

Matrix Relaxations in Rubber-Toughened Thermoplastics

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Synopsis

In several systems involving a rubber dispersed in a higher modulus polymer, we have found that both the storage modulus at temperatures below the major softening process and the maximum value of the loss modulus are proportional to the square of the volume fraction of the matrix. This agrees with a relationship for foams derived theoretically by Termonia using a finite-difference approach. Similar relationships have been found for the glass transition in polymethyl methacrylate and for crystalline relaxations in polyethylene, polyoxymethylene, and polytetrafluoroethylene which involve large decreases in modulus.

INTRODUCTION

Elastomers are frequently added to high-modulus thermoplastics to improve toughness. This always involves some sacrifice of modulus, and a great deal of effort has gone into finding ways to achieve an optimum combination of properties. Dynamic mechanical measurements can provide information about the energy absorbed in viscoelastic relaxations associated with the matrix or the dispersed phase.

In approaching this subject, it is appropriate to bear in mind two aspects of dynamic mechanical behavior.¹

1. The loss modulus is proportional to the energy absorbed per cycle provided the strain amplitude is held constant. This study employed the Dupont Dynamic Mechanical Analyzer (DMA Model 982) which operates in this manner.
2. For a given relaxation, the maximum value of the loss modulus is proportional to the difference between the unrelaxed and relaxed storage moduli. If the relaxed modulus is very small, the maximum loss modulus will be approximately proportional to the storage modulus at temperatures below the relaxation.

It was expected that in a blend of two polymers which are not miscible on a molecular level the maximum in the loss modulus would be proportional to the concentration of the component in which it originates. As shown in Figure 1, this is the case for the γ relaxation of polyoxymethylene in blends with polyurethane rubber. This is a low-temperature phenomenon which is attributed to the motion of short segments in the amorphous regions. However,

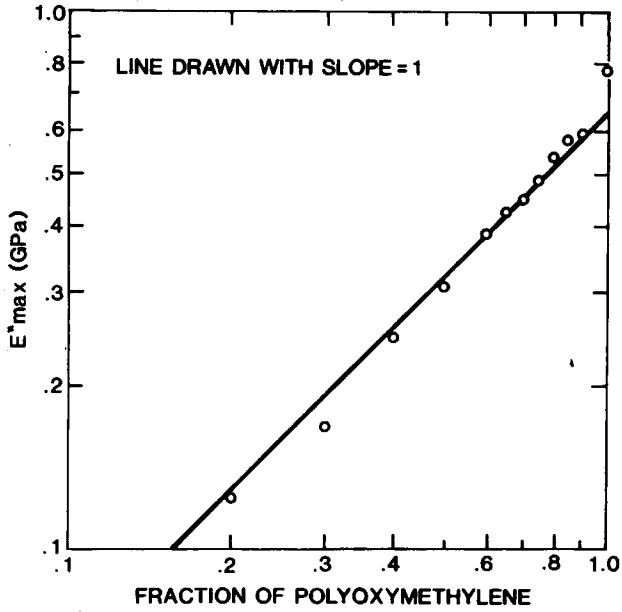


Fig. 1. Dependence of the maximum in the loss modulus for the γ relaxation of polyoxymethylene in blends with polyurethane rubber.

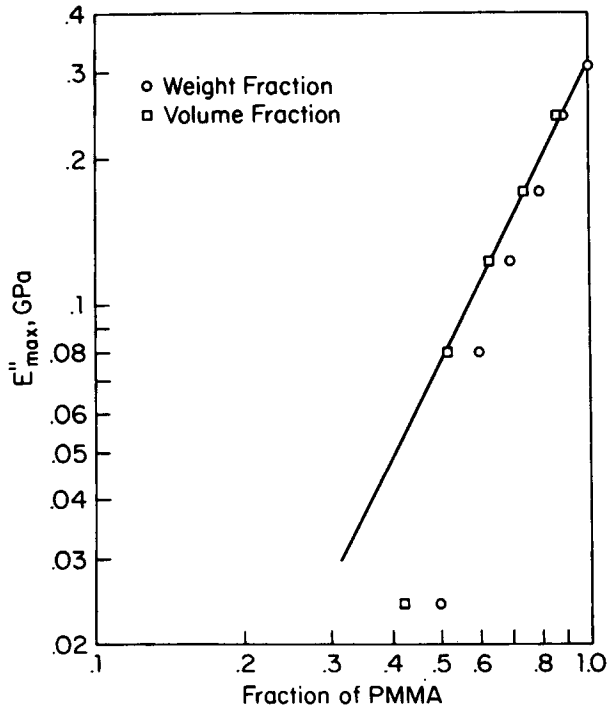


Fig. 2. Dependence of the maximum in the loss modulus for the glass transition of polymethyl methacrylate in blends with polyisobutylene. Line drawn with a slope of 2.

this turns out not to be a general rule for relaxations involving a large change in modulus.

GLASS TRANSITION

Polymethyl methacrylate (PMMA) was melt blended with 10–50% polyisobutylene by weight and compression-molded. The data plotted in Figure 2 show that the maximum loss modulus for the glass transition of PMMA is proportional to the square of volume fraction of PMMA down to about 0.5. At higher levels of polyisobutylene, phase inversion probably occurs with a sharp reduction in the deformation of PMMA. The storage modulus is also proportional to the square of the volume fraction of PMMA at temperatures from 0 to 130°C (Fig. 3). This confirms the expectation that the maximum loss modulus would be proportional to the storage modulus at temperatures below the relaxation. At -100 and -50°C , the modulus is less dependent on the composition because of the proximity to the glass transition of polyisobutylene.

CRYSTALLINE RELAXATIONS

The α relaxation in polyoxymethylene is a process which occurs in the crystalline regions at about 130°C at a frequency of 1 Hz.¹ It is the major

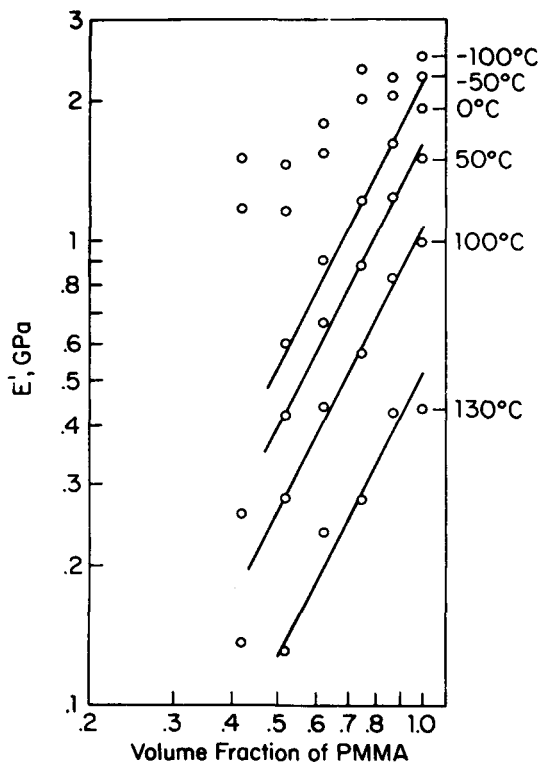


Fig. 3. Storage modulus of blends of polymethyl methacrylate and polyisobutylene. Lines drawn with a slope of 2.

STARKWEATHER

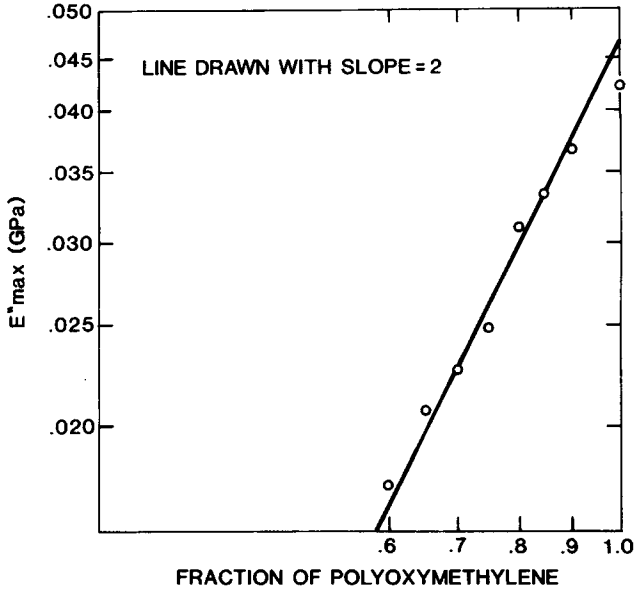


Fig. 4. Dependence of the maximum in the loss modulus for the α relaxation of polyoxymethylene in blends with polyurethane rubber.

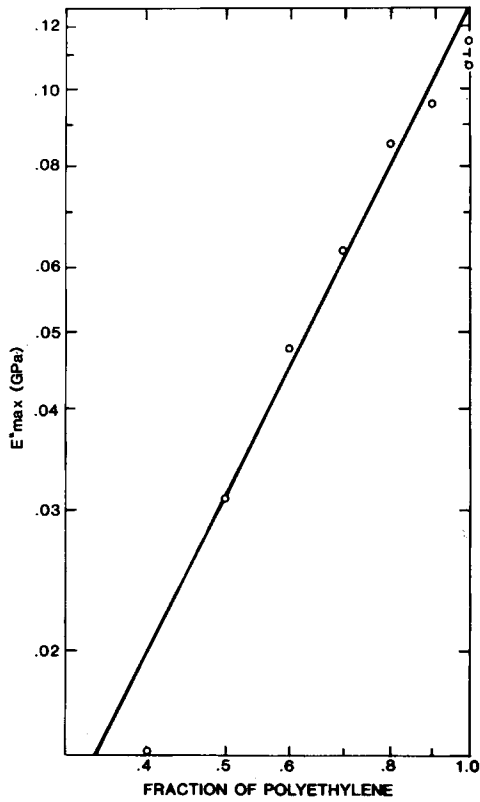


Fig. 5. Dependence of the maximum in the loss modulus for the α relaxation of linear polyethylene in blends with polyisobutylene. Line drawn with a slope of 2.

softening process in this polymer. A study of the dependence on temperature and frequency indicated that it has little if any cooperative character.² The dependence of the maximum in the loss modulus on the fraction of polyoxymethylene in blends with polyurethane rubber is shown in Figure 4. Unlike the behavior of the lower temperature γ relaxation shown in Figure 1, the strength of the α relaxation depends on the square of the fraction of polyoxymethylene. Between room temperature and the α relaxation, the storage modulus is also approximately proportional to the square of the fraction of polyoxymethylene. This is analogous to the behavior of polymethyl methacrylate in blends with polyisobutylene. In both cases, a rigid polymer matrix is blended with a soft rubber as a dispersed phase.

The α relaxation in polyethylene is also associated with the onset of motion in the crystalline regions. High-density polyethylene was melt-blended with polyisobutylene in various proportions and compression-molded. As shown in Figure 5, the maximum value of the loss modulus for the α relaxation depends on the square of the fraction of polyethylene over most of the range of composition. Between 0 and 80°C, the storage modulus is also proportional to the square of the fraction of polyethylene. Thus, the polyethylene/polyisobutylene and polyoxymethylene/polyurethane rubber blends behave in an analogous manner.

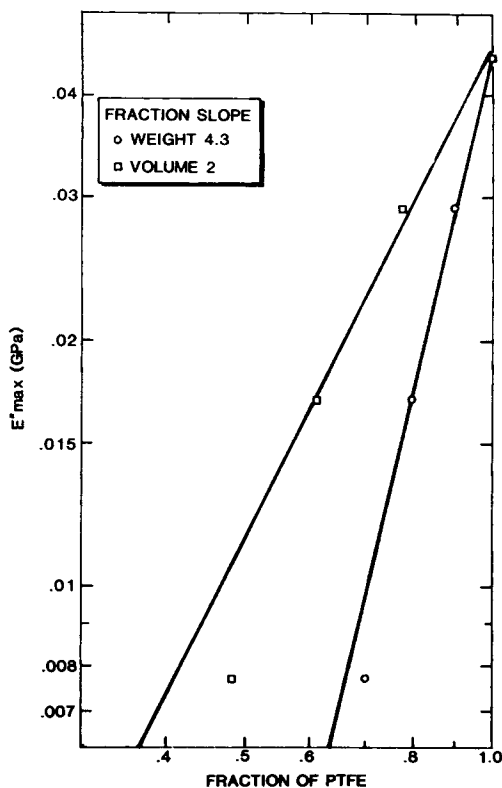


Fig. 6. Dependence of the maximum in the loss modulus for the β relaxation of polytetrafluoroethylene in blends with Nordel.

The β relaxation in polytetrafluoroethylene (PTFE) is associated with first-order crystalline transitions at 19 and 30°C. The dynamic mechanical loss peak reflects a change in the distribution of relaxation times at the 19°C transition.³⁻⁵ It was difficult to find an elastomer with adequate stability at the melting point of PTFE, but an ethylene/propylene rubber, Nordel 1635 EPDM, was finally selected. The desired amount of Nordel was dissolved in toluene, and the appropriate weight of Teflon 6 fine powder was stirred into this solution. The mixture was dried under vacuum at 60°C and compression molded at 360°C for 5 minutes. As shown in Figure 6, the maximum loss modulus for the β relaxation in PTFE decreases rapidly when diluted with rubber. The slope of a log log plot of the maximum value of the loss modulus vs the weight fraction of PTFE is 4.3. The difference between the densities of the components is quite large and the maximum loss modulus. Actually, E'' max depends on the square of the volume fraction of PTFE up to 20% Nordel[®] by weight (about 39% by volume). The behavior of the storage modulus is complicated by the proximity of the glass transition of Nordel.

DISCUSSION

It appears that there are generally applicable empirical relationships governing the viscoelastic properties of blends consisting of a relatively high-modulus matrix and a low-modulus dispersed phase. Both the storage modulus at temperatures below the major softening process of the matrix and the maxi-

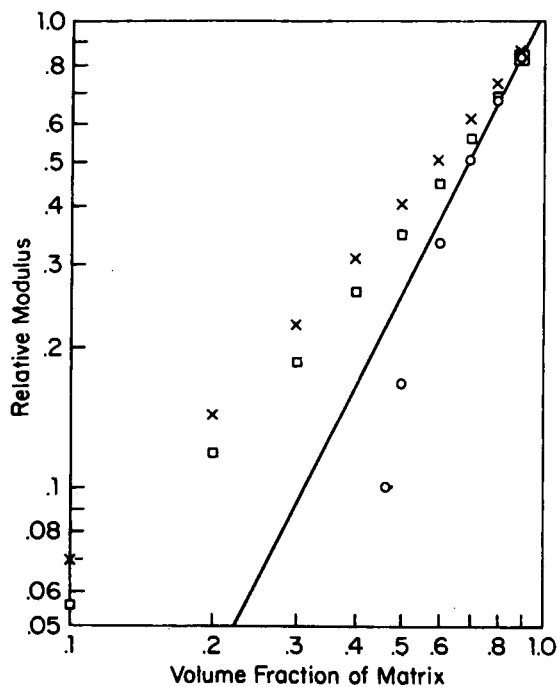


Fig. 7. Mathematical models for the modulus of rubber-toughened plastics. Line drawn with a slope of 2. \odot Hill, \square Kerner, \times Halpin.

imum value of the loss modulus depend on the square of the volume fraction of the matrix.

Mathematical models for the modulus of this type of blend have been given by Kerner,⁶ Hill,⁷ Budiansky,⁸ and Halpin and Kardos.⁹ These relationships are compared with the empirical one in Figure 7. The treatments of Kerner and Halpin and Kardos understate the reduction of the modulus by the dispersed rubber. The self-consistent method of Hill fits the data quite well up to about 30% rubber by volume.

The linear relationship between the modulus and the square of the volume fraction of the matrix agrees with the empirical data on foams and a theoretical relationship found by Termonia¹⁰ using a finite-difference approach. It is of interest to note that the modulus of the composite apparently does not depend on the compressibility of the dispersed phase.

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