Direct Observation of Two Glass Transitions in Silica-Filled Polymers. Implications for the Morphology of Random Ionomers

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The unusual behavior of polymer interfaces formed near solid surfaces has been the subject of considerable interest for both fundamental and practical reasons. Such interfaces are formed, for example, when polymers interact with dispersed solid particles[1] (e.g., talc,[2] carbon black,[3-6] or calcium carbonate[7]), or fibers, or when they are deposited directly onto solid surfaces (e.g., mica[8]). It is observed that many polymer properties (viscosity, diffusion coefficient, NMR T_2 relaxation time, etc.) in these interfacial regions are dramatically altered due to the restrictions on mobility that the chains experience in the vicinity of the surfaces. Some possible causes of the chain mobility reduction include crowding and/or local ordering of chains at the interface as well as loss of configurational entropy of the polymer segments near the solid surface.

The existence, thickness, and glass transition of the adsorbed-polymer layer around the filler particles have been studied by several techniques such as mechanical analysis,[4,9] dilatometry,[5] DSC,[6] and NMR.[3] It was concluded that indeed there is a polymer layer (*ca.* 20 Å thick) adsorbed on the surface of the particles. In one case, i.e., that of poly(dimethylsiloxane) filled with high surface area silica particles, it was suggested that the adsorbed layer has a different glass transition from that of the bulk polymer, as demonstrated by the occurrence of a second tan δ peak.[9] A carbon-black-filled styrene–butadiene rubber was also thought to have two glass transitions as indicated by the two slope changes in the specific volume versus temperature curve.[5] On the other hand, mechanical analysis and DSC measurements on high surface area carbon-black-filled rubbers[4,6] as well as several silica-filled polymers[6,9] (PS, PEG, PMMA, EP rubber) did not reveal any second glass transition. Some insight into the morphology of carbon-black-filled rubbers, which did not contain any unbound polymer, was obtained from NMR relaxation time (T_2) measurements.[3] The relaxation time (T_2) was found to consist of two components. One did not change when the samples were heated through the T_g, while the other responded to the glass transition, although the T_2 was an order of magnitude smaller than that of the unfilled rubber at temperatures above T_g. Hence, the morphology postulated was that some rubber chains are strongly adsorbed on the particles and do not participate at all in the glass transition, while others do participate but suffer from mobility constraints.

The above discussion provides some relevant examples which show that adsorbed polymer chains interact strongly with the surface of filler particles. These interactions restrict the chain mobility, as indicated for two systems by the occurrence of a second glass transition or by the existence of a different relaxation time. However, because the second glass transition has been observed only in two polymer systems, it is difficult to conclude whether the effect is a general one.

In another area, restrictions on chain mobility have recently been invoked to explain the existence of two glass transition temperatures in some random ionomers.[10] According to the multiplet/cluster (or EHM) model, multiplets (ionic assemblies consisting of several ionic groups) restrict the mobility of ionomer segments around them. As the ion content increases, the number of regions of restricted mobility grows and they start to overlap. At some specific ion content, the aggregates become large enough to exhibit their own glass transition; above that point they are called clusters. Thus the second peak in the tan δ versus temperature curves, observed for many ionomers, is due to the glass transition of the regions of restricted mobility (clusters). Confirmatory evidence of the restricted mobility concept of the EHM model was obtained in the case of telechelic ionomers from dielectric spectroscopy.[11] In other studies, a significant reduction in the chain mobility of the segments next to the ionic groups was observed by NMR measurements on block ionomer and telechelic reverse micelles in solution[12] as well as telechelic ionomers in the solid state.[13] In the case of sulfonated polystyrene random ionomers, it was concluded, based on DSC results that the mobility of styrene units adjacent to multiplets was constrained.[14]

In a recent paper from this laboratory[15] it was suggested that the process of clustering and its effect on ionomer properties should be similar to that of the incorporation of filler particles into polymers, which, as was discussed above, creates regions of restricted mobility at the polymer–filler interface. It was suggested that in the case of polymers containing very small (nanosize) particles, subject to strong interactions with the polymer (e.g., chemical bonds), a second glass transition should be observable, in a manner analogous to that of the ionomers (ref 15, p 2801).

In order to prove this similarity experimentally and also demonstrate that regions of restricted mobility in polymers generally exhibit their own glass transition, provided that the regions of restricted mobility are large enough, we measured the dynamic mechanical properties of poly(vinyl acetate) (PVAc), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(4-vinylpyridine) (P4VP) homopolymers filled with silica particles. PVAc as well as the silica particles were obtained from Aldrich, PS and PMMA from Polysciences, and P4VP from Scientific Polymer Products. To prepare the composites, the polymers were dissolved in THF (DMF in the case of P4VP) and the desired amount of silica was added to give composites that contained 10 wt % filler. After stirring the slurries for 48 h, the solvent was allowed to evaporate under stirring. The solid samples were dried under vacuum for 48 h at 130 °C. Composite samples containing silica particles of two different average diameters were prepared. One set was made from particles of 7 nm nominal diameter, while the other was made from particles smaller than 44 μm in diameter, as determined by passage through a specified sieve. A Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) was used to carry out the measurements. Data were collected at five different frequencies so as to allow the calculation of the activation energy of the observed transitions from an Arrhenius type plot.

Figure 1 shows the tan δ versus temperature curves for PVAc samples measured at 0.33 Hz. The main feature of the curve for the unfilled PVAc sample (open circles) is the peak with a maximum at *ca.* 60 °C, due

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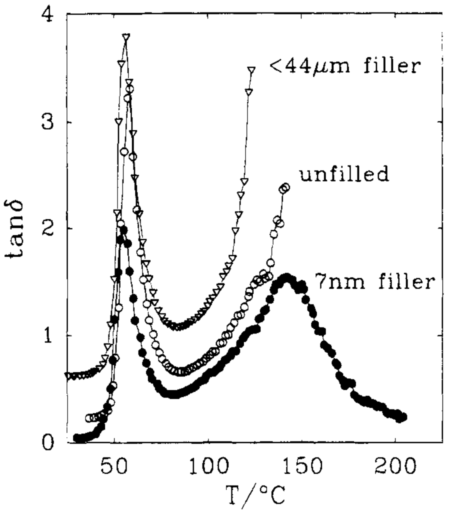

Figure 1. tan δ versus temperature curves for PVAc samples: unfilled (○); filled with 10 wt % of large silica particles (▽); filled with 10 wt % of fine silica particles (●). The top two curves have been shifted vertically for clarity by 0.2 and 0.5, respectively. The lines through the experimental points serve as a guide to the eye.

to the glass transition of PVAc. From the variation of the temperature of peak maximum with frequency, the activation energy was calculated to be 360 kJ·mol^{-1}. We also note that, above 100 °C, the sample starts to flow, as reflected by the upturn of the curve. The PVAc sample containing 10 wt % of large particles (d < 44 μm) exhibits similar behavior (triangles). On the other hand, a PVAc sample filled with 10 wt % of very fine silica particles (d = 7 nm) shows a dramatically different behavior (filled circles) as depicted in Figure 1. Although the position of the tan δ peak has not changed, its height has decreased by about 35% in comparison with the corresponding peak for pure PVAc. This indicates that a significant number of chain segments in this composite sample does not participate in this glass transition. The activation energy for the peak was calculated to be 340 kJ·mol^{-1}, in good agreement with the value for pure PVAc. Most importantly, we note that there is another peak located at *ca.* 150 °C and that the sample does not start to flow even at 200 °C. The position of the maximum of this second peak exhibits a significant variation with the frequency of measurement, and the activation energy was calculated to be 240 kJ·mol^{-1}. The position of this peak, as well as the fact that the phenomenon it represents is characterized by such a high activation energy, suggests that it is associated with the glass transition of the PVAc chains that are restricted in mobility because of their interaction with the silica surface.

The difference between the effects of the large and small particles lies in their specific surface areas (SSA). Although both kinds of particles reduce the mobility of chains in their immediate vicinity, the volume fraction of polymer that is affected by the large particles (SSA ≅ 1 m^2·g^{-1}) is negligible compared with the one interacting with the small particles (SSA ≅ 400 m^2·g^{-1}). In addition to this surface area effect, it should also be borne in mind that the thickness of the layer of restricted mobility material around the particle may not be large enough to allow for the detection of an independent glass transition. This is believed to be the situation in the region surrounding the multiplets in ionomers.[10] Under these circumstances, it is the overlapping regions of restricted mobility which surround different particles that give rise to the glass transition. If this is also the case here, then the total volume of restricted mobility material would be extremely small for large particles but would be substantial for the nanosize particles, especially when the latter are distributed heterogeneously throughout the polymer. Therefore, the second glass transition is detectable only in the case of very small particles.

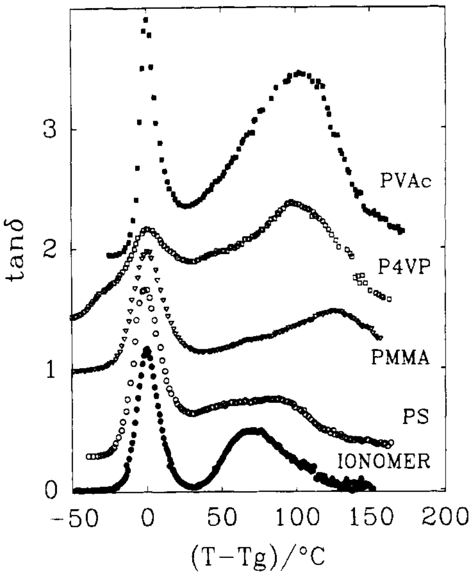

Figure 2. tan δ versus $T - T_g$ curves for a poly(styrene-*co*-4.5 mol % sodium methacrylate) ionomer (●) and the following polymers filled with 10 wt % of 7 nm silica particles: PS (○), PMMA (▽), P(4VP) (□), and PVAc (■). The curves of the filled polymers have been shifted for clarity by 0.2, 0.9, 1.4, and 1.9, respectively.

Results similar to those found in PVAc were obtained for polystyrene. Incorporation of 10 wt % of large silica particles does not affect the mechanical properties, while the tan δ curve of the sample containing 10 wt % of very fine silica particles exhibits two peaks (Figure 2). One is located at *ca.* 100 °C (glass transition of pure PS) and the other at *ca.* 160 °C. The activation energy for the first transition is 480 kJ·mol^{-1}, while for the second it is 130 kJ·mol^{-1}. It is also seen in Figure 2 that PMMA and P4VP which contain 10 wt % of the fine silica particles also have tan δ curves with two peaks. The first is found at the T_g of the unfilled polymers (*ca.* 100 °C for PMMA and 140 °C for P4VP), while the second is located at *ca.* 245 °C for both materials. Again, as for PVAc, we attribute this second peak to the glass transition of chains experiencing a mobility reduction.

The above-mentioned results for PVAc are in excellent agreement with the recent findings of Landry *et al.*,[16] who observed two peaks in the tan δ curve for that system filled with 30 wt % of silica. They ascribed the second peak to motions of chains that are restricted at the surface of the particles. There is also qualitative agreement of our observations with the data of Sokolof *et al.*,[17] who found that PS chains adsorbed on an oxidized silicon surface have sufficient energy to diffuse away from the surface only above 160 °C, in contrast to self-diffusion, which would already be activated at considerably lower temperatures. Many other observations of the unusual behavior of polymers near surfaces have been made.[1-9] In general, the tan δ data presented here suggest that this unusual behavior may well be due to the appreciable increase in the glass transition temperature of the near surface polymer regions. However, for large flat surfaces a second glass transition may not be detectable if the thickness of the restricted mobility layer is too small (see also comment above regarding overlapping regions).

At this point, it is useful to compare the mechanical properties of a typical ionomer with those of the silica-filled polymers. Such a comparison is also presented in Figure 2. The ionomer selected for comparison is a poly(styrene-*co*-sodium methacrylate) copolymer with 4.5 mol % ion content; the results were taken from ref 15. To make the comparison simpler, the tan δ profiles in Figure 2 are plotted versus $T - T_g$, where T_g is taken to be the maximum of the first peak of the five different polymers. For clarity, the curves of the filled polymers were shifted vertically to avoid overlap. For the same reason, an exponential background is subtracted before presenting the ionomer data. For the justification of this procedure the reader is referred to ref. 15. Background subtraction was not found necessary in the case of the filled polymers.

The similarity between the ionomer and the filled polymers is striking. Both types of samples exhibit two peaks. The first one corresponds to the glass transition of the matrix polymer, while the second, which is significantly broader in all cases, is due to polymer chains with reduced mobility. In all cases examined, both in ionomers and in the filled polymers, the size of the first peak is smaller compared to the size of the corresponding peak for the pure homopolymers. Furthermore, the difference in the position of the maximum of the two peaks, ΔT_g, is seen to vary from 60 to 140 °C for the filled systems. This range is comparable to that found in styrene–sodium methacrylate ionomers for ion contents ranging from 1 to 15 mol % (60–100 °C). It is also seen that, for the ionomer sample, the activation energy of the first glass transition (530 $\mathrm{kJ \cdot mol^{-1}}$) is considerably higher than the activation energy of second one (310 $\mathrm{kJ \cdot mol^{-1}}$).[15] A similar trend was found for the other filled samples, as discussed previously. This comparison suggests that the morphology of ionomers is very similar to that of polymers filled with very fine particles. The latter systems are heterogeneous, as can be seen from the existence of polymer regions characterized by two different regimes of chain mobility, which manifest themselves by two different glass transitions. For ionomers, the EHM model suggests that the two glass transitions also reflect heterogeneously distributed regions of different mobility.

It is worth noting that, on the basis of the WLF equation, the second glass transition would be expected to have a larger activation energy than the first. However, the opposite trend is observed for the filled polymers and random ionomers. Although several arguments can be invoked to explain this trend and its physical significance, it should be borne in mind that the time–temperature superposition principle, and consequently the WLF equation, had been shown to fail for clustered random ionomers[18] at an ion concentration which was later found to coincide with the percolation threshold for clusters.[15] Thus, while no physical significance is attached at this time to the fact that the second glass transition is characterized by a lower activation energy than the first, it should be emphasized that the same trend is observed for both filled polymers and random ionomers and may well be due to the same underlying phenomena in both systems.

In conclusion, it has been shown that several polymers filled with nanosize silica particles exhibit two loss tangent peaks, which are ascribed to glass transitions on the basis of their activation energies. This behavior appears to be general, since it is observed in very different polymers. We also suggest that this behavior is analogous to that seen in clustered ionomers. In both sets of materials, the height of the first peak is smaller than the height of the corresponding peak in pure homopolymers. The higher temperature peak is broader than the first and has a lower apparent activation energy. In addition, the temperature difference between the two peaks, ΔT_g, lies in the range of *ca.* 60–100 °C for both the ionomers and the filled systems. The above comparison reveals that both types of systems behave in similar ways and suggest that they should have similar morphologies. The results and discussion presented here support strongly the validity of the EHM model for ionomer morphology.

The effects of various additional factors, such as filler content, molecular weight, and thermal history on the two glass transitions of filled polymers are currently under study; the results will be reported later.

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