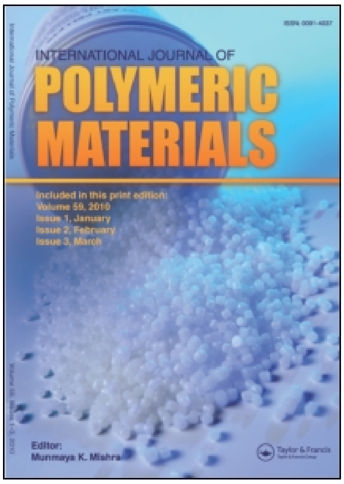

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On the Damped Debye Lattice Model for Modified Amorphous Polymeric Systems

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The steepness index (SI) of the stress relaxation master curves is shown to vary in a predictable way when the structure of the polymer is changed by the addition of fillers or by copolymerization, plasticization, or chemical substitution. The changes in SI can be associated with changes in the degree of inter-chain coupling produced by the various modifications. It is proposed that the peculiar differences in the value of SI between otherwise similar amorphous polymers, as PS and PMMA, may be related to certain thermal parameters, as is the case in the calculation of the Grüneisen constants.

INTRODUCTION

The stress relaxation behaviour of amorphous polymers in the primary transition region, i.e. around the glass transition temperature, T_g, has not been explained in a satisfactory way. This applies especially to the variation from one polymer to another of the maximum negative slope of the log (modulus) – log (time) master curve in this region. This slope, termed the steepness index (SI),[1,2] takes on a high value for polystyrene (SI $\approx$ 3/2), while it is considerably lower for polymers like polyisobutylene and poly(methyl methacrylate) (SI $\approx$ 0.5–1.0).[3,4] The reason for this difference is not fully understood; however, the concept of the damped Debye lattice (DDL) appears to provide some valuable guidelines.[1–4] It has been proposed that the steepness of the transition depends on the dimensionality of the system.[1–4] Polystyrene (PS) is considered to be a three-dimensional lattice corresponding to SI $\approx$ 3/2, while, e.g., polyisobutylene represents a one-dimensional chain (SI $\approx$ 0.5), which corresponds to the familiar results of Rouse[5] and Bueche.[6] The dimensionality of the damped Debye lattice as reflected in the value of SI depends on the balance between inter- and intrachain interactions.[1-4] In the one-dimensional case the intrachain interactions are dominant, while in the three-dimensional case interchain coupling becomes significant.

It is the purpose of the present note to summarize literature data supporting the view that a three-dimensional lattice in the sense of DDL becomes decoupled, i.e. assumes a lower dimensionality, when the polymer is plasticized, filled, chemically substituted, or otherwise modified. Conversely, polymers with weak interchain interactions may assume a higher dimensionality by similar measures.

STEEPNESS INDEX OF MODIFIED SYSTEMS

An example of the destabilization of a 3-D lattice to a lower dimensionality is the plasticization of polystyrene, where the weakening of the interchain interactions by the plasticizer in fact results in a lower SI-value.[1,2] This applies, however, only to solvents having a solubility parameter (δ) sufficiently different from that of PS. When theta-solvents are used, the 3-D character of the original polymer is not changed.[1,2]

A similar decrease in the SI-value due to plasticization is also noted for poly(vinyl chloride) (PVC) treated with dioctyl phthalate (20 w/o). In this case, SI-values around 0.6 for rigid PVC ($\delta = 9.5\ (\text{cal/cm}^3)^{1/2}$) have been reduced to about 0.3 by plasticization with dioctyl phthalate ($\delta = 7.9\ (\text{cal/cm}^3)^{1/2}$).[7]

Another instance of an SI-lowering effect is phenyl substitution of PS.[2]

It appears to be possible to destabilize the interchain interactions and reduce the SI-value also by other means than plasticization and substitution. Consider, for example, poly(vinyl acetate) (PVAC), which represents a 3-D lattice, (SI $\approx 3/2$). If this polymer is filled with carbon black[8] (Figure 1), the SI-value, calculated from relaxation data, decreases substantially depending on the amount of filler, in this case from *c.*1.4 (unfilled PVAC) to *c.*0.6 (20 v/o carbon black). In this case the carbon black particles had an average diameter of 200 Å and had also a high specific area. If instead a grade with a low area and an average diameter of 2000 Å is used, the reduction of SI will be lower,[8] from *c.*1.4 to *c.*1.2 (20 v/o carbon black). The degree of reduction of SI thus appears to be associated with the activity of the filler, i.e. the interaction between the filler particles and the polymer chains.

Relaxation data for a styrene-butadiene random copolymer reported by Oono[9] suggest a similar behaviour, Fig. 1. When the polymer was filled with carbon black having an average particle diameter of 280 Å, the SI-value decreased from 1.0 to 0.3 at 100 pph carbon black. This also shows that SI-values lower than 0.5 (1-D chain) can be obtained, indicating that also the

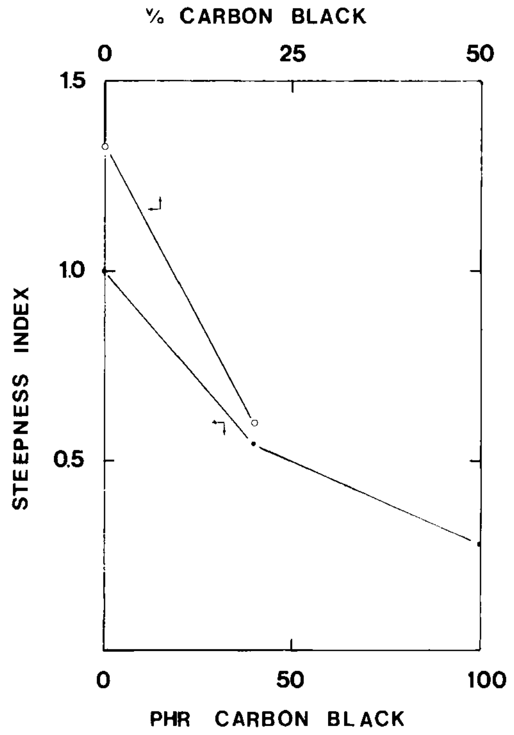

FIGURE 1 Influence of carbon black on the steepness index of PVAC (○) and SBR (●).

intra-chain interactions may be affected. An inert silica filler did not significantly influence the shape of the master curve in this case.[9]

Blending of two incompatible polymers also affects the inter- and intrachain interactions, and the same is true of copolymerization. Evaluating the SI-values for PVAC and lightly cross-linked poly(methyl methacrylate) (PMMA) from Kaplan and Tschoegl's stress relaxation data[10] yields 1.3 and 0.6, respectively. Blending of the two polymers in equal amounts yields a system with SI $\approx$ 0.7, indicating the disappearance of the 3-D character of PVAC. Horino *et al.*[11] also studied stress relaxation of blends of PVAC and PMMA. The PMMA was used in two states, uncross-linked and lightly cross-linked. The results for PVAC-cross-linked PMMA are in good agreement with those reported in Ref. 10, i.e. the 3-D state of the PVAC is destroyed. If PMMA is not cross-linked, the SI-value is higher, 0.75, the corresponding value of the blend being *c.*0.9. Thus, a similar behaviour is noted, with or without cross-linking, the steepness index of PVAC is reduced and closer to that of PMMA. Figure 2 shows the influence of acetylation on the SI-value of poly(vinyl alcohol)

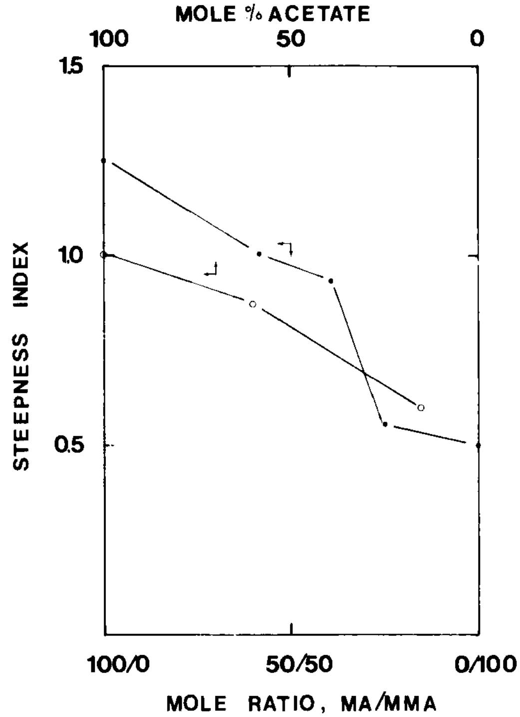

FIGURE 2 Influence of chemical composition on the steepness index. Upper curve: PVOH with varying degree of acetylation. Lower curve: PMA/PMMA-copolymers of varying composition.

(PVOH) as calculated from data obtained by Fujino *et al.*[12] Here, the SI-value decreases from *c.* 1.0 to 0.2 depending on the degree of acetylation of PVOH. A similar behaviour is observed for copolymers of PVOH and poly(vinyl formal).[13] Increasing the amount of poly(vinyl formal) to 75% (mole) increases the steepness index up to 1.1.

In Figure 2 also the steepness index of random copolymers of poly(methyl acrylate) (PMA) (SI = 1.3) and PMMA (SI = 0.5) from Ref. 14 is shown. Again, a decrease in SI with an increasing amount of PMMA is noted.

OTHER SYSTEMS

Inherent in all discussions on the dimensions of the damped Debye lattice is the balance between the inter- and intrachain interactions. It is obvious from the discussions above and Refs. 1, 2 that it is rather easy to affect especially the three-dimensional lattice. Lin and Aklonis[4] found that SI for PMMA was not markedly affected by plasticizers, remaining rather constant and lower than 3/2 ($SI \approx 1.0$); i.e. a two-dimensional lattice. They suggested that the insensitivity of the SI-value to plasticization could be due to the fact that the interchain interactions were stronger than those within the chains. If the two types of interactions are of the same order, this would yield an SI-value of 3/2 (three-dimensional system).

This would also account for the behaviour of styrene-based ionomers.[15,16] In these polymers the interchain forces are higher than in the pure system. This results, for example, in a higher glass transition temperature and also in a significant decrease of SI, as demonstrated for styrene-sodium methacrylate copolymers.[15,16] Thus also strengthening of the interchain interactions may disturb the balance between inter- and intrachain forces, which apparently is a prerequisite for a 3-D type of behaviour of the system.

CONCLUSIONS

One of the main parameters extracted from the DDL-concept of representing stress relaxation data is the steepness index (SI). It is equal to the exponent m in the relation

$$E(t) = E_1(1+t/\tau)^{-m}+E_2 \tag{1}$$

proposed to describe the relaxation modulus $E(t)$ in the transition region.[17] Here, E_1 and E_2 denote the glassy and rubbery modulus ($E_1 \gg E_2$), respectively, t the time and τ a time constant. The exponent m, i.e. SI, is obtained from the usual double-logarithmic plots (master curves) of stress or modulus *vs.* time.

Equation (1) is closely related to the power law[18] for stress relaxation

$$\dot{\sigma} = d\sigma/dt = -A(\sigma-\sigma_i)^n \tag{2}$$

where A and n are constants. The exponents n and m of Eqs. (1) and (2) are connected as $n = 1+1/m$.

Apart from the double-logarithmic representation of relaxation data, also stress (ln time)-plots are used. When normalizing the stress (or modulus) with regard to the internal stress, one finds outside thermal transition regions

$$F = (0.1 \pm 0.01)(\sigma_0-\sigma_i) \tag{3}$$

where F is the maximum (inflexion) slope $(-d\sigma/d \ln t)_{\max}$ of the $\sigma(\ln t)$-plots, σ_0 the initial applied stress (at $t = 0$) and σ_i the internal stress, i.e. the equilibrium stress attained after a sufficiently long time. This peculiar relationship, found to be valid for both polymers and metals[19,20] has not been explained hitherto, even though there are indications that it may emerge from a cooperative flow mechanism.[21]

Evaluating m from Eq. (2), one can relate the slopes m and F as follows,[22]

$$F = [m/(m+1)]^{m+1}(\sigma_0 - \sigma_i). \tag{4}$$

This interconversion is shown graphically in Figure 3.

Below T_g, the slope of the log σ^* − log t or the log E − log t plots, is comparatively low. When approaching T_g, the slope increases, eventually assuming a maximum value in the transition region, and then it again decreases. This maximum value is the steepness index occurring in the DDL-theory.

A similar variation is found for F/σ_0^*. The value of 0.1, cf. Eq. (3), normally found sufficiently far from thermal transitions, corresponds to $m \approx 0.20$.

The double-logarithmic representation of relaxation data is closely related to the power law of flow, cf. Eq. (2), while the linear-logarithmic plots reflect an exponential variation of the flow rate with the effective stress.[18,19] The various aspects of the two representations have been discussed in detail earlier.[18,19] One might add that in the transition region both representations give a fair description of the relaxation process.[23] The corresponding physical background is too weak for a decision to be made in favour of any of the current theoretical approaches. The same applies also to the DDL-concept, which although plausible, cannot account for the differences in the SI-value between similar polymers like PMMA and PS.

In contrast to certain other methods, like the WLF-approach,[24] the analysis

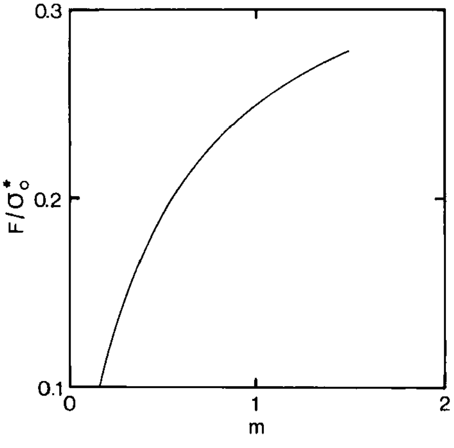

FIGURE 3 The ratio F/σ_0^* vs. the slope (m = SI) of the relaxation curve in a log σ^* − log t diagram according to Eq. (4).

of the SI-behaviour appears to reveal some highly tangible differences between otherwise similar polymers. Despite the obvious significance of these differences, the attempts to explain them appear to be unsuccessful. It is, however, not unlikely that they may be associated with certain thermal properties as is the case in the calculation of the Grüneisen parameter. For instance, the specific heat associated with the interchain vibrations in PS (3-D lattice) and PMMA (1-D lattice) has been reported to differ by *c*.20‰, the higher value applying to PS.[25] Also calculations of the Grüneisen parameter γ give somewhat different values.[26–28] To this come certain differences in the bulk modulus entering the Grüneisen parameters.[27] It is, on the other hand, known that both experimental and theoretical determinations of γ are subject to substantial uncertainty, due mainly to difficulties in properly assessing the intermolecular interactions. In view of the primary role played by the dimensionality of a lattice in the Grüneisen concept, the link between the corresponding thermal parameters and flow mechanisms in polymers in general, and the steepness index in particular, appears plausible.

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