

# Structure-Property Relationships in Copolymers to Composites: Molecular Interpretation of the Glass Transition Phenomenon

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## Synopsis

Structure is taken as the main theme in outlining the mechanical properties of polymer composites. Examples of two-component polymer systems are selected from the literature showing their morphology, as evidenced from electron micrographs, and their corresponding mechanical properties, as evidenced by dynamic mechanical spectra. A compatibility number,  $N_c$ , is defined in a continuous scheme from a compatible system (one glass transition,  $N_c \rightarrow \infty$ ) to an incompatible system (two glass transitions,  $N_c \rightarrow 0$ ). The point at which semicompatibility occurs,  $N_c \cong 1$ , is taken as the approximate universal segmental length associated with a glass transition. This length of 150 Å allows for 100 to 5000 C—C bonds for an associated glass transition. The ramifications of this molecular interpretation of a glass transition are discussed, resulting in a denouncement of the time-temperature correspondence principle and a new interpretation of short-segmental block copolymers.

## INTRODUCTION

Polymer science has entered an era in which great emphasis is now being placed on the technological applications of existing polymers rather than the development of new monomers. The art of tailoring polymers has emerged which relies on the mixing of two or more homopolymers with differing properties to obtain some synergistic effect. In light of this importance placed on heterogeneous systems, this work will discuss the fundamental relationships between the morphology of a two-component polymer system and the observed glass transition phenomena.

Early work done on two-component systems was in the area of the copolymerization of two different monomers to give properties similar to that of a new homopolymer, i.e., one glass transition. Concurrently, a technology was developed which involved the mechanical blending of two polymers to give a two-phase system, i.e., two glass transitions. From the copolymer perspective, it has recently been observed that nearly all copolymerizations involve some degree of phase separation.<sup>1</sup> From the two-phase composite perspective, new synthesis methods have now been developed which can greatly control the degree of phase separation, which was limited previously to the basic chemical incompatibility of the two components. Examples of controlled composite structures are graft copolymers, block copolymers, and interpenetrating polymer networks (IPN's). This work seeks to bridge the gap in the structure-property relationship that

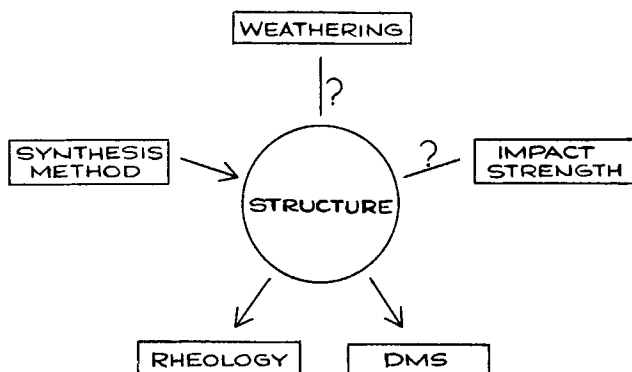


Fig. 1. Schematic diagram with structure as the central theme.

exists between the two approaches of copolymer theories and the present technology of two-phase polymer blending.

A unified approach is given here which emphasizes the importance of the resulting morphology of a two-component system and not the synthetic routes taken to reach such a morphology. This approach deemphasizes the terms copolymer, blend, and graft copolymer as a means of identifying materials. Rather, structure is taken as the central basis for identifying materials. Figure 1 shows a schematic of this theme. It says that one cannot directly relate a synthesis technique to a resultant physical property. Comparisons can only be made on an indirect basis by first defining the individual relationships involved. The symbol ( $\rightarrow$ ) in Figure 1 is called a conditional in Eulerian logic. It means that, for example, if the synthesis conditions are fully documented, the resultant structure can be predicted. It does not mean the reverse is true, however, since there are several synthesis methods which may have given the same resultant structure. A similar conditional relationship exists between a material's structure and its dynamic mechanical spectra (DMS). Other relationships have not yet been determined, such as the structure-impact strength case. Reference 3 investigates this very relationship.

False generalizations have arisen by not recognizing this type of logic. For example, it has been widely accepted that the procedure of grafting the rubber modifier onto the glassy matrix improves impact strength. We now have seen cases where the opposite is true.<sup>2</sup> In fact, what is crucial for impact improvement is an optimum rubber particle size. The amount of grafting required for impact strength depends on the compatibility of the components and other variables which control the particle size required. Another attempt at making a synthesis-property correlation has been to equate a low temperature loss peak in DMS with impact strength. Through the scheme of Figure 1, it can be shown,<sup>3</sup> by basic rules of logic, that such a loss peak is neither a necessary nor a sufficient condition for impact strength, substantiating experimental evidence.<sup>4</sup>

In this paper, one particular relationship will be examined—the structure-dynamic mechanical properties relationship. Examples of two-component systems are selected from the literature which show electron micrographs (EM) and their corresponding DMS. From this discussion will emerge an estimation of the segmental size necessary for an observed glass transition of a homopolymer,

an index for defining compatibility, the use of DMS as a tool for predicting ultimate properties such as impact strength, and a new interpretation of short-segmental block copolymers.

### COMPATIBILITY DEFINED

Chemical compatibility is defined in classical chemistry as complete molecular mixing. With respect to macromolecules, whose molecular size can be large, this molecular definition loses its significance. Many heterogeneous systems would be considered homogeneous by this molecular mixing definition, even though two phases are seen in electron micrographs and two  $T_g$ 's are observed with mechanical techniques. What we are really interested in with macromolecules is the mixing of segments of the polymer chains.

The compatibility or homogeneity of a composite can only be defined by the technique used to measure the system.<sup>5</sup> Thus, compatibility is a relative term which can be defined by a compatibility number

$$N = \frac{\text{exp. probe size}}{\text{domain size}} \quad (1)$$

The experimental probe size in a mechanical test, for example, would be the segmental length associated with the  $T_g$  phenomenon. The domain size is the average length in which only one component exists:

when  $N_c \rightarrow \infty$ , compatible system

when  $N_c \rightarrow 1$ , semicompatible system

when  $N_c \rightarrow 0$ , incompatible system

Figure 2 is a schematic representation of a composite which illustrates the full range from that of an incompatible to a compatible system. The top figures represent what would be seen in an EM, and below are the corresponding DMS. The arrows represent the probe size. When  $N_c \rightarrow 0$ , two transitions are observed, representing the  $T_g$ 's of the individual components. A change in volume fraction of the components would merely result in a change in peak heights but not a shift along the temperature axis.

For the compatible system ( $N_c \rightarrow \infty$ ), the composition fluctuations are small enough to average out over the probe distance so that only one main transition is observed, i.e., copolymer behavior. A change in volume fraction of the components results in a shift along the temperature axis.

For the semicompatible case ( $N_c \rightarrow 1$ ), a broadened modulus curve is observed. The  $\tan \delta$  curve shows a great deal of damping over the entire temperature range from the low to the high transition of the original components. Note that at no time is there a case where the two transitions are shifted inward due to some interaction of the components.

Figure 3 summarizes the progression in the  $\tan \delta$  curves from Figure 2 in going from an incompatible to a compatible system. This is the first attempt at describing the entire progression in going from a one to a two transition material. The estimation of the domain size at which this inversion takes place ( $N_c \rightarrow 1$ ) can be taken as a measure of the experimental probe size. *Therefore, the first known means of determining the size of the molecular distance which is*

$$N_c = \frac{\text{EXPERIMENTAL PROBE SIZE}}{\text{DOMAIN SIZE}}$$

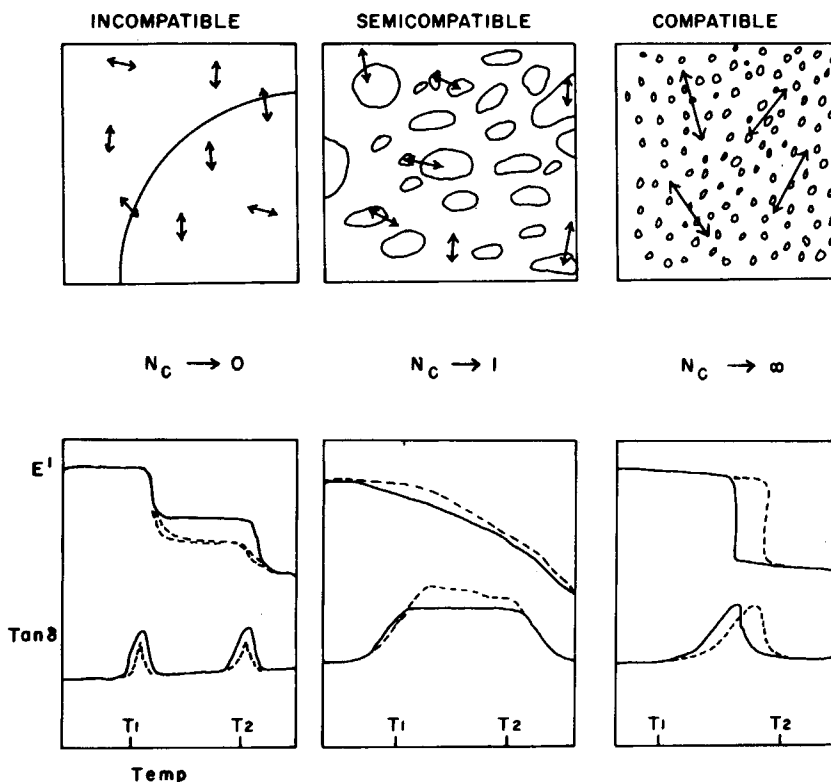


Fig. 2. Schematic diagram of electron micrographs of two-phase systems and the corresponding DMS below. Arrows represent probe size.

*undergoing a glass transition motion from a molecular standpoint has now been formulated.*

The ability to discriminate between one or two transitions must not be confused with a problem in resolution. Figure 4 shows a problem which is involved with resolution. When two polymers are mixed, the  $T_g$ 's of the components must be separated far enough apart on the temperature axis to distinguish between peaks. In this case, the two polymers are copolymers of poly(methyl methacrylate) (PMMA) and poly(butyl acrylate) (PBA). The copolymer with the higher PMMA content has a higher transition temperature than the copolymer of lower PMMA content. Only when the difference in PMMA content is greater than 25–30%, i.e., the  $T_g$  temperatures are separated far enough apart, can the mechanical peaks representing each copolymer be distinguished.

Figure 5 illustrates the real problem of this discussion. When butyl acrylate (BA) and methyl methacrylate (MMA) are copolymerized, a distribution of compositions results. At the start of the reaction, a PMMA-rich copolymer forms, whereas at the end of the reaction, a PBA-rich copolymer forms. The  $T_g$ 's of the two phases are well separated. However, only when the molecular weight i.e., the domain size, of the PBA-rich phase is large enough can an associated transition be observed.

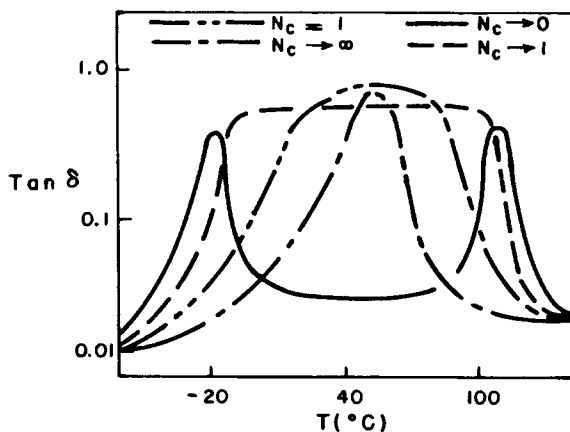


Fig. 3. Schematic progression of  $\tan \delta$  vs. temperature curves from an incompatible to a compatible system.

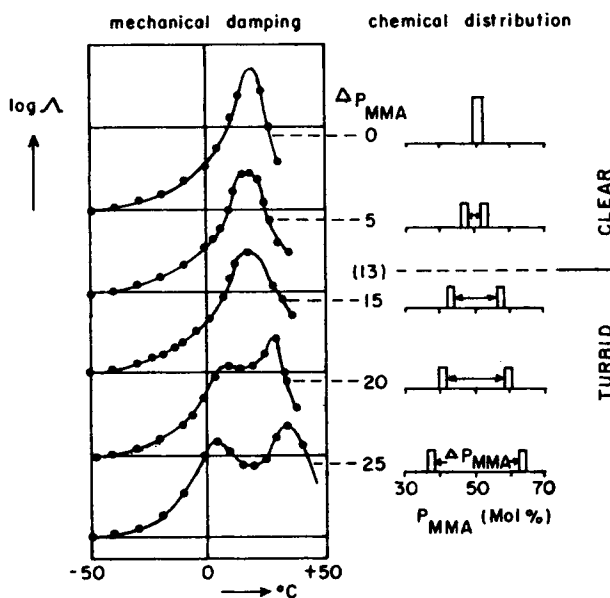


Fig. 4. Mechanical damping curves for various PMMA/PBA copolymers. Redrawn from reference 1.

### EM's VERSUS DMS\*

Frisch et al.<sup>6</sup> show an EM of a composite of a polyurethane and a polyacrylate system formed by a precipitated latex method. The polyurethane dispersed phase is of the order of 1 micron or larger. The DMS is shown here in Figure 6;  $E''$  indicates two  $T_g$ 's and is clearly an incompatible case.

Sperling et al.<sup>7</sup> show EM's of a polybutadiene/polystyrene (PB/PS) IPN. The high *cis*-PB case has a cellular domain structure of about 500 to 1000 Å. The

\* A discussion of synthesis methods is not in the scope of this paper. Examples were chosen because of the resultant structure, their ability to be observed in EM's, and the availability of DMS data at one frequency.

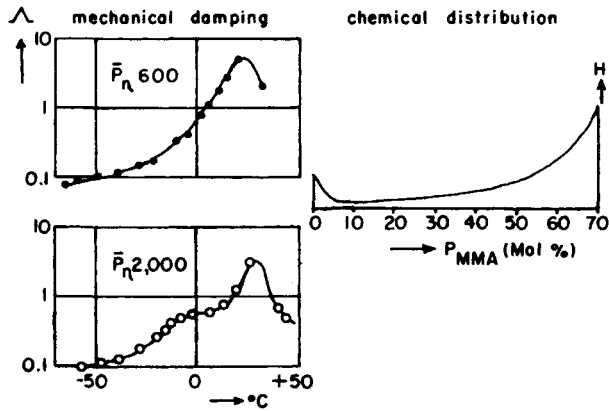


Fig. 5. Mechanical damping curves for a PMMA/PBA copolymer with a given chemical distribution.  $P_n$  is the degree of polymerization. Redrawn from reference 1.

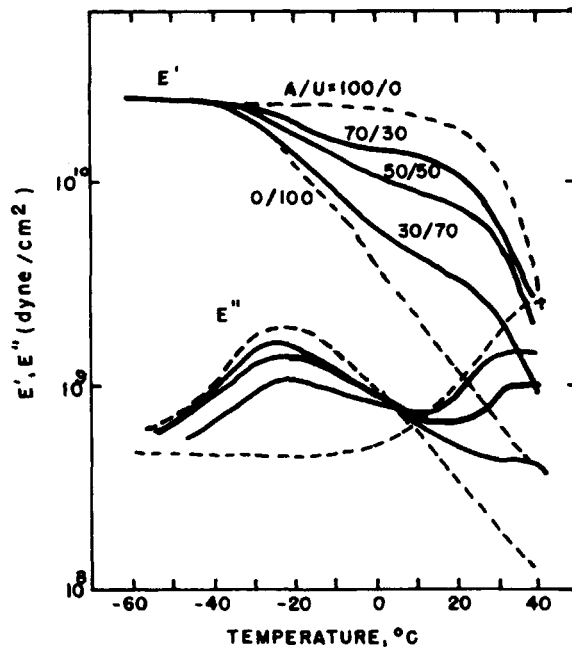


Fig. 6. DMS of a polyacrylate/polyurethane IPN system at 110 Hz. Redrawn from reference 6.

modulus curves of Figure 7 begin to show a broadening at this domain size, and thus we have an indication of the probe size.

In a study by Sperling et al.,<sup>8</sup> the compatibility of a poly(ethyl acrylate) (PEA)/PS IPN system was increased gradually by substituting PS with PMMA. Figure 8 shows the gradually decreasing heterogeneities. The cellular structure, rich in PEA, formed a web of about 1000 Å in size. A fine structure of about 100 Å was observed within the cell walls. Figure 9 shows that for a 1000 Å heterogeneity, two  $T_g$ 's are observed. When the cells decrease in size to about 100 to 300 Å (that of the fine structure), one broad transition occurs. It is the existence of this fine structure that can cause the inward shifting of transitions from a

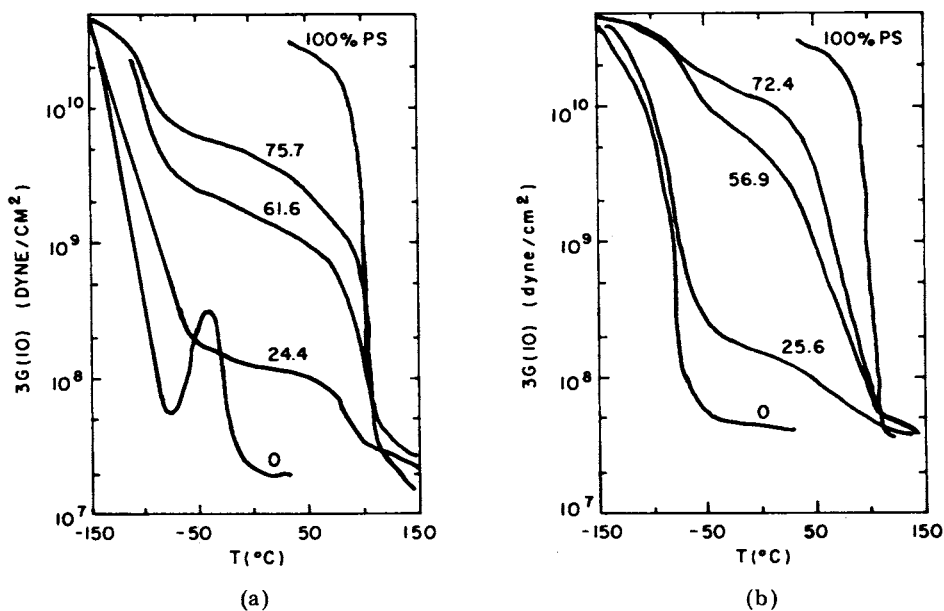


Fig. 7. DMS of (a) PB (high cis)/PS IPN and (b) PB (random)/PS IPN at 110 Hz. Redrawn from reference 7.

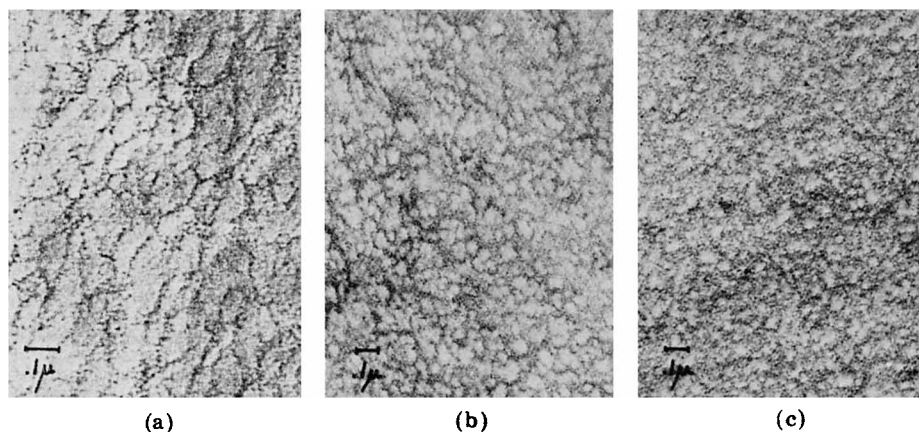


Fig. 8. Electron micrographs of (a) 49 PEA/51 PS, (b) 48 PEA/(14S-Co-38 MMA), and (c) 47 PEA/53 PMMA. Dark regions are the PEA domains. Taken from reference 8.

material with two  $T_g$ 's. Neither the glassy domain nor the cell walls are pure. They behave as copolymers which are richer or poorer in rubber content.

Matsuo<sup>9</sup> has done a similar study in compatibility control. In the blending of an acrylonitrile butadiene rubber (NBR) with poly(vinyl chloride) (PVC), increasing the AN content increases the compatibility of the rubber with PVC. Figure 10 shows an EM of such a series, with the corresponding DMS shown in Figure 11. This series dramatically indicates what was described in the schematic of Figure 1 when going from  $N_c \rightarrow 0$  to  $N_c \rightarrow \infty$ . With heterogeneities below about 200 Å, the composite behaves as a one- $T_g$  material. At the 200 to 1000 Å domain size range, broad transitions are observed.

It appears from these examples presented here that a "universal" domain size

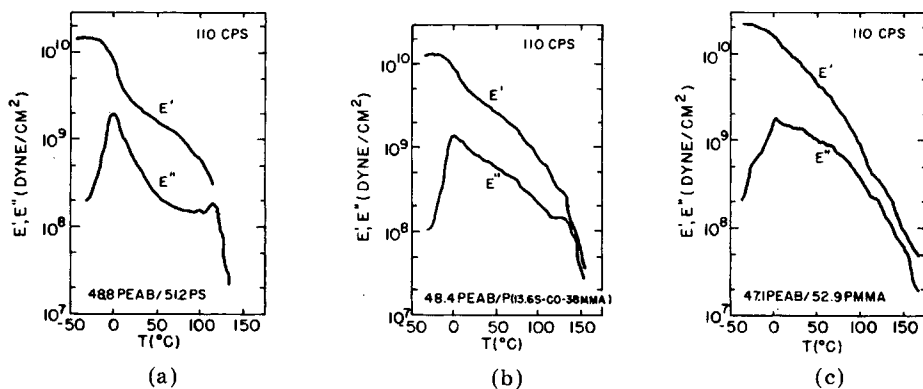


Fig. 9. (a)–(c) DMS of the materials shown in Fig. 8 at 110 Hz. Redrawn from reference 8.

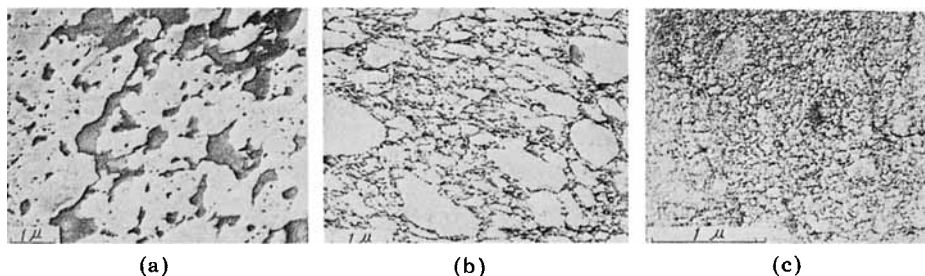


Fig. 10. Electron micrographs of (a) PVC/PBD (100/10) blend, (b) PVC/NBR-20 (100/5) blend, and (c) PVC/NBR-40 (100/15) blend. Dark areas are rubber domains. Taken from reference 9.

exists in which two-component polymers change from a two- $T_g$  material to a one- $T_g$  material. The domain size at the inversion point ( $N_c \rightarrow 1$ ) will be taken to be 150 Å. The use of EM's for determining particle size is only a crude one. Added to this are the problems of wide particle size distributions, irregular shapes, and cocontinuous networks. The 150 Å figure is admittedly only a crude approximation. The "universality" of such a number could also be questioned. The examples given here, incorporating components of polybutadiene, polyurethane, poly(ethyl acrylate), polystyrene, poly(vinyl chloride), and poly(methyl methacrylate), are certainly only a small fraction of the large number of common polymer components possible. It is a substantial enough representation of commonly used polymers, however, to suggest that the 150 Å size is, in fact, a "universal" constant.

## RAMIFICATIONS OF THE 150 Å RULE

### Glass Transition Phenomenon

The single most important parameter in characterizing the mechanical behavior of amorphous polymers has *never* been identified in terms of molecular structure other than to assume that  $T_g$  is associated with some "long range coordinated chain motion." The glass transition is experimentally observed by a break in the thermal expansion, modulus, or heat capacity versus temperature. From the previous argument, we can now say that the glass transition



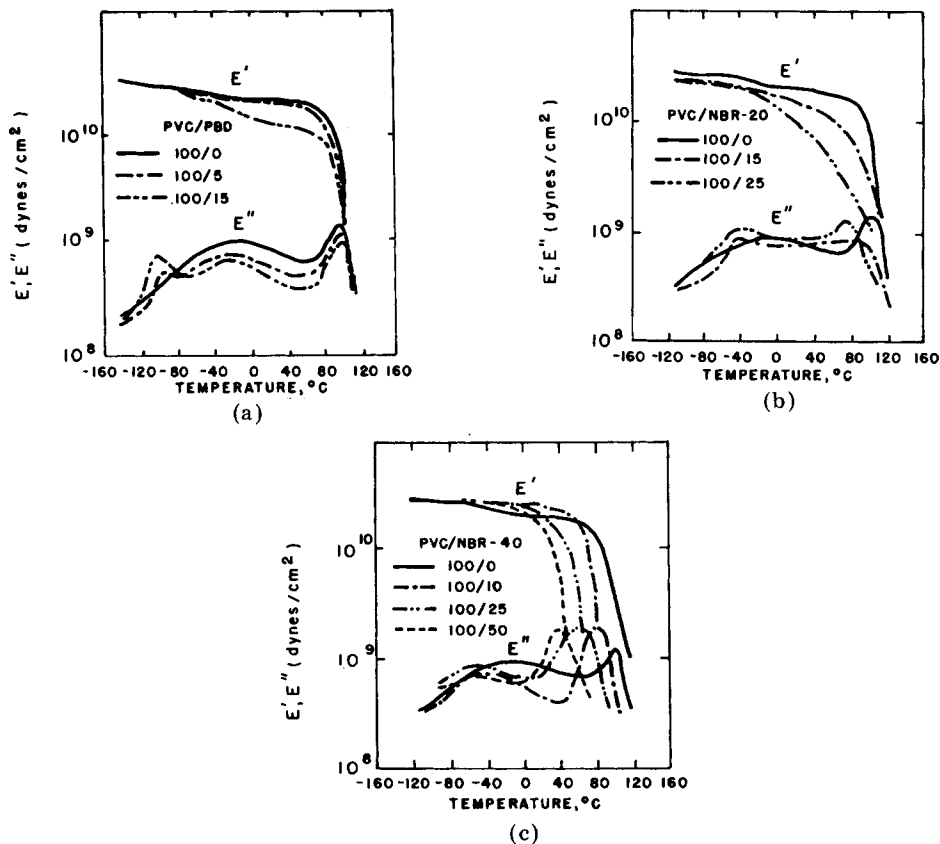


Fig. 11. (a)–(c) DMS of materials shown in Fig. 10, respectively, at 110 Hz. Redrawn from reference 9.

(at 110 Hz) is associated with an end-to-end distance of approximately 150 Å. This theory of a “universal” length is consistent with the Simha and Boyer<sup>10</sup> theory that the free-volume fraction is a constant. The number of monomer units per associated motion is then dependent upon the statistical conformation of the polymer. For a freely oriented C—C chain, the average end-to-end distance is given by<sup>11</sup>

$$\bar{r}^2 = 2nl^2 \quad (2)$$

where  $n$  is the number of C—C bonds,  $l$  is the length of the C—C bond, and  $\bar{r}^2$  is the mean squared end-to-end distance. Given  $l = 1.5 \text{ \AA}$  for a C—C bond, it would take about 5000 bonds for a coordinated motion. If the same polymer were in a “good” environment, and thus extended, or perhaps the monomer were stiff, then, as an extreme case,

$$r = nl \quad (3)$$

Then only about 100 units would be involved. The glass transition for a stiffer molecule then involves less monomer units but the same average end-to-end distance. The higher temperature needed for a transition of a stiffer molecule is a result of the higher threshold energy needed for the same end-to-end distance motion as that of a more flexible chain.

The fact that the two glass transitions of most composites are essentially the same as those of the components indicates that the conformations are basically the same in the individual phases as they are in the homopolymer state. It should be noted that this particular method of using a compatibility series to determine the size of a main transition (often termed  $\alpha$ ) could also be used to make assignments of secondary or minor transitions, e.g.,  $\beta$ ,  $\gamma$ ,  $\delta$ .

### Time-Temperature Superposition

The 150 Å rule was determined from DMS data measured at 110 Hz. It remains to be seen whether other frequencies give the same value. If this were also the case, it would then verify the correspondence between time and temperature. If, however, a change in frequency represents a differing end-to-end distance of a molecular motion, then the time-temperature superposition principle would not be fundamentally correct, since the shift of  $T_g$  due to a time change would not represent the same phenomenon as a shift due to a temperature change. It is known from an empirical basis that ductility and impact strength of rubber-modified glassy polymers require different domain sizes for different rates of impact. There is thus a hint of the possibility that varying the rate changes the size of the molecular motion.

The glass transition is a second-order thermodynamic transition in that there is a discontinuity of the second-order properties, e.g., thermal expansion and heat capacity. However, the glassy state is a nonequilibrium state due to the kinetic limitation on the rate of internal adjustment. The Gibbs and Di Marzio<sup>12</sup> theory takes this nonequilibrium effect into account by dealing only with  $T_2$ , the true second-order transition temperature, calculated to be about 50°C below  $T_g$ .

Barring that difference in a nonequilibrium glass state, the  $T_g$  measured from a volume expansion is an indication of the structural change, i.e., free volume. The  $T_g$  measured by DMS is an indication of the motions which are manifestations of the structure. That is, the  $T_g$  measured by DMS or any other means of applying stress can be indirectly correlated with the thermodynamic  $T_g$  only because the motions under stress are strongly dependent on the free volume. However, observing a  $T_g$  by a change in temperature (no stress) results in a different molecular superstructural reorganization than would a  $T_g$  observed isothermally by a long-time stress relaxation experiment. In other words, the *time-temperature correspondence principle as applied to main glass transition temperatures is not a fundamentally correct principle.*

Although it has been shown by Tobolsky<sup>13</sup> and Williams, Landel, and Ferry<sup>14</sup> that the superposition principle is limited to materials above  $T_g$ , it is commonly used as a tool for predicting long-term properties of glassy polymers from relatively short-time tests. Let us look carefully at the meaning of a master curve of a glassy polymer like polystyrene, constructed from a stress relaxation experiment with a reference temperature of 25°C. The predicted  $T_g$  would be about 8 decades of time from zero time, or more than 30 years. Clearly, the molecular motion occurring over 30 years under stress at 25°C in the glassy state, with a small free volume, would be different than that of the motions associated with a  $T_g$  observed from a dilatometry experiment. The pitfall here has been to assume that the glass transition is a kinetic phenomenon and then to apply

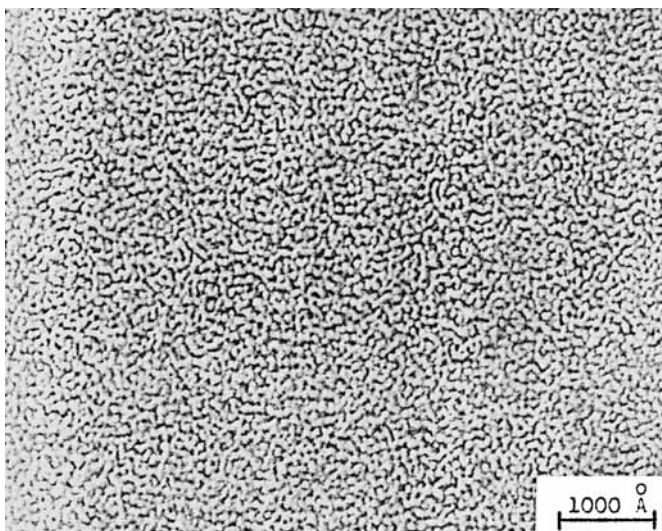


Fig. 12. Electron micrograph of a polyester urethane block copolymer. Taken from reference 16.

a time and temperature equivalence. The glass transition is a nonequilibrium thermodynamic phenomenon which is, for all practical purposes, independent of time.

Most polymer physicists have probably asked themselves the question: How many decades of time must I extrapolate a  $T_g$  measured from a dynamic experiment in order to correlate it to a  $T_g$  measured from a static experiment? The solution to this dilemma is that there is no such correlation, since the two experiments are representing different types of molecular motions.

### New Assignment of Short-Segmented Block Copolymers—Analysis of Polyurethanes

Figure 12 represents an EM of a polyester urethane block copolymer, and Figure 13 shows the DMS of a polyester and polyether urethane taken from a comprehensive study by Cooper et al.<sup>15,16</sup> The accepted interpretation has been to associate the low-temperature transition ( $\approx 0^\circ\text{C}$ ) with the transition of the soft polyether or polyester segments and to associate the higher temperature transition ( $>150^\circ\text{C}$ ) with the transition of the hard isocyanate segments. As the block lengths are increased (curves B to A), the  $E'$  curve begins to broaden. This broadening was accredited to the increases in crystallinity that can occur with longer blocks. However, Figure 14 shows that in the annealed, quenched, and control sample, they all show a broadened transition regardless of heat treatment. The classical assignments thus fall short of an explanation. Furthermore, no adequate explanation can be given for the decrease in the low-temperature  $T_g$  with increasing segmental length.

Under the new scheme presented in this work, the heterogeneities shown in Figure 12 are well below the  $150 \text{ \AA}$  level, and therefore the material should be considered as a copolymer. The  $\alpha_a$  transition ( $\approx 0^\circ\text{C}$ ) is the transition for the hard and soft segments. This assignment can also be substantiated by the fact that the  $T_g$  peak ( $\alpha_a$ ) shifts with variations in relative amounts of soft and hard

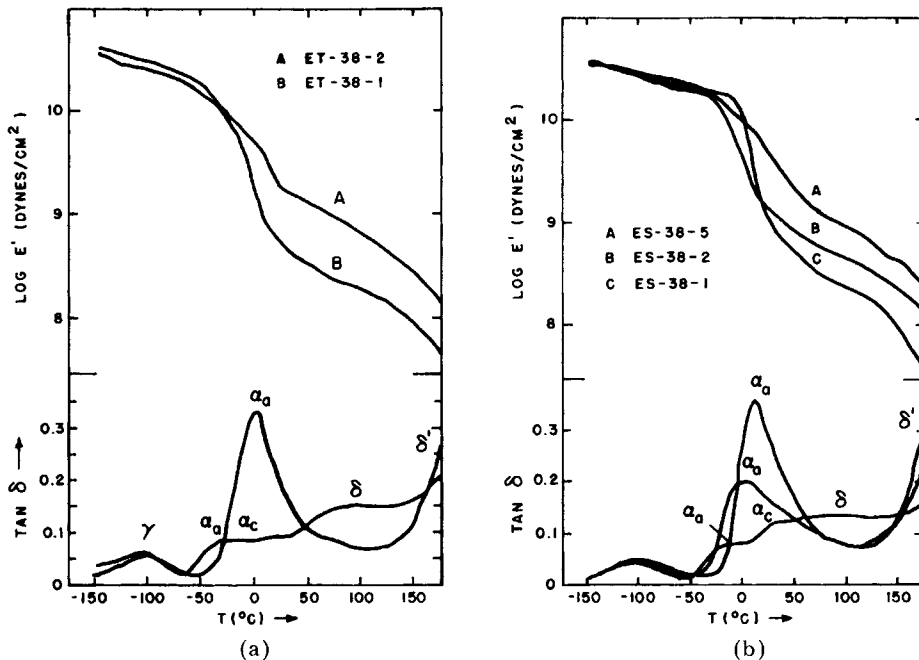


Fig. 13. (a) DMS of a polyether (ET) and (b) a polyester (ES) urethane block copolymer at 110 Hz. Redrawn from reference 17. ET-38 represents 38% of the soft polyether segment. ET-38-2 represents the same ether content but block lengths of twice the size of ET-38-1.

segments. The following equation for predicting a copolymer transition will be used:

$$\frac{1}{T_{gc}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (4)$$

where  $W_1$  and  $W_2$  are weight fractions of the components and  $T_{gc}$  is the calculated transition of the copolymer. Assume a value of  $-50^\circ\text{C}$  for the  $T_g$  of the soft polyether segments and a value of  $127^\circ\text{C}$  for the  $T_g$  of the hard isocyanate segments. Then, the  $T_g$  for the copolymer would be  $-23^\circ\text{C}$  for a 38% polyether content (62% isocyanate content) and  $-5^\circ\text{C}$  for a 24% polyether content (76% isocyanate content). This is what has been experienced for the  $\alpha_a$  transition in Figure 15.

As the block lengths are increased, a broadening occurs owing not to crystallization but to an increasing heterogeneity size ( $N_c \rightarrow 1$ ). This satisfactorily describes the shift of  $\alpha_a$  to lower temperatures with increasing block length.

For short block lengths of 1000 to 2000 MW (which includes many commercial urethane elastomers), the mechanical properties can be treated as behaving like a copolymer ( $N_c \rightarrow \infty$ ). For block lengths of 8 to 10,000 MW or larger ( $N_c \rightarrow 0$ ), two glass transitions are normally seen. For block lengths of intermediate size, a semicompatible ( $N_c \rightarrow 1$ ) situation exists.

### Application of DMS

In addition to determining mechanical transitions in polymers, DMS can now be used as an analytical tool for approximating domain size in two-phase systems

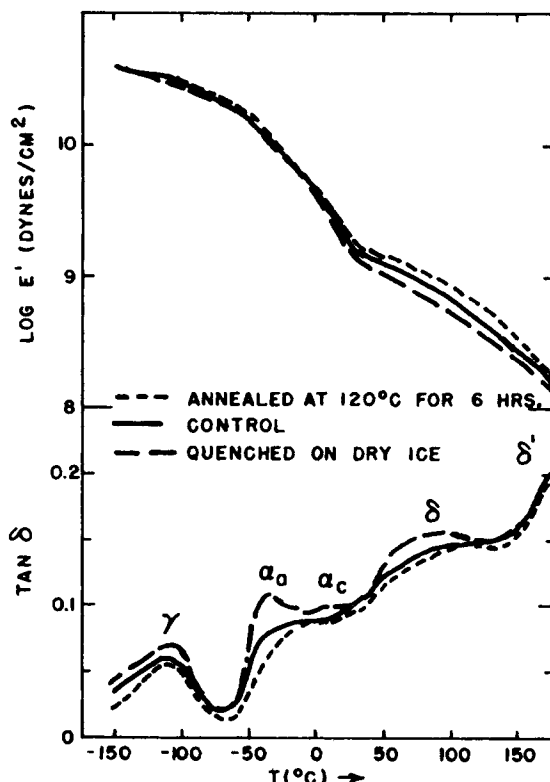


Fig. 14. Effect of thermal history on the DMS of ET-38-2 at 110 Hz. Redrawn from reference 17.

in terms of discrimination between heterogeneities of smaller or larger than 150 Å sizes.

A low-temperature loss peak is often used as basis for indicating impact strength. We now know the approximate end-to-end distance of a coordinated motion associated with a main glass transition ( $\approx 150$  Å). We now can make the following conclusions about loss peak-impact strength correlations. For most glassy matrices, rubber particles of at least 1500 Å and above are necessary for impact enhancement. Materials which exhibit impact enhancement by rubber modification will, therefore, exhibit a low-temperature transition. For rubber particles of 150 to 1500 Å, no impact improvement will be observed, even though a low-temperature loss peak will be seen with DMS. For rubber particles sizes below 150 Å, neither impact strength nor a low-temperature loss peak would be observed. This is an explicit example of the direct nature that results from correlating different physical properties through the central theme of structure (Fig. 1).

## CONCLUSIONS

1. An index has been presented for adequately defining all ranges of compatibility.
2. Electron micrographs were compared with dynamic mechanical spectra in order to generalize about the structure-property relationships in a continuous

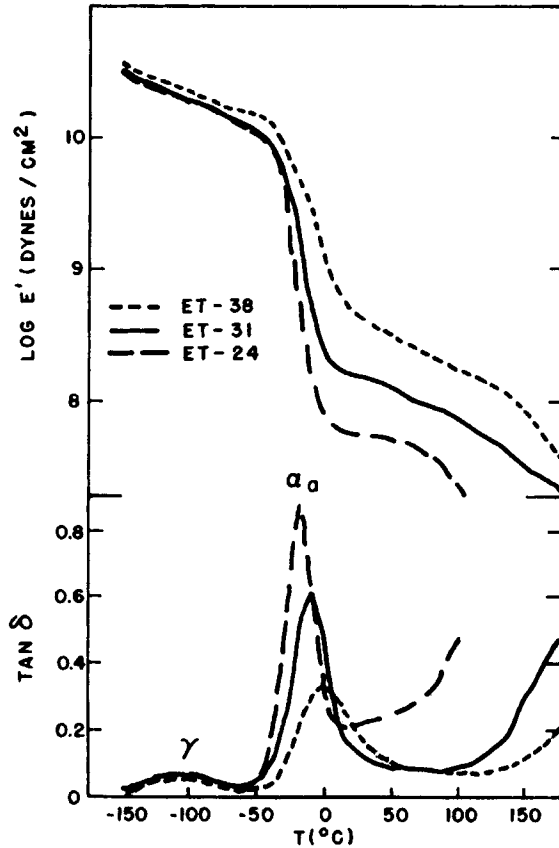


Fig. 15. DMS of a polyether urethane block copolymer at various soft to hard segment concentrations. Redrawn from reference 17. ET-38 represents 38% soft segment and 62% hard segment.

scheme from a compatible ( $N_c \rightarrow \infty$ ) to an incompatible ( $N_c \rightarrow 0$ ) system.

3. The universal domain size necessary for an observed glass transition temperature in DMS was determined to be about 150 Å at 110 Hz. The end-to-end distance representing the coordinated motion of a polymer chain in a glass transition (observed in a dynamic experiment at 110 Hz) was taken to be 150 Å. Glass transitions can represent anywhere from 100 to 5000 C—C bond units, according to whether the polymer conformation is highly restricted or freely orienting.

4. A new interpretation of short-segmental polyurethane block copolymers was given. Segment molecular weights of 1 or 2000 give block copolymers with only one observed main glass transition.

5. With a greater understanding of the molecular interpretation of a glass transition motion, it was proposed that the time-temperature superposition principle is not a fundamentally correct concept. Furthermore, glass transitions observed from isochronal measurements cannot be compared with transition observed from isothermal measurements, nor can  $T_g$ 's from dynamic measurements be compared with  $T_g$ 's from transient experiments.

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