

Diffusion of Miscible Polymers in Multilayer Films

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Synopsis

Thermal and optical properties of multilayer films of miscible polyethyloxazoline (PEOx) and poly(styrene-co-acrylonitrile) have been studied as a function of time and temperature. Differential scanning calorimetry showed that the distinct, characteristic T_g 's of the component polymers of the original films disappear after only short heating periods above T_g , and a single transition appears. The new transition region is broad at first, but narrows on subsequent heating. The measurement of light transmittance as a function of wavelength through the heat-treated films also confirms the diffusion of the miscible polymers and gives results which are comparable to the thermal measurements. Films from immiscible polymers of polystyrene and PEOx retain their properties after various heat treatments. A qualitative discussion of the diffusion process as examined by the thermal measurements is presented.

INTRODUCTION

As indicated by the recent literature,¹⁻²⁵ there is a growing interest in diffusion of polymer chains through a molten matrix of other polymer chains. This includes the special case of self-diffusion, where all the chains are identical except for a fraction which are tagged in some way as an experimental necessity for following the diffusion process, and the more general situation of mutual diffusion involving two types of chains which differ in molecular size (or architecture) or in chemical composition as in miscible polymer pairs. This interest has been driven by new theories for polymer-polymer diffusion,¹⁻⁷ including mechanisms such as reptation, and issues related to the processing, fabrication, and uses of multicomponent polymer systems as an outgrowth of the rapid discovery of new miscible polymer pairs over the past 10-15 years.^{8,9} Practical questions requiring some knowledge about such diffusion processes include: (a) the rate of molecular scale homogenization during mechanical melt mixing of two thermodynamically miscible polymers; (b) the kinetics of demixing upon traversing boundaries on blend phase diagrams¹⁰⁻¹⁸; and (c) development of adhesion between two polymers by a diffusional mechanism^{19,20} during lamination operations, coextrusion of film and fibers, crack healing, at weld lines, and between a matrix and impact modifier particles having a graft layer, to mention some of the most obvious.

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Of course, the diffusion coefficients for polymer-polymer transport are quite small and special techniques are needed to quantify them. One approach used recently by a number of groups has been to follow the kinetics of phase demixing or mixing after a temperature jump across an equilibrium phase boundary of a binary blend using microscopy¹⁰ or scattering techniques¹¹⁻¹⁸ (light, X-ray, or neutron) to monitor the course of this process. Many of these studies are concerned more with the mechanism of the demixing,¹⁰⁻¹⁸ i.e., spinodal decomposition or nucleation and growth, than with understanding the underlying diffusional process. A number of other studies have used the more straightforward approach of following the time dependence of the spatial composition profile about the original interface created by juxtaposition of the two polymer melts. Owing to the short distances over which diffusion can occur in a reasonable time, rather special techniques for obtaining the composition profile are needed such as microdensitometry with infrared²¹ or dispersive energy analysis^{22,23} for detection. These techniques are limited by the chemical nature of the components or some means to tag them for analysis. An apparently more general approach involves measurement of the rate of displacement of embedded markers (metal particles) using Rutherford backscattering from an ion beam.^{6,7} Bartel et al.²⁴ recently described a technique of diffusion across multiple interfaces created by laminating a number of alternating layers of tagged and untagged polymers. The progress of diffusion was followed by monitoring the small angle neutron scattering by the composite film (tagging was by deuteration). Smith et al.²⁵ cleverly created such a geometry by using photobleaching to write an alternating layer pattern in a polymer system containing fluorescent species on some of the chains. The diffusion process was followed by monitoring the redistribution of fluorescence as a function of time.

The purpose of the review given above has been to point out that while polymer-polymer diffusion is a subject of great practical importance, all of the experimental techniques used to date are very complex, requiring sophisticated instrumentation and data analysis. They also are often limited by the need to tag one species chemically. There is an obvious need for simpler techniques which do not require such specialized facilities and materials. The concept of diffusion in multilayer structures as mentioned above seems especially attractive since these layers can be made quite thin by techniques like coextrusion so that the diffusional process can be completed in a reasonable period of time. We show here that simple techniques like differential scanning calorimetry and optical transmission of such multilayer films can be used to follow the progress of the diffusion process in at least a qualitative way; however, we believe such approaches can be made more quantitative.

EXPERIMENTAL

The various polymers used in this study are identified and described in Table I. Multilayer films were prepared from combinations of these materials by two different techniques described next. These films were dried prior to any measurements in a vacuum oven at a temperature just below the glass transition for the component of the film having the lowest T_g .

TABLE I
 Polymers Used in This Study

Polymer	Designation	Source and description
Polyethyloxazoline	PEOx	Dow Chemical, $\bar{M}_w = 450,000$, $\bar{M}_w/\bar{M}_n = 4$
Polystyrene	PS	Dow Chemical, Styron 658D
Poly(styrene-co-acrylo nitrile)	SAN	Dow Chemical, Tyril 876B, 25% AN
Polyhydroxy ether of bisphenol A	Phenoxy	Union Carbide, PKHH

Solution casting methods were used to prepare multilayer films having relatively thick component layers for use in preliminary experiments. For the polyethyloxazoline (PEOx)–styrene/acrylonitrile copolymer (SAN) and the PEOx–polystyrene (PS) systems, the procedure was as follows: First, a tetrahydrofuran solution, containing 1% by weight of the styrenic polymer, was poured into an aluminum pan followed by ambient evaporation and then thorough drying *in vacuo* at 120°C. Second, a similar weight of isopropanol solution, containing 1% by weight of PEOx, was poured onto the dry styrenic polymer film followed by evaporation and drying at 68°C *in vacuo*. Discs of the two layer film were punched out, and six such discs were stacked into a sample pan for the differential scanning calorimeter (DSC). This composite was placed on a hot plate for about 30 s to bond the bilayers and to provide good contact with the sample pan. From the total thickness of the composite film, it was estimated that each component layer was about 25 μm thick. A similar procedure was used to prepare multilayer films from PEOx and the polyhydroxy ether of bisphenol A, Phenoxy.

Multilayer films having much thinner component layers were prepared from PEOx with each of the two styrenic polymers for us using a coextrusion process²⁶ by The Dow Chemical Co. The extrusion temperature was about 245°C. This process layers the two polymers inside a feedblock that feeds a film die. At this point the individual layers are relatively thick; however, upon emerging from the die, the thickness is reduced by about 30-fold prior to solidification on chill rolls. The contact time between the layers in the melt state is of the order of minutes before the drawdown but only seconds during and after the drawdown. Thus, the opportunity for significant interdiffusion when the components are miscible is very limited owing to the thickness of the layers prior to drawdown and the short contact time in the melt state afterwards. A photomicrograph of a typical extrudate solidified without stretching is shown in Figure 1. Sharp boundaries between the layers are evident. Each multilayer film consists of 48 layers of PEOx and 49 layers of the styrenic polymer. The total film thickness after stretching was 1 mil. Based on elemental analyses of the film and component densities, it was estimated that the individual PEOx layers are about 0.15 μm thick while the styrenic layers are about 0.35 μm thick. All films were stored in a desiccator prior to use because of the hydrophilic nature of PEOx.

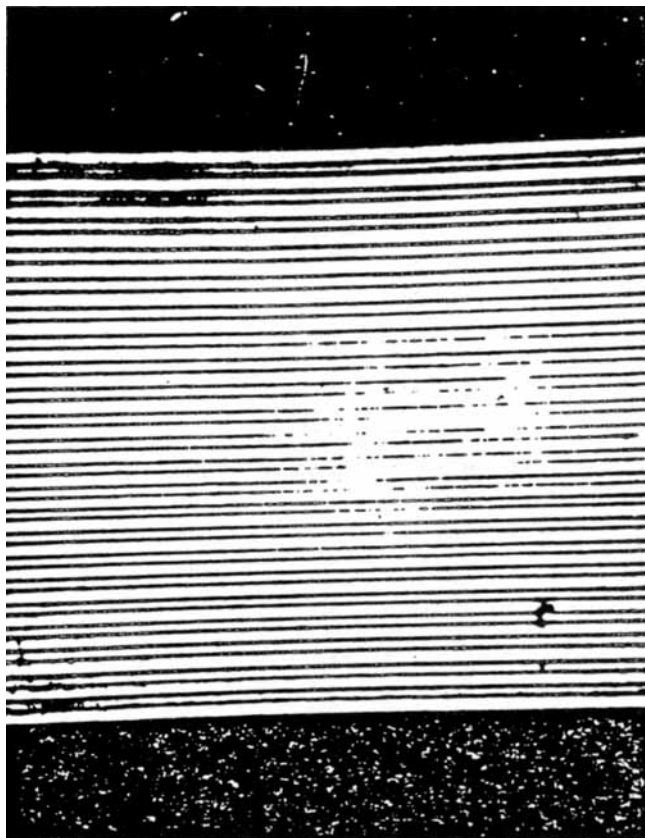


Fig. 1. A photomicrograph showing layer boundaries in a web of a multilayer extrudate before stretching. PEOx layers are dark and SAN layers are light. After stretching the layer thicknesses are about $0.15\ \mu\text{m}$ (PEOx) and $0.35\ \mu\text{m}$ (SAN).

Thermal analysis to examine glass transition behavior of the multilayer films was done on a Perkin-Elmer DSC 2 equipped with a Thermal Analysis Data Station. Usually, the dry films were stacked to obtain a total sample mass of 10–20 mg. The heating rate was normally $20^\circ\text{C}/\text{min}$. and cooling was at $320^\circ\text{C}/\text{min}$.

Light transmission characteristics of the multilayer films, after various thermal treatments, were measured as a function of wave length from 400 to 800 nm using a Beckman Spectrophotometer Model ACTAM VI.

BACKGROUND

The film fabrication procedures described above should produce sharp boundaries between the components even when the two polymers are miscible. At room temperature these structures should persist indefinitely. However, heating the film to temperatures above T_g should provide mobility that will allow interdiffusion for a miscible pair, the extent of which will depend on the value of the mutual diffusion coefficient and the time at the heat treatment temperature. Figure 2 illustrates composition profiles which can be expected in such systems as a function of the time for diffusion. In the initial stages, the

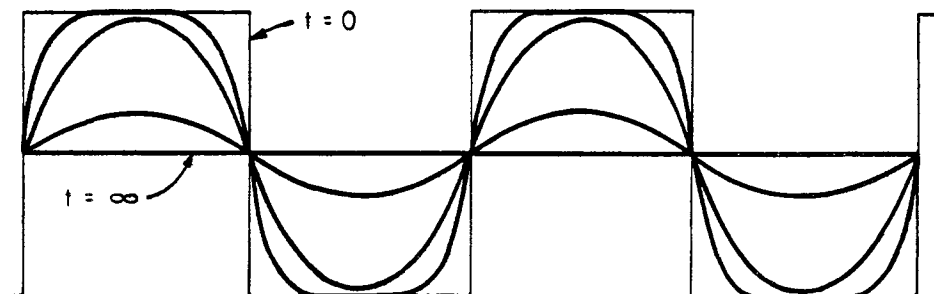


Fig. 2. Schematic illustration of concentration profiles as a function of diffusion time for a multilayer film. For simplicity all layers are shown to have equal thickness.

principal event is to create a diffuse interface while retaining regions of each component unaffected by diffusion. As time progresses, the extent of the latter diminishes and such unaffected regions eventually disappear. Finally, the periodic profile relaxes to a perfectly uniform composition equal to the overall film composition. This state is approached asymptotically in time and would only appear to be complete when the sensitivity of the technique for examination is surpassed.

An initial DSC scan of a multilayer film should yield steps in the heat capacity corresponding to the T_g 's and the amounts of the components comprising the film whether the pair is miscible or not. For a miscible pair, scans after a thermal history allowing diffusion should reflect the events mentioned above. At early times, the onset of the lower T_g and the completion of the upper T_g should remain fixed while intermediate regions of the heat capacity vs. temperature relation would begin to become smeared and eventually lose the steplike character of individual transitions. At intermediate times the low T_g onset and the high T_g completion will begin to shift toward each other as the regions of pure materials disappear. Finally, there will appear to be one broad transition region which with time sharpens to become identical to that for the homogeneous blend. Ideally, an immiscible pair should show no changes at all as a result of heat treatment.

Alfrey et al.^{27,28} have analyzed the optical reflectance characteristics of ideal multilayer films like those described here. They showed theoretically that the reflectance of such films has minima and maxima as a function of the wavelength of the incident light but is not a simple periodic function. These expectations were confirmed experimentally. Obviously, similar responses are to be expected for the transmission characteristics. Once diffusion is complete for a miscible pair, no such behavior is expected. Thus, one expects the initial minima and maxima in optical transmission to decay as diffusion occurs and to disappear upon completion of this process at some point, depending on the sensitivity of measurement. Analyses and experiments for scattering from related kinetic systems have been described.^{29,30}

The purpose of the present paper is to show qualitatively that DSC and optical measurements follow the expectations outlined above. More quantitative analyses can provide estimates of the diffusion coefficients, but this is not pursued in this preliminary study.

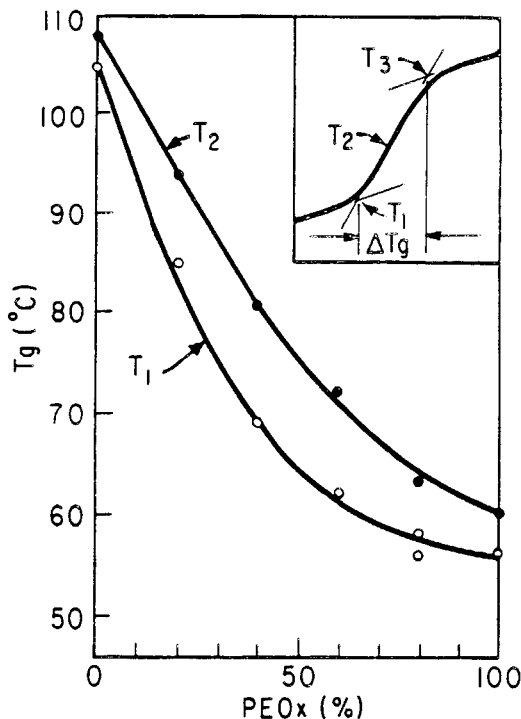


Fig. 3. T_g of PEO_x/SAN blends: (O) "initial" T_1 ; (●) "midpoint" T_2 ; $T_3 = \Delta T_g + T_1$. Also, please see Table II.

RESULTS AND DISCUSSION

Blends of PEO_x with SAN 25 and with Phenoxy have been shown to be miscible while blends with PS are not.³¹ Figure 3 shows the single T_g observed for PEO_x/SAN 25 blends by DSC along with other details of the transition region. The thermal events in the glass transition region are strongly influenced by previous history of the PEO_x as shown recently.³² The following present thermal and optical results for heat treated multilayer films composed of these various pairs.

Thermal Measurements

Preliminary experiments on solvent cast multilayer films having 12 layers were conducted to ascertain qualitative differences in thermograms for selected miscible and immiscible polymer combinations. For the miscible pair PEO_x/SAN 25, heat treating the multilayer film at 230°C for 1 h resulted in a single T_g on the DSC trace; however, further heating for 1 h at 250°C caused noticeable narrowing of this T_g region. Figure 4 shows two T_g 's for an initial scan on a film which had not been heat-treated (curve A), the single but broad T_g after treating for 1 h at 230°C (curve B), and the subsequent narrowing of the T_g region on further heat treatment (curve C). Details of these changes will be discussed more fully later. Multilayer films of PEO_x and Phenoxy showed a single T_g after only 10 min at 230°C, whereas a film consisting of the

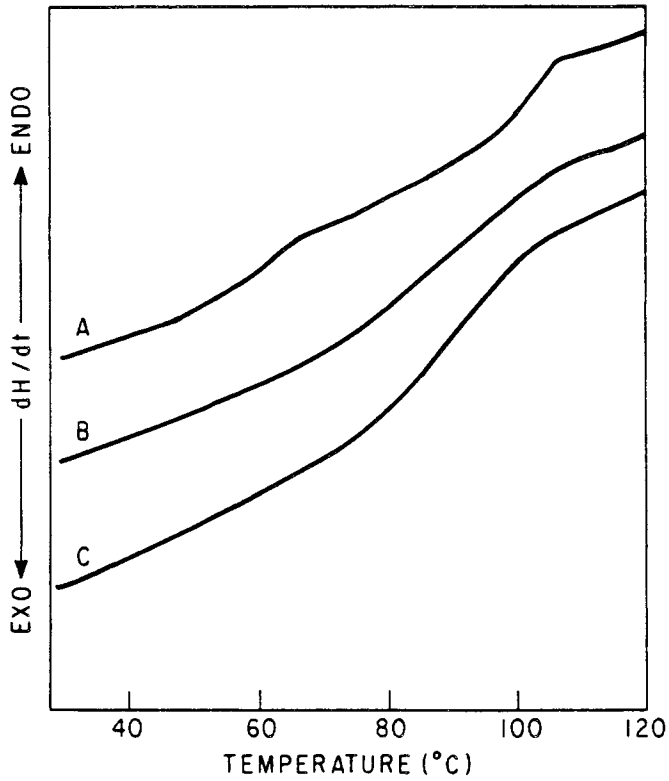


Fig. 4. Thermogram of solution cast multilayer film of PEO_x/SAN: (A) Initial run, no heat treatment; (B) 1 h at 230°C; (C) 1 additional h at 250°C.

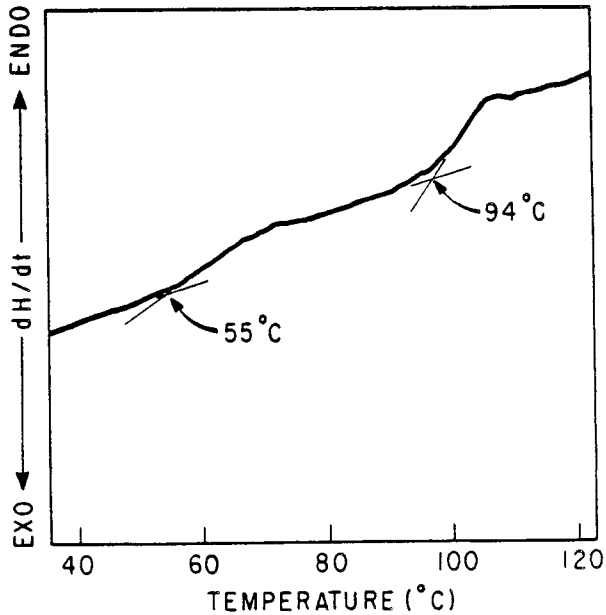


Fig. 5. Thermogram of solution cast multilayer film of PEO_x/PS after 1 h at 230°C.

TABLE II
Thermal Data for PEO_x/SAN Melt Blends

PEOX/SAN Ratio	T_1 (°C)	T_2 (°C)	ΔT_g^* (°C)	After 5 min at 300°C			ΔC_p at T_g (cal/g °C)
				T_1 (°C)	T_2 (°C)	ΔT_g (°C)	
0/100	105	108	6	—	—	—	0.20
20/80	85	95	23	85	94	18	0.20
40/60	69	81	25	71	83	23	0.16
60/40	62	72	24	64	73	19	0.20
80/20	56	63	16	64	67	7	0.14
100/0	56	60	9	—	—	—	0.20

* $\Delta T_g = T_3 - T_1$; for definitions please see Figure 3.

immiscible pair PEO_x and PS retained the original individual component T_g 's after such heat treatments, as seen in Figure 5.

More detailed experiments were performed on microlayer films made by coextrusion based on PEO_x and styrenic polymers since the more precise control of geometry and thinner individual layers should provide a more convenient time scale for following the diffusion process. However, before examining the results of these experiments, more needs to be said about the transition temperature behavior of miscible PEO_x/SAN 25 blends. The insert in Figure 3 defines the temperature for the onset, T_1 , the midpoint, T_2 , and the completion, T_3 , of the glass transition region. Each of these characteristic temperatures is shown as a function of composition for fully mixed blends, prepared by melt blending, for this miscible pair. The breadth of the glass transition, $\Delta T_g = T_3 - T_1$, is broader for the blends than for the pure compo-

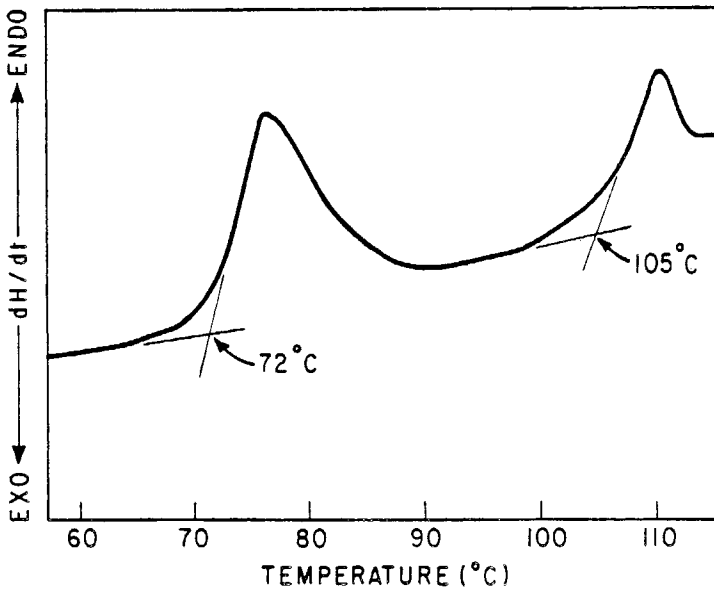


Fig. 6. Thermogram of coextruded multilayer film of PEO_x/SAN. Film aged > 30 days at room temperature.

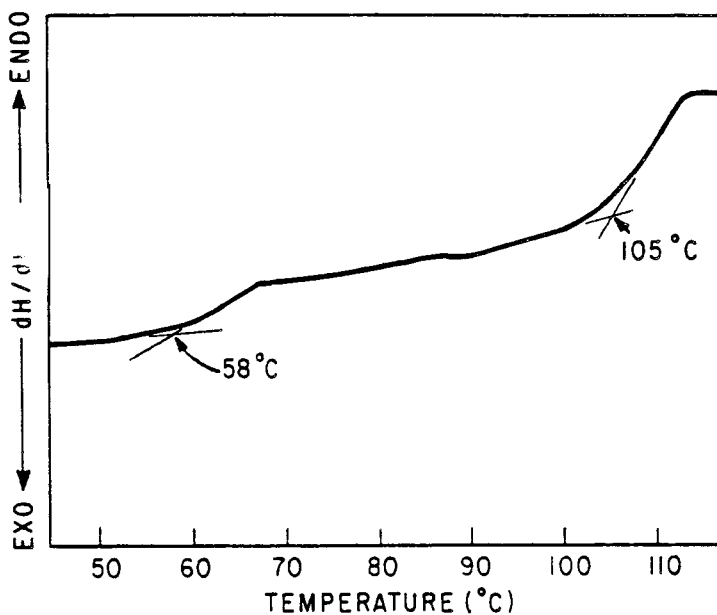


Fig. 7. Thermogram of a multilayer film of PEOx/SAN. Sample heated to 117°C and quenched to 7°C prior to running the experiment.

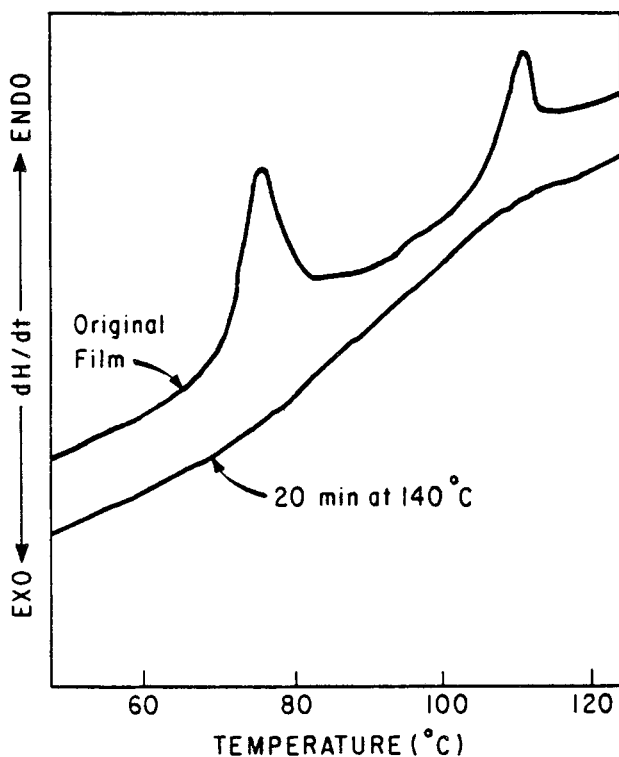


Fig. 8. Thermogram of the original PEOx/SAN multilayer film and the one after 20 min at 140°C.

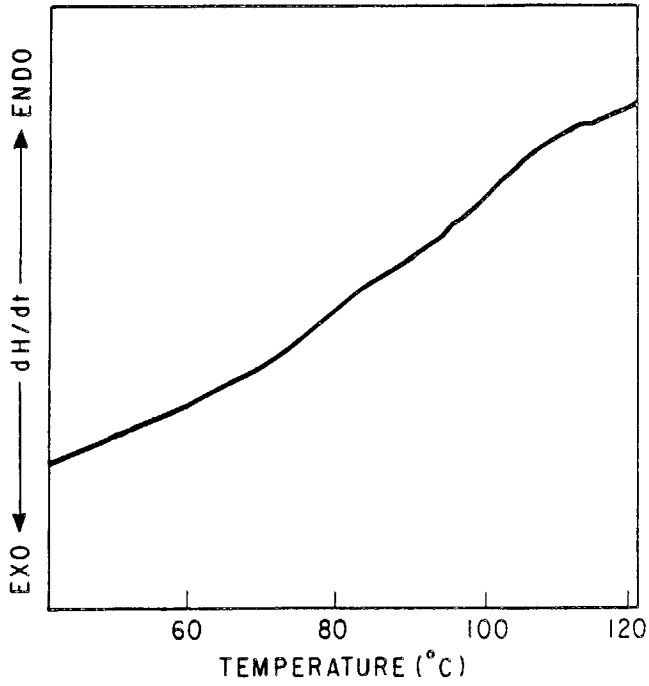


Fig. 9. Thermogram of a multilayer film of PEOx/SAN after 10 min at 140°C.

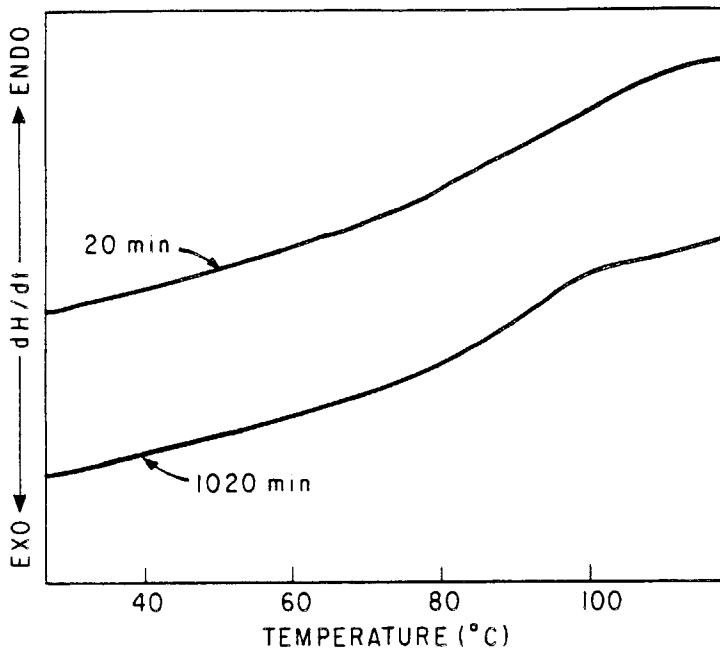


Fig. 10. Thermograms of multilayer films of PEOx/SAN showing narrowing of the transition region on heating at 140°C.

nents which is rather typical for blends and is believed to be the result of equilibrium composition fluctuations.³³ Other miscible systems show even broader transition regions than these.³³ This breadth is slightly dependent on prior thermal history while the step change in the heat capacity at the transition is relatively constant (see Table II).

Various heat treatments for immiscible PEO_x/PS microlayer films resulted in no change in the two T_g 's observed for the two component polymers, similar to observations in the preliminary experiments. However, films based on the miscible PEO_x/SAN 25 pair showed significant changes even after short periods of time above the T_g of SAN. During the first DSC scan of these films, excess enthalpy peaks for both the PEO_x and the SAN were clearly observed as shown in Figure 6. This scan was terminated at 117°C, and the film was immediately quenched to 7°C at 320°C/min. A repeat scan made immediately thereafter shown in Figure 7 did not show the enthalpy relaxation peaks but did reveal the T_g 's of the component polymers at their expected temperatures.³¹ Both transitions are quite distinct, indicating the absence of significant

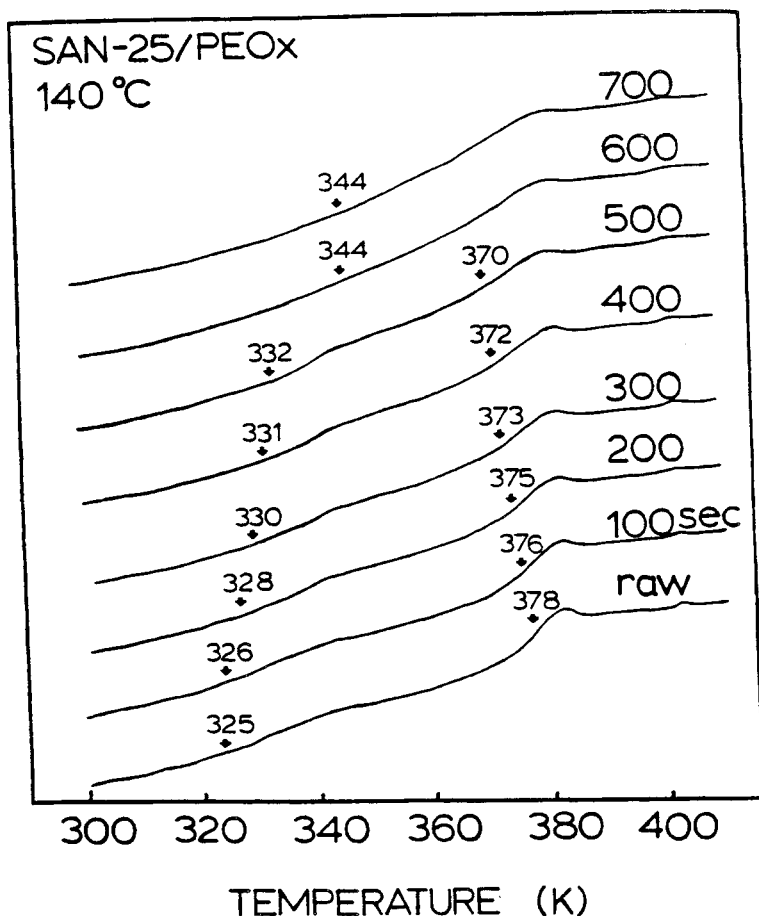


Fig. 11. Thermograms of multilayer films of PEO_x/SAN after heating for various times, up to 140°C (University of Massachusetts study).

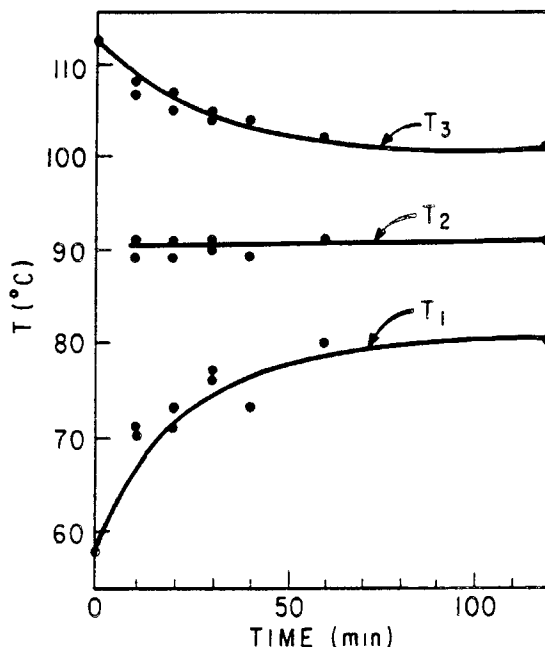


Fig. 12. Changes in the glass transition region (please see Fig. 3) of multilayer films of PEO_x/SAN after heating at 140°C for various lengths of time (to 120 min).

interdiffusion of the components. Figure 8 compares the thermograms for these films after heat treatment in the DSC for 20 min at 140°C with that of the original scan (Fig. 6). After this heat treatment there is a single but broad transition region having $T_1 = 68.5^\circ\text{C}$ and $T_3 = 88^\circ\text{C}$. After only 10 min at 140°C, the intermediate region is not as diffuse but vestiges of the completion of the lower T_g and the onset of the higher T_g are still evident, as shown in Figure 9. Thus, the boundaries between the various film layers becomes totally diffuse somewhere between 10 and 20 min at 140°C as judged by the DSC. As described later, this distinction in phase boundaries seems to be lost at 10 min as judged by optical transmission. Further heating at 140°C results in continued narrowing of the transition as seen by comparing the thermograms in Figure 10 after 20 and 1020 min. Figure 11 shows a complete chronology of thermograms obtained after heating for various times at 140°C (results of a University of Massachusetts study). Figure 12 shows the change in the three characteristic temperatures defined in Figure 3 as a function of time the film was held at 140°C. As seen, the transition region progressively narrows with time and eventually approaches values characteristic of the homogeneous blend comparable to those in Figure 3. Figure 13 shows similar results for the original microlayer film and after heating for 10 min at various temperatures (reflecting the increase in diffusion coefficient with temperature). Also shown on this plot are the characteristic temperatures after heating for 1020 min at 200°C. The results in Figures 12 and 13 suggest that within the sensitivity of this technique that diffusion is substantially complete after 60 min at 140°C and after 10 min at 160°C for the microlayer thicknesses used. A comparison of T_1 and T_3 for the original microlayer film with corresponding

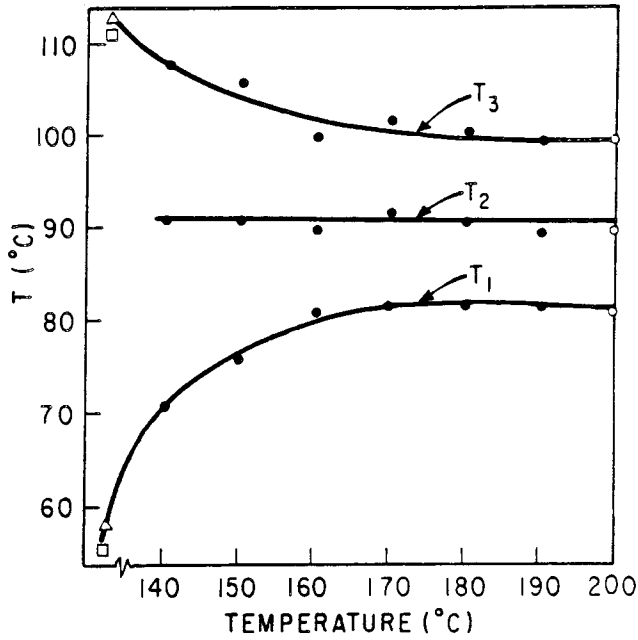


Fig. 13. Changes in the glass transition region of multilayer films of PEO_x/SAN after heating for 10 min at various temperatures: (Δ) original film; (\square) separate determination of the two polymers; (\bullet) heat-treated films; (\circ) heat-treated for 1020 min.

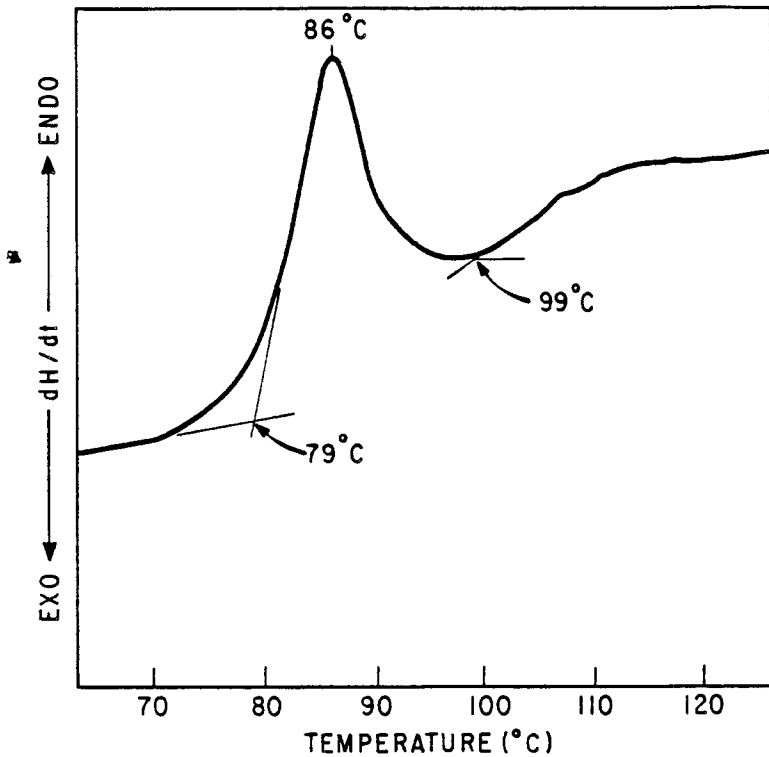


Fig. 14. Thermogram of multilayer film of PEO_x/SAN which had been heated for 10 min at 140°C and stored for 10 months before the experiment.

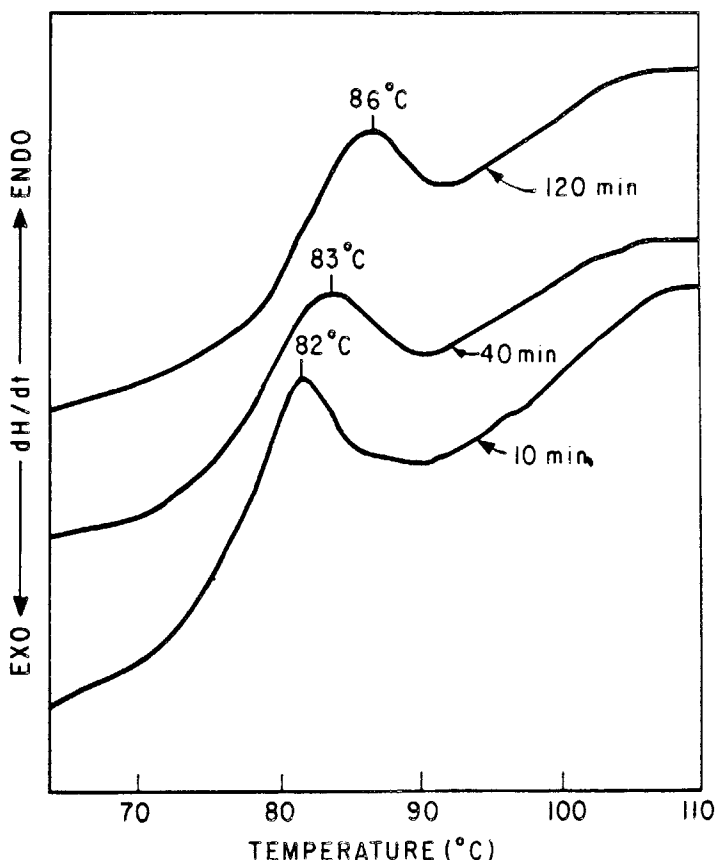


Fig. 15. Thermograms of multilayer films of PEOx/SAN. Samples were heated at 140°C for different lengths of time and stored for 17 days before running the experiment.

values determined separately for PEOx and SAN 25 (see Fig. 13) indicate that negligible PEOx-SAN diffusion occurred during the coextrusion process.

As a final point on thermal behavior some observations relating to the effects of physical aging are noted. Microlayer film of the miscible pair PEOx and SAN 25 which had been heated at 140°C for 10 min were reexamined by DSC following 10 months of storage in a dessicator at room temperature. Figure 14 shows the thermogram for such a sample obtained while heating to 137°C. An excess enthalpy peak due to this aging appears at a temperature about 10°C higher than would be expected for pure PEOx aged in a similar manner.³² There is no such peak for SAN-rich phases, which is not surprising based on its higher T_g and previous experience. A second scan after immediate quenching from 137°C erased this peak to give a scan entirely comparable to an unaged film which had been heated at 140°C for 10 min (see Fig. 9).

The nature of this enthalpy relaxation process was further explored by examining samples which had been heat treated at 140°C for varying lengths of time and subsequently aged at room temperature for a relatively brief period of 17 days. As seen in Figure 15, the peak of the heat capacity overshoot that developed on aging shifts from about 82 to 86°C as the thermal

treatment time increased from 10 to 120 min. There is also a slight rise above the melt base line near the end of the broad transition region. The net result of increased time for diffusion at 140°C is to shift the enthalpy relaxation peak which develops on room temperature aging to higher temperatures. This is reasonable based on the increase in T_g caused by increased addition of SAN to the PEO_x-rich end of the composition spectrum. Apparently the very high T_g for the SAN-rich end of the spectrum does not permit significant physical aging at room temperature. We mention these observations for two reasons. First, the results demonstrate that, even though there is only a single but broad T_g for these films after intermediate times for diffusion, there is a concentration gradient resulting in a spectrum of T_g 's that continuously overlap to appear as one and, thus, there is a spectrum of propensities for sub- T_g annealing. Second, the development of enthalpy relaxation peaks during storage can add a complicating element to the thermal analysis for diffusion progress, but it can be eliminated by a careful thermal pretreatment protocol.

Optical Measurements

Optical transmittance of the as received microlayer film based on PEO_x and SAN 25 was measured as a function of wavelength as mentioned previously (see lower curve in either of the four parts of Fig. 16). As expected, this film consisting of microlayers having different refractive indices and relatively sharp interfaces produces a complex pattern of minima and maxima similar to those described by Alfrey et al.^{27,28} for reflectance. As this film was heated to temperatures where diffusion toward a spatially homogeneous concentration occurs, the optical transmittance progressively changed with time. No attempt is made here to analyze these changes quantitatively; however, the most significant issue is the progressive relaxation of the amplitude between the various minima and maxima. After sufficient time, which varied with temperature of heating as seen in Figure 16, this process became essentially complete relative to the sensitivity of this measurement. Based on these apparent times to completion for the various temperatures, an activation energy of about 8 kcal/mol was estimated for the diffusion process. There is good qualitative agreement between the time scales for the progress of diffusion as judged by the optical and the thermal measurements.

SUMMARY

These results show that some qualitative information about the rate of mutual diffusion between miscible polymer pairs can be obtained from relatively crude multilayer films made by solution casting methods using thermal analysis to follow the change in glass transition behavior as a means to monitor the relaxation of the initial square wave concentration profile. Coextrusion technology can be used to create more precise layering and to reduce layer thickness to a point where the diffusion process is completed on a more rapid time scale which is important for systems having very low diffusion coefficients. Furthermore, creating microlayers of thickness of the order of the wave length of light or less allows one to use a relatively simple optical technique for following the progress of diffusion. It was found that for

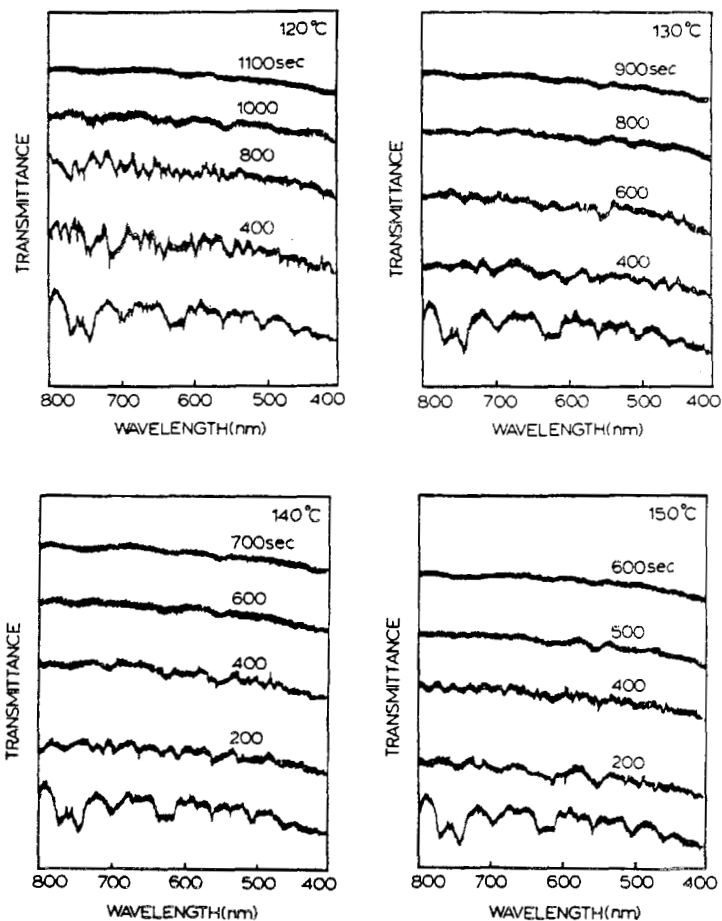


Fig. 16. Transmittance of light through the multilayer film of PEOx/SAN as a function of the heat history of the film and the wavelength. In each case the lower trace represents the transmittance through the as-received film.

a microlayer film based on PEOx and SAN that use of thermal and optical measurements to follow the diffusion progress gave results which are in good qualitative agreement. We believe that methods of analysis are possible which could make either the optical or the thermal approach for following the progress of diffusion more quantitative.

An inherent assumption of the thermal approach is that diffusion is slow enough that very little change in the concentration profile occurs during the course of a thermal scan. Application of this approach must be careful to avoid complications associated with physical aging and to allow for the breadth of the glass transitions of blends at diffusional equilibrium as these can be significantly larger than those for the pure components in some systems.

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