

The Melt Elasticity of Polymer Blends: Polystyrene/ Poly(methyl Methacrylate)

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Synopsis

Samples of general-purpose polystyrene and poly(methyl methacrylate) were melt blended in a special mixer-extruder over the complete range of compositions from 100% polystyrene to 100% poly(methyl methacrylate). The blends were characterized for their melt rheological characteristics in a melt elasticity tester which measured their stress-strain behavior and strain recovery characteristics as a function of time. In addition, the blends were processed through a laboratory fiber spinning apparatus wherein the spinline tension was measured. Large maxima in the amount of recoverable strain, in the time for the strain recovery to finish, and in the melt tension were observed at a weight percent composition of 40% polystyrene and 60% poly(methyl methacrylate). The melt stress-strain curves showed double yield points at certain compositions. The results are discussed in terms of a model consisting of two interpenetrating continuous phases.

INTRODUCTION

There is a great deal of interest today in blends or "alloys" of both compatible and incompatible polymers. The practical motivation for this interest is the achievement of enhanced end product properties as, for example, increased impact strength in the case of rubber-modified polystyrene or rubber-modified polypropylene. It is well known that the melt flow behavior in processing of polymer blends is complex and does not follow a simple additive relationship.

The objective of the research described here is the presentation of data on the melt properties of blends that may assist in the understanding of this complex behavior. The selection of the two polymers studied, polystyrene and poly(methyl methacrylate), was not made on the basis of the end product properties of their blends; rather, they were selected to give a relatively simple system for greater possibility of understanding the melt rheology of blends. Both are essentially linear polymers which do not crystallize and have reasonably close glass transition temperatures.

EXPERIMENTAL

Materials and Blend Preparation

The polystyrene used was a general-purpose, crystal, extrusion-grade material with a glass transition temperature T_g of 104°C. The poly(methyl methacrylate) was a general-purpose injection molding-grade material with a T_g of 112°C.

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The melt blending was performed in an elastic melt extruder, (EME).^{1,2} This type of mixing extruder has been found to be very useful in the preparation of blends of both compatible and incompatible polymers over wide ranges of molecular weight and melt viscosity. The pellets of the feed composition are introduced to the extruder and are first subjected to a melting and random mixing experience to produce a uniform spatial distribution of the components. Then, as the melt progresses through the EME, it is subjected to a large magnitude of stringing out, or extensional deformation, that causes the domains of the two polymers to achieve very large areas of intimate contact.

This process of melt blending has been found to produce blends of two continuous-phase morphologies.³ For example, if polystyrene and polyethylene are melt blended in an EME and the extrudate is then immersed in toluene, the polystyrene is solution extracted leaving behind the polyethylene in a form that somewhat resembles an open-cell foam, indicating that the polystyrene was a continuous phase in the open cells of the polyethylene. This two-phase interpenetrating network morphology has been found even in extreme cases, such as when 1% polyethylene is blended with 99% polystyrene and when the polystyrene is solvent extracted a fine, three-dimensional cobweb of polyethylene remains.

The blends of polystyrene and poly(methyl methacrylate) were prepared by first weighing out pellets at 5% intervals of composition and then tumbling the individual batches. Each individual composition was then fed into the EME. The $\frac{1}{8}$ -in.-diameter extrudate was then pelletized and injection molded into preforms for the melt elasticity tests.

In the case of the materials used for the melt spinning tension tests, the blending was done in an EME that was an integral part of the fiber spinning line. A schematic sketch of this apparatus is shown in Figure 1. The same polystyrene and poly(methyl methacrylate) were weighted out for the various compositions, dry tumbled, and then fed to the EME. The approximately $\frac{1}{8}$ -in.-diameter extrudate was melt drawn at a constant rate to form an approximately 0.0014-in.-diameter fiber. The temperature of the melt as it came from the extruder was 220°C. As the fiber was drawn, it passed through a pulley arrangement that measured the melt tension.

Melt Elasticity Test Procedure

The melt elasticity tester⁴ has been described in detail elsewhere,⁵ but a brief description here may be of assistance in interpreting the results. The preformed specimen is placed in a heated cuplike member. A central cylindrical member

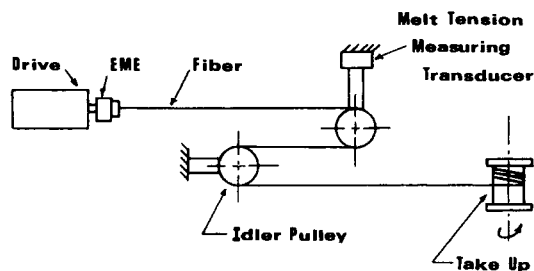


Fig. 1. Melt spinning tension apparatus, schematic.

is then placed on top of the specimen in a coaxial manner with respect to the cup. As the material melts, the specimen fills the annular space between the inside of the cup and the central cylindrical member, as shown in Figure 2.

After thermal equilibrium has been established at the desired test temperature, the cup is rotated about its axis of symmetry while the internal central cylindrical member is restrained by the restraining arm acting against a stationary force transducer. As a result, the specimen is sheared in a manner similar to a Couette viscometer. Since the rate of rotation is preset and known, the amount of strain γ_a applied is known as a function of time. Concurrently the force transducer, through the lever ratio of the restraining arm, measures the resulting stress. The result is a stress-strain curve for the melt.

After the desired amount of strain γ_a has been applied, the rotation of the cup is abruptly stopped and the restraining arm is concurrently released from the force transducer. The central cylinder then rotates according to the elastic strain recovery of the specimen. The motion of the central cylinder is recorded as a function of time by a photographic technique. The result is a plot of elastic strain recovery γ_r as a function of time.

All melt elasticity tests reported here were performed at 200°C, at an applied shear magnitude γ_a of approximately 10 strain units and at an applied shear rate $\dot{\gamma}_a$ of approximately 2 sec⁻¹.

RESULTS

The strain recovery curves as a function of time up to 900 sec for 100% polystyrene and blends of polystyrene and poly(methyl methacrylate) up to 40% polystyrene and 60% poly(methyl methacrylate) are shown in Figure 3. The following observations should be noted:

(1) The magnitude of the melt elasticity as shown by the amount of recoverable strain increases as the poly(methyl methacrylate) content increases from zero, pure polystyrene, to 40% polystyrene, 60% poly(methyl methacrylate).

(2) For compositions from 100% polystyrene to 75% polystyrene plus 25% poly(methyl methacrylate), the amount of recoverable strain increases slightly, but each strain recovery curve in this range of compositions shows a rapid initial recovery and the strain recovery process is finished in a short period of time.

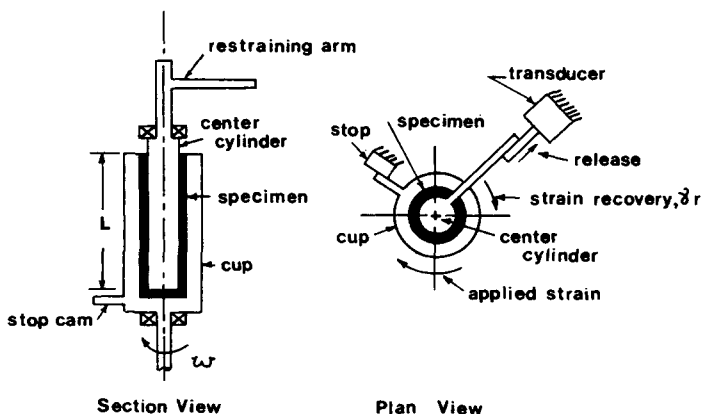


Fig. 2. Melt elasticity tester apparatus, schematic.

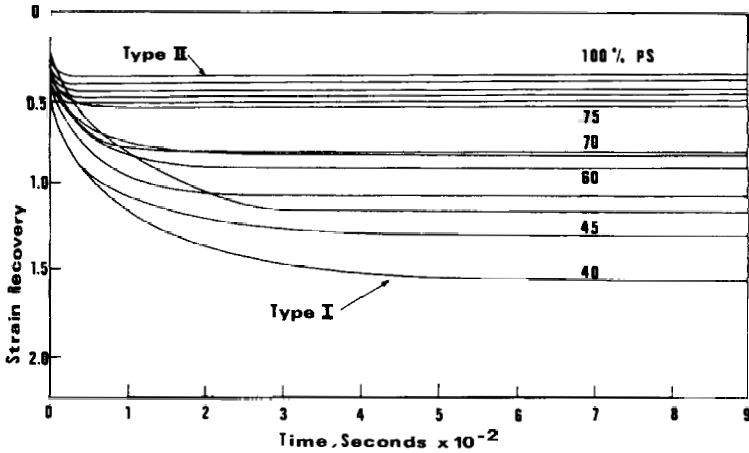


Fig. 3. Strain recovery of blends of polystyrene and poly(methyl methacrylate) up to 40% PS-60% PMMA.

(3) For compositions containing less polystyrene and greater percentages of poly(methyl methacrylate), for example, 70% polystyrene and 30% poly(methyl methacrylate), there is an abrupt change in the shape of the time-dependent strain recovery curve. The initial recovery rate is slower. The total amount of recovery is larger, and as the composition goes to 40% polystyrene with 60% PMMA, the strain recovery process is still going on after 900 sec.

The strain recovery curves fall into two distinct categories: recovery that continues for long periods of time to large magnitudes of strain recovery (for reference purposes this will be called type I) and recovery that is smaller and finished in a short period of time (type II). The initial recovery rate, 0-1 sec, often appears to be more rapid in type II than in type I, but this is not universally the case.

For compositions containing less polystyrene and more PMMA, the amount of elastic strain recovery decreases, as shown in Figure 4. In the composition

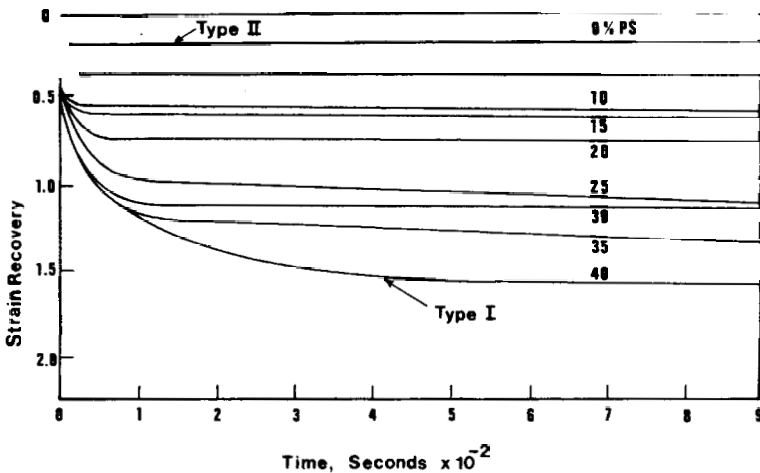


Fig. 4. Strain recovery of blends of polystyrene and poly(methyl methacrylate) from 40% PS-60% PMMA to 100% PMMA.

range containing a moderate amount of polystyrene, the strain recovery is large and takes a long time, type I. But as the 100% PMMA composition is approached, the elastic strain recovery becomes less in magnitude and is finished more rapidly, type II.

In summary, as the composition of the blend is changed from 100% of one polymer to 100% of the other polymer, the elastic strain recovery changes from type II, small, to type I, large and slow, and then back to type II. The "transition" from type I to type II takes place at approximately 25–75% weight compositions at each end of the composition scale.

The data of the two previous figures are summarized in Figure 5. Here the total amount of recoverable strain and the time for the strain recovery process to be finished are plotted as a function of blend composition. There is a very large maximum in both the total amount of elastic strain recovery and the time for the strain recovery process to be finished at a composition of 40% PS and 60% PMMA. The time for the strain recovery process increases smoothly to the maximum from both ends of the composition scale. The total amount of strain recovery increases in an irregular manner from both ends of the composition scale. This is in keeping with the "transition" or change of shape of the time-dependent strain recovery curve from type II to type I as a function of composition at constant temperature.

The fiber melt spinning tension as a function of composition is also shown in Figure 5. There is a maximum in the melt tension at the same composition, 40% PS and 60% PMMA, at which the maximum is observed in the total strain recovery and the time for the strain recovery process to be finished. It would appear that there is a correlation between the elastic strain recovery characteristics and the tension in melt spinning.

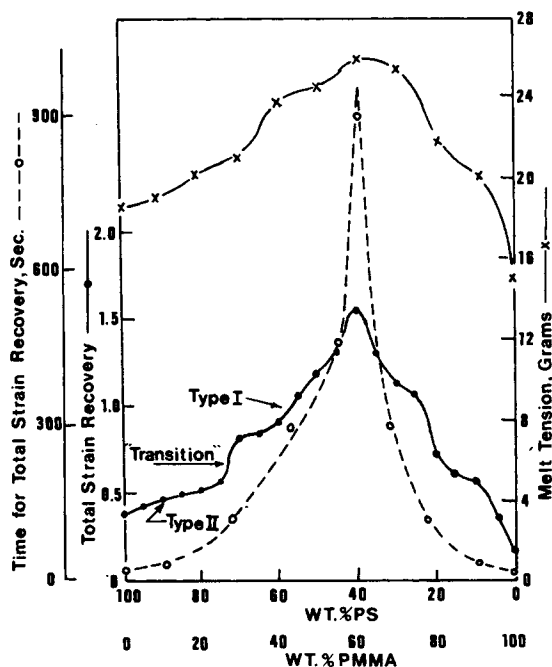


Fig. 5. Total recoverable strain, time of finish of strain recovery, and melt spinning tension as function of composition.

The stress-strain curves for pure PS and pure PMMA, together with the stress-strain curve for the 40% PS and 60% PMMA, the composition of the maximum melt elasticity, are shown in Figure 6.

The stress-strain curves for the two pure polymers both exhibit the standard expected behavior. As the strain is applied at a constant rate, the stress rises in an essentially linear manner, then reaches a yield point, or stress overshoot, and falls to a constant value associated with steady-state flow. For the case of the 40% PS and 60% PMMA, the result is quite different. The stress rises to a yield point, decreases, and then rises again to a second yield point. The stress then decreases monotonically and is still decreasing at a strain magnitude of ten strain units. This double yielding is also observed at other compositions near 40% PS and 60% PMMA, as shown in the three-dimensional plot of stress-strain as a function of composition in Figure 7. It should also be noted that the yield stress or stress overshoot of the blends is much higher than that of melts of either pure component.

DISCUSSION

Polymer blends prepared by melt mixing in the EME as mentioned in the section on blend preparation have been found to have a morphology consisting of two continuous phases. It has not been found possible to verify this morphology in the present system of PS-PMMA by the solvent extraction method, but certain secondary information leads to an indication that this same structure exists in this system of blends.

Polystyrene and poly(methyl methacrylate) are considered to be incompatible by classical definition. This is consistent with the observation that the blends in both the glassy and melt states are opaque and have a very bright white appearance. This indicates that two phases are present and that the incident light is reflected by the phase interfaces.

To confirm that two phases are present in the blends the samples were tested in a differential scanning calorimeter (DSC). The results are shown in Figure 8. The test conditions were as follows: specimen weight approximately 12 mg, heating rate 10°C/min, high sensitivity.

The 100% PMMA shows a T_g at 112°C, and the 100% PS shows a T_g at 104°C.

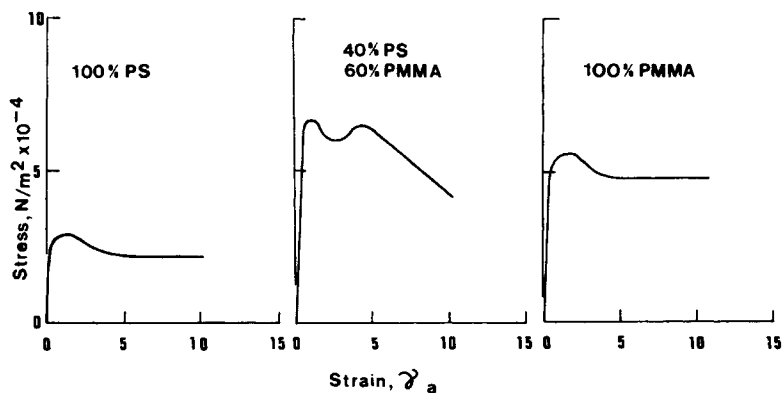


Fig. 6. Stress-strain curves of 100% PS, 40% PS-60% PMMA, and 100% PMMA.

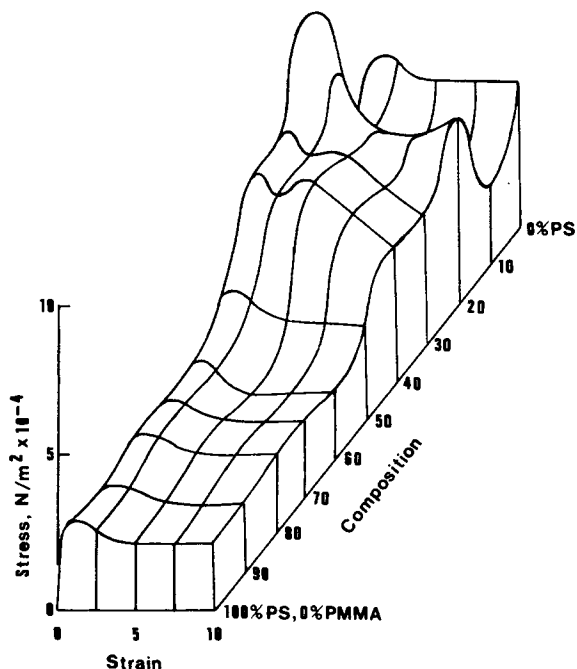


Fig. 7. Stress-strain behavior as function of composition.

The blends show two distinct glass transition temperatures. This is a strong indication that two phases are present. It is interesting to note that as polystyrene is added to poly(methyl methacrylate), the PMMA glass transition increases from 112 to 119°C at 40% PS and 60% PMMA and also becomes sharper,

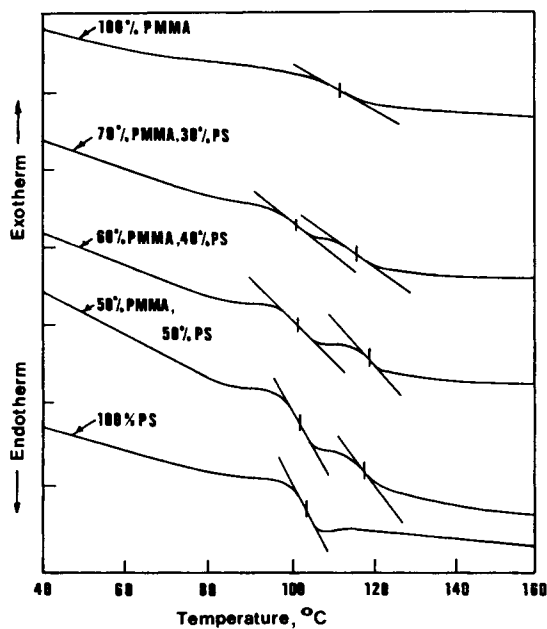


Fig. 8. Differential scanning calorimeter curves as function of composition.

as indicated by the slope in the DSC curve. As poly(methyl methacrylate) is added to polystyrene, the PS glass transition temperature does not change and its sharpness decreases. These observations may indicate some interaction of one polymer with the other.

The stress-strain curves of the blends may be interpreted in terms of a continuous two-phase model. As the external strain is applied to the melted blend, both phases experience essentially the same internal strain. One phase yields, thereby reducing the measured stress, but the applied strain is still increasing in the other phase, and the stress again rises until this phase yields. This would be the response of a model consisting of two ductile materials with different yield strains coupled in parallel. If a series model corresponding to one continuous phase with the second discontinuous phase dispersed in it was used, one would expect only one yield point corresponding to the continuous phase's response, and the discontinuous phase would act simply like a filler in the yielded and flowing continuous phase. The point is that in the continuous two-phase model the externally applied strain is felt approximately equally by both phases, but in the series model, once the continuous phase has yielded, the discontinuous phase only feels a stress transmitted through the continuous phase, not a monotonically increasing externally applied strain.

It may also be possible to interpret the elastic strain recovery data in terms of the continuous two-phase model. If both phases have experienced essentially the same externally applied strain, then both phases will contribute to the strain recovery in an additive manner. That is, if both phases were highly elastic, the composite would exhibit a high recoverable strain. If one phase was highly elastic and the other phase was not, the composite would also exhibit a high recoverable strain. On the other hand, if the continuous phase is not elastic in the series model, there will be little if any strain recovery even if the discontinuous phase is elastic.

In any two-component system the question of phase inversion must be considered. In a model consisting of a continuous phase and a discontinuous phase, an inversion takes place as a function of composition such that the phase that was continuous becomes the discontinuous phase, and vice versa. If this were the case here, there would be an abrupt change in the strain recovery characteristics at the phase inversion composition. On each side of the inversion composition the strain recovery characteristics would be essentially those of the continuous phase. With this model involving a phase inversion it would be difficult to explain the very large maximum in elastic recoverable strain.

The maximum in the amount of recoverable strain of 40% PS and 60% PMMA blend is approximately four times the recoverable strain of either of the two individual components. This would indicate that there is an interaction between the two components that increases the melt elasticity. It would be premature to give a positive explanation of this interaction on the basis of present information, but one could speculate that on the basis of a continuous two-phase model there is a strong physical interaction between the phases at their interfaces which causes a high recoverable strain.

Although these two polymers are incompatible, it should be recognized that in the melt blending process used, there is a high probability that some molecules of one polymer are mixed into the phase that is predominantly the other polymer, and vice versa. These molecules could then be physically trapped in the phase

composed predominantly of the other polymer and because of the very low diffusion rate of large molecules they would stay there. This might take place most often in the region near the phase boundary.

Another possible clue can be seen in Figure 5. In the composition range from 100% PS to about 75% PS plus 25% PMMA, the amount of recoverable strain is small and only increases slightly with the addition of PMMA. This has been designated type II behavior. Further addition of PMMA causes a sharp "transition" in the amount of recoverable strain to type I, large and slow. A similar situation is indicated at the other end of the composition spectrum. As PS is added to PMMA the recovery characteristics change from type II to type I. This is also seen in Figures 3 and 4.

Previous studies⁵ have shown that in pure polystyrene there is a "transition" from type I to type II strain recovery behavior as the temperature of the melt is increased. A similar "transition" as a function of temperature has been observed in pure poly(methyl methacrylate).⁶ The temperature of the strain recovery tests on the PS-PMMA blends described herein was 200°C. This is above the temperature-dependent "transition" for both pure PS and pure PMMA. As a result type II response is observed at both ends of the composition spectrum.

But the interesting point is that type I response, large, long, and slow, is observed in the strain recovery response in the middle range of compositions. A possible explanation is the following:

As the blend is melt mixed in the EME, some molecules of polymer A are transported physically into regions of predominantly polymer B because of the high elongation orientation experience in the shear zone of this mixing extruder [Fig. 9(a)]. When the material leaves the extruder, the externally applied shearing stops and the molecules of both polymers A and B recoil to seek their lowest energy state, [Fig. 9(b)]. Since the molecules of polymer A are incompatible with those of polymer B, they seek to recoil in a manner to bring their own segments in close proximity to each other because they are compatible with themselves but not with the surrounding B molecules. In the process of this recoiling upon themselves, there is a high probability that some segments of molecules B will be caught by the recoiling A molecules. When the segments of molecules A have finished recoiling upon themselves, they have reached a low-energy state but have also trapped some segments of polymer molecules B in the process. The result is the formation of a local region which prevents free motion of molecules of polymer B. When the externally applied strain is applied during the melt elasticity test [Fig. 9(c)], the molecule B resists being disrupted from the low-energy state associated with being coiled back on itself due to compatibility. The result is somewhat like a network point and thereby makes possible a large, elastic recoverable strain. If we consider polymers A and B to be the pure polymers at the ends of the composition scale, then it would seem reasonable to expect a maximum in the recoverable strain in some middle range of composition.

This model may also be used to explain the large maximum in the yield stress, or stress overshoot, in the middle range of compositions. If the structure shown in Figure 9(b) exists in the phase interfaces of these compositions, then it would be expected that a larger stress would be required to overcome the entrapment caused by molecule A on molecules B before this network like an interaction point would be broken down to allow the usual flow process to take place.

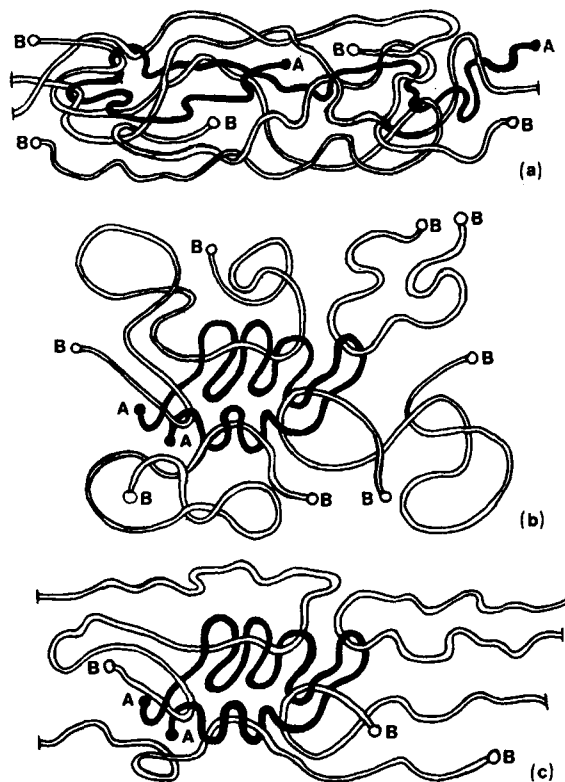


Fig. 9. Schematic molecular model.

It is not the intention of the authors to present an absolute, definitive model of the process involved in the results of these experiments. Rather, the intent is to present these thoughts for the purpose of consideration and discussion in the hope that a greater understanding of the behavior of blends may be achieved in the future.

The idea of molecular mixing, or mixing at the molecular level, of incompatible polymers is not popular. Many studies of blends of incompatible polymers have indicated that domains of 1–50 μm are formed depending on the method of preparation of the blend. In the research described above, the mixing was carried out in an extruder which subjects the polymers to very high elongational deformations at high deformation rates. It would seem possible that under these conditions some molecules of polymer A would be mixed into domains of polymer B, and vice versa, and because of the very slow diffusion rates of macromolecules they would not have the opportunity to diffuse back into their own domains.

A perhaps overly simplistic picture of the concept of molecular mixing would be the following: Suppose the extruder is operated with a feed of pure polymer A. Then one molecule of polymer B is introduced into the feed. It would be trapped somewhere in the mass of A. The number of molecules of B that could be introduced into A in this manner before domains of B would be formed is open to question, but some, perhaps only a few, could be mixed at the molecular level.

CONCLUSIONS

(1) Blends of polystyrene and poly(methyl methacrylate) produced by melt mixing exhibit a very large maximum in their strain recovery magnitudes and times of recovery in the melt state at a composition of 40% polystyrene and 60% poly(methyl methacrylate).

(2) Blends of the same composition exhibit a maximum in melt tension in a fiber spinning operation.

(3) These blends also exhibit double yield stresses.

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