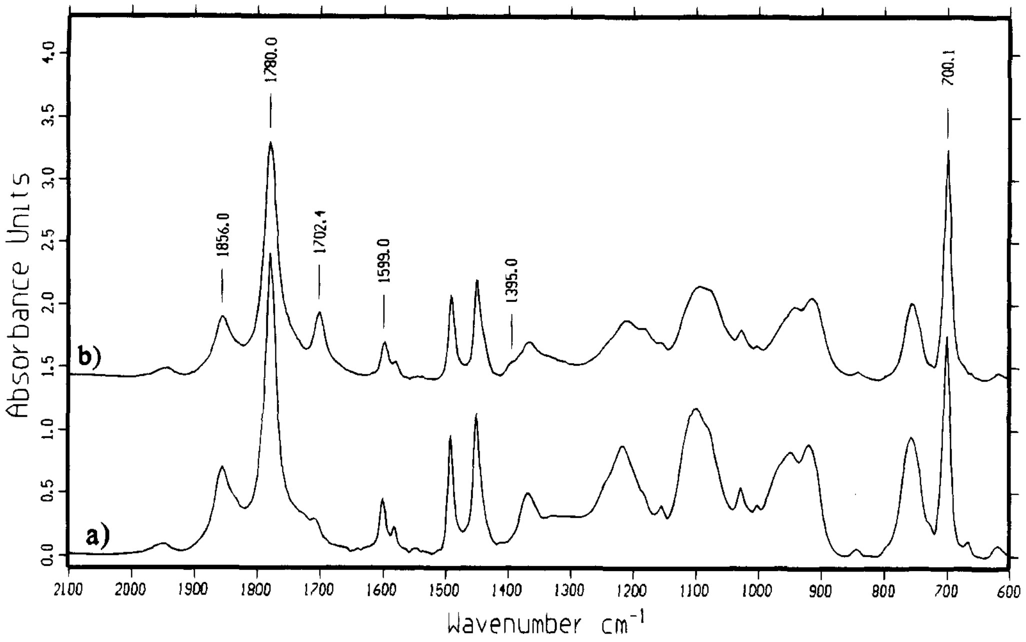

Figure 4. FTIR spectra of two-layer specimens of SMA and PTHF (a) before chemical reaction and (b) after a reaction time of 122 min at 210 °C.

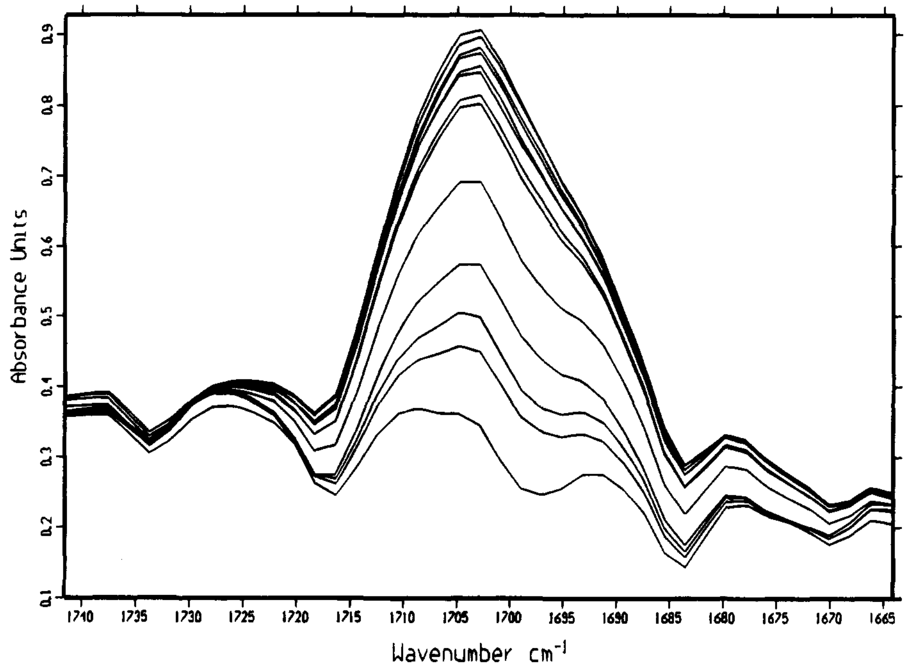

Figure 5. Imide peak at 1702 cm^{-1} as a function of reaction time at 170 °C. The peaks are taken every 7 min up to 98 min.

min. These measurements were also carried out at 230, 210, and 190 °C. Figure 6 shows the imide formation as a function of time for four different temperatures. It should be noted that Figure 6 gives the imide content as a function of time. The imide content was obtained from a calibration curve. The calibration is described in the appendix. The initial slope of the reaction is increasing with the temperature. The curves show a plateau which means that the reaction slows down significantly after a certain time. This might be related to the network formation, which hampers the diffusion of the components, or to the reaction being confined only to areas near the interface. It is known that the interface of immiscible, high molecular weight polymers should be in the range of a few nanometers.[16] However, the interfacial thickness might be significantly larger if one oligomer is involved and the interactions are not too repulsive.[17] The initial slope is proportional to the reaction rate constant. It changes from $k = 2.5 \times 10^{-4}$ s^{-1} at 230 °C to $k = 3.6 \times 10^{-5}$ s^{-1} at 170 °C. This order of magnitude is comparable to other reported literature values of the reaction of SMA with amines.[18] An apparent activation energy obtained by an Arrhenius plot yields a value of 57 kJ/mol. This is, of course, only an apparent value because the reaction is controlled by diffusion as will be shown below. Scott and Macosko obtained an activation energy for the reaction of an SMA and an amine-terminated butadiene–acrylonitrile copolymer of about 120 kJ/mol.[19] But they prepared cast films of the polymer mixtures from a mutual solvent in order to avoid diffusion influences. The reaction mechanism shows that the anhydride and the amine component react first to a secondary amine salt before the cyclic imide is formed.[19]

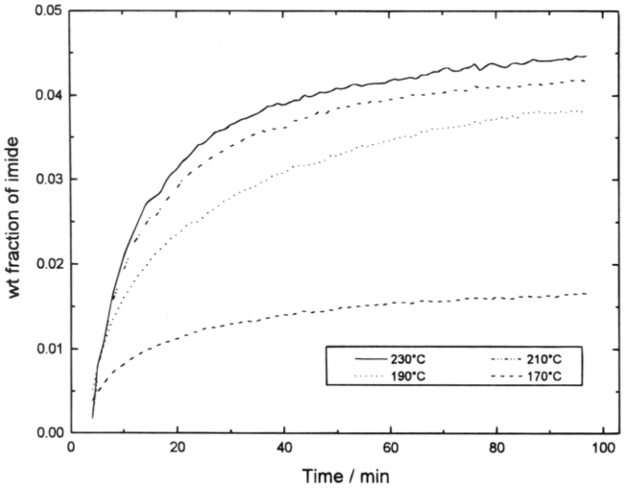

Figure 6. Imide content versus time for the reaction of SMA and PTHF-1100 at four different temperatures.

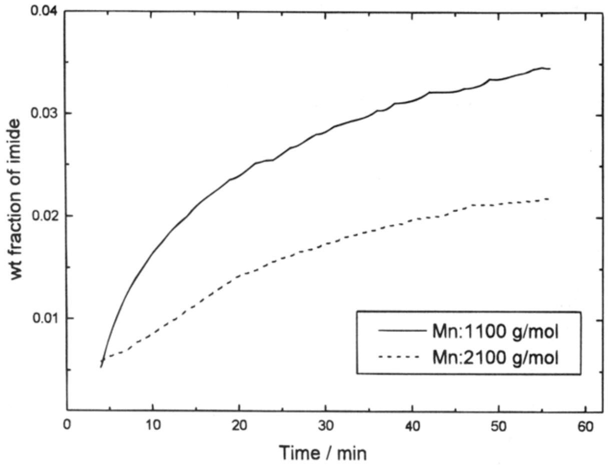

Figure 7. Imide content versus time for the reaction of SMA with PTHF-1100 and PTHF-2100, respectively, at 190 °C.

The influence of the molecular weight of the PTHF on the reaction rate was studied at 190 °C by using two different molecular weights (see Figure 7). The reaction is significantly slowed down by an increase of the molecular weight. This might be attributed mainly to a lower concentration of reactive end groups, as well as to an increase in viscosity. For the molecular weight of M_n = 1100, the reaction rate constant, k, obtained from the initial slope, is 1.16×10^{-4} s^{-1}. For a molecular weight of M_n = 2100, k is 7.05×10^{-5} s^{-1}. This decrease with increasing molecular weight is nearly proportional to the decrease of the concentration of amine end groups.

In the second part of this report, the diffusion behavior of the SMA/PTHF-2100 system will be discussed. It has been found that FTIR microscopy is a suitable tool to study extremely broad interfaces or diffusion profiles of polymeric systems in the micrometer range.[20,21] Figure 8 depicts FTIR spectra taken at different distances from the interface (upper picture) and the corresponding contour plot (lower picture). All spectra are baseline corrected. The spectra in front belong to the pure PTHF-2100 phase, whereas the spectra in the back belong to the neat SMA phase. The SMA phase can be identified by the characteristic band of the anhydride at 1780 cm^{-1}. The peak area at 1702 cm^{-1} represents the spatial resolution of the imide formation which can also be seen in the contour plot. The density of the lines is related to the differences in the peak heights of the respective spectra at a fixed wavenumber. It can also be seen that the imide formation occurs within the SMA phase. The optical phase boundary was determined by microscopy. Another proof of this fact is provided in Figure 9. The light micrograph clearly shows three distinguishable phases. The thin section of the sample was prepared by a special technique. The sample was cut relatively quickly with a microtome at −18 °C. The lower zone consists of pure PTHF-2100. The observed structures are caused by crystallization of PTHF. In the SMA phase, a raster of dark and bright vertical strips is formed by delamination of the brittle SMA phase, which stops exactly at the original phase boundary before the reaction starts (optical phase boundary). After reaction, a broad interphase can be seen (the middle phase at Figure 9). The horizontal strips are caused by cutting marks of

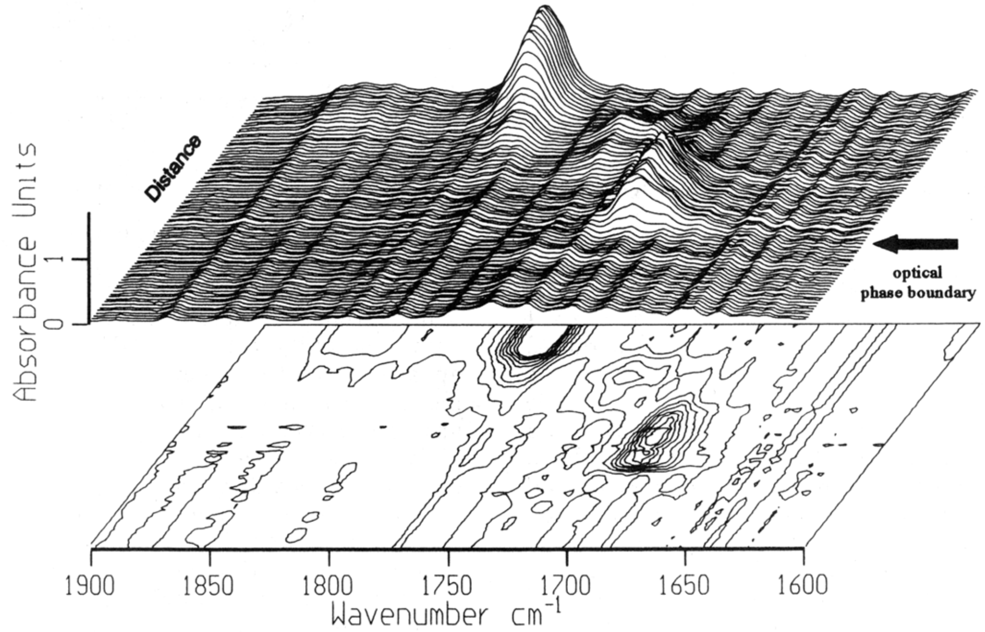

Figure 8. Distance-resolved FTIR spectroscopy at the interface of PTHF and SMA annealed at 170 °C for 23.5 h. The lower diagram represents the corresponding contour plot.

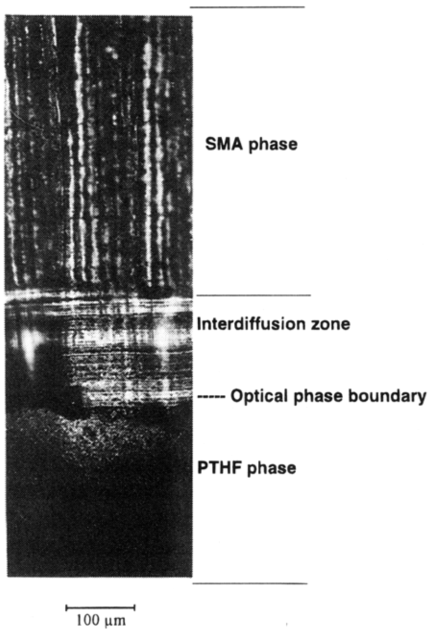

Figure 9. Optical micrograph of the interfacial area of the system PTHF-2100 and SMA annealed at 170 °C for 23.5 h.

the softer interdiffusion zone. This is exactly the interdiffusion area seen by FTIR. Because the dark and bright vertical strips can also be seen in this phase, it can be concluded that PTHF diffused into the SMA phase prior to imide formation. These results are in agreement with FTIR measurements.

It is not possible to obtain information about the spatial arrangement of the unreacted PTHF from Figure 8. Therefore, the FTIR spectra in the range from 1200 to 650 cm^{-1} across the interface have been added and shown in Figure 10. Two additional characteristic bands can be observed. The band at 700 cm^{-1} is the out-of-plane deformation vibration which was also taken as an internal standard for kinetics measurements. The band at 1113 cm^{-1} stems from the C$-$O$-$C ether bond of the PTHF. It can be seen that the PTHF-2100 penetrates the SMA phase deeper than the imide area. Thus, it can be concluded that PTHF-2100 diffused into the SMA phase prior to the imide formation. As well, the peak at 700 cm^{-1} shows that the imide formation takes place inside the SMA phase, because this peak is still present when the peak of the maleic anhydride at 1780 cm^{-1} has already vanished. There is clearly a faster diffusion across the interface than the reaction between amine and anhydride.

These characteristic peaks at 1780 and 700 cm^{-1} (SMA phase), 1702 cm^{-1} (imide area), and 1113 cm^{-1} (PTHF phase) can be integrated. The integration values of the peak areas versus distance are shown in Figures 11 and 12. The distance of 0 was given by the optical interface. The imide formation starts at the optical interface and has an extension of about 180 μm into the SMA phase (see Figure 11). In this area, the anhydride peak at 1780 cm^{-1} disappeared almost completely and then it increased to the value of the bulk phase. Figure 11 shows also schematically the measured resolution function. The imide profile next to the optical interface is almost identical to the resolution function; i.e., there is a stepwise transition into the imide area. By contrast, the imide profile in the SMA phase shows a real diffusion contribution.[22] This is an indication that there is diffusion prior to imide formation. Therefore, various bands, which are independent of the imide formation, are integrated as a function of distance and are depicted in Figure 12. These are the C$-$O$-$C ether vibration band at 1113 cm^{-1}, which represents the PTHF component, and the out-of-plane deformation vibration band of the phenyl ring at 700 cm^{-1}, which characterizes the SMA component. Also the imide area shown in Figure 11 is added into Figure 12. It is clear that there are two plateaus of the PTHF-2100 and the SMA components in the imide formation area. Thus the concentration of both components in this area is constant. The steep concentration profiles of both components near the optical interface are confirmed again. It can also be seen that the PTHF-2100 penetrates the SMA phase much deeper than the imide formation area. This demonstrates, as well, that the lower molecular weight component (PTHF-2100), which has also the lower viscosity, diffuses first into the high molecular weight area of the SMA phase before the reaction under imide formation starts.

Conclusions

This model experiment provides more insight into the kinetics and diffusion process at the interface of PTHF/SMA. It has been demonstrated by FTIR spectroscopy, FTIR microscopy, and optical microscopy that the interdiffusion of the low molecular weight component (PTHF) occurred prior to the imide formation inside the high molecular weight area of the SMA phase. Thus,

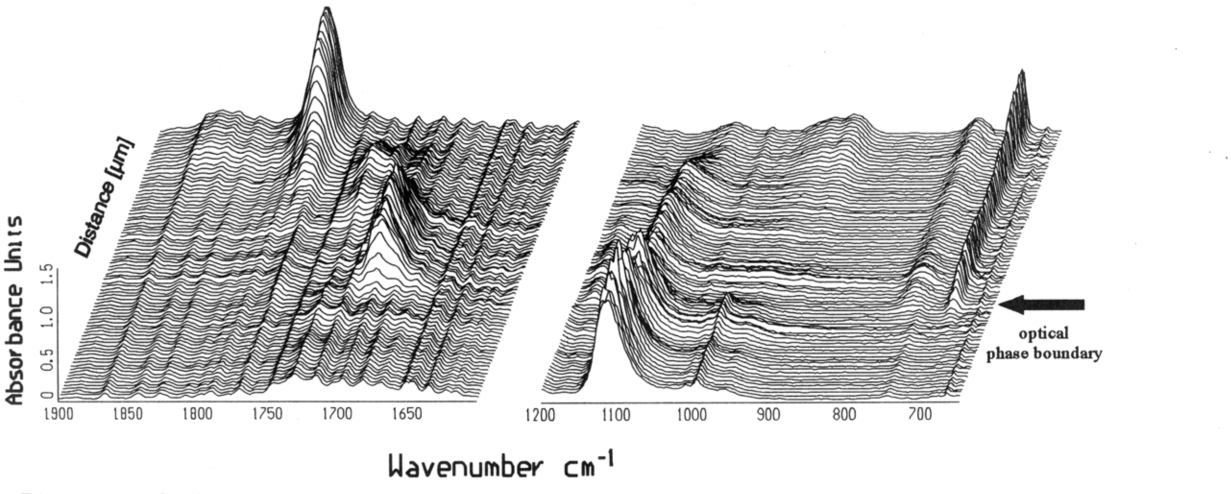

Figure 10. Distance-resolved FTIR spectroscopy of the system PTHF-2100 and SMA annealed at 170 °C for 23.5 h in the ranges from 1900 to 1600 cm^{-1} and from 1200 to 650 cm^{-1}.

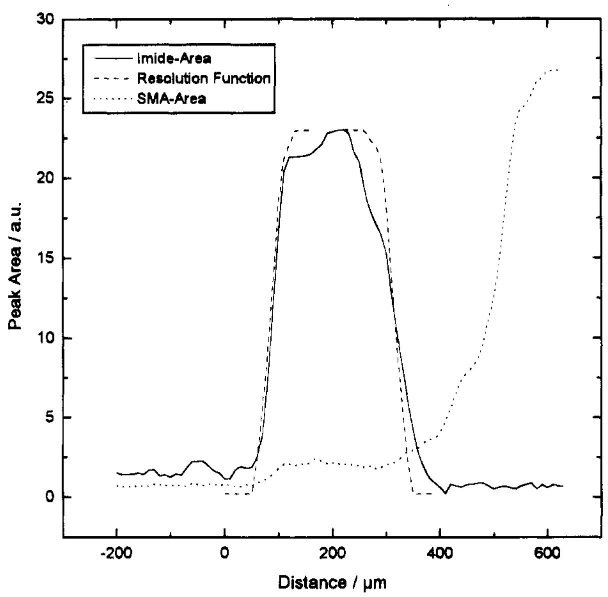

Figure 11. Relative concentration versus distance of the SMA component (1780 cm^{-1}) and the imide area (1700 cm^{-1}). The dashed line represents the resolution function.

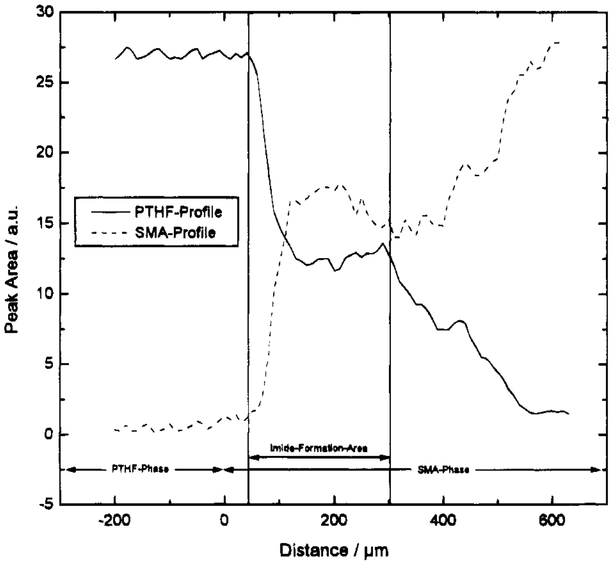

Figure 12. Relative concentration versus distance for the SMA area (700 cm^{-1}) and the PTHF area (1113 cm^{-1}).

the imide formation near the interface is diffusion-controlled. The reaction rate increases with higher temperature and simultaneously with lower molecular weight.

Appendix

Bis(imide)-terminated PTHF was prepared by the reaction of bis(amine)-terminated PTHF with succinic anhydride.[23] The bis(amine)-terminated PTHF and the succinic anhydride were dissolved in acetone and stirred for 1 h at room temperature. Acetic anhydride, triethylamine, and $Ni(OAc)_2$ were added, and the solution was stirred for another 8 h at 70 °C. The bis(imide)-terminated PTHF was cleaned in a thin-layer evaporator. Then different blend ratios of SMA and bis(imide)-terminated PTHF were prepared and thin films for FTIR studies cast. Then the imide peak was related to the internal standard (out-of-plane deformation vibration of styrene at 700 cm^{-1}). These relative peak areas can then directly be related to absolute values of the imide content.

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