Small-Angle X-Ray Scattering Studies of Zinc Stearate-Filled Sulfonated Poly(ethylene-co-propylene-co-ethylidene norbornene) Ionomers

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ABSTRACT: The crystallization, melting, and dissolution behavior of zinc stearate (ZnSt) in ZnSt-filled sulfonated poly(ethylene-co-propylene-co-ethylidene norbornene) (SEPDM) ionomers was studied by synchrotron small-angle X-ray scattering (SAXS). The melting temperature of ZnSt in the ionomer was considerably lower than in the pure state, which was consistent with the existence of very small ZnSt crystalline domains and a specific interaction between the metal sulfonate groups of the SEPDM and the metal carboxylate groups of ZnSt. Temperature-resolved SAXS showed that, on melting, some or all of the ZnSt rapidly dissolved into the ionomer. Ionic aggregates in the neat ionomer persisted up to 300°C. Microphase separation was also observed at elevated temperatures for the ZnSt-filled ionomers, but the composition of the microdomains was believed to be quite different than that of the microdomains in the neat SEPDM. The time and temperature dependence of the ZnSt crystallization in the filled ionomers was characterized by time-resolved SAXS experiments following a temperature quench from the melt. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 3141–3150, 1999

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INTRODUCTION

Ionomers are polymers that contain a small amount of bonded salt groups, generally less than 10 mol %.1 Their unique properties arise from microphase separation of associated ionic groups that produces properties similar to those of cross-linked polymers. However, the physical cross-links that arise from the ionic aggregation may dissociate under stress at elevated temperatures, which allows the material to exhibit viscous flow.

The thermo-reversible nature of the ionic associations makes ionomers with low glass-transition temperatures ($T_g$) attractive candidates for thermoplastic elastomers (TPEs), which are polymers that behave as cross-linked rubbers at use temperatures but can be melt processed like thermoplastics at elevated temperatures. Typical examples of commercial TPEs are segmented polyurethanes and styrene-diene block copolymers. In those systems, a rubbery continuous phase contains crystalline or glassy domains that serve as physical cross-links at low to moderate temperatures, but when the crystalline melting point or $T_g$ is exceeded, melt flow may be achieved.

One particular ionomer developed as a TPE is a sulfonated terpolymer of ethylene, propylene, and a diene monomer, sulfonated EPDM (SEPDM).2 Substantial improvements in the modulus and tensile strength of EPDM are achieved by introducing small amounts (~10–50 meq/100 g rubber (phr)) of bonded metal sulfonate groups. At temperatures usually encountered in conventional plastics processing operations (i.e.,
150–250°C), the ionic associations are weakened and, in principle, should allow for melt flow of the ionomer. In practice, however, the strong persistence of the ionic associations in neat SEPDM at temperatures above 200°C produces very high viscosity melts and makes melt processing by conventional techniques difficult. A significant reduction of the melt viscosity of SEPDM can be accomplished by selectively plasticizing the ionic microphase with polar diluents such as stearic acid or metal stearates. Although most plasticizers that disrupt the ionic associations also have a detrimental effect on the room-temperature mechanical properties, one particular additive, zinc stearate (ZnSt), not only reduces the melt viscosity but actually improves mechanical properties such as tensile strength and elongation to break.

The decrease in melt viscosity of SEPDM at elevated temperatures by the addition of ZnSt is presumed to be due to the association of molten ZnSt with the ionomer sulfonate groups, which solvates the intermolecular dipole–dipole associations of the sulfonate groups. Mechanical property improvements at temperatures below approximately 80°C have been attributed to the formation of a separate crystalline ZnSt phase that behaves as a reinforcing filler. Although phase separated, the crystalline ZnSt phase is compatible with the ionomer at concentrations of up to 50 wt %. As with the nomenclature commonly used for polymer blends, in this paper we distinguish between the terms miscible and compatible. Miscible denotes a single-phase mixture, whereas compatible signifies a mixture with useful mechanical properties regardless of whether it is single phase or phase separated. Although ZnSt is immiscible with SEPDM (i.e., it forms a separate phase), it is compatible with the ionomer in that it forms a stable mixture without noticeable blooming. In contrast, ZnSt is incompatible with non-sulfonated EPDM; it readily exudes from EPDM at concentrations as low as 1 wt %. These observations suggest that specific interactions between the sulfonate groups of the ionomer and the metal carboxylate groups of the plasticizer are responsible for the nonfugitive nature of the ZnSt phase in plasticized SEPDM. Also, the relative optical clarity of ZnSt-filled SEPDM indicates that the dispersed ZnSt domains are very small, which also suggests an associative interaction between the metal stearate and the ionomer.

In this paper, temperature-resolved small-angle X-ray scattering (SAXS) measurements were used to study the temperature-dependence of the ZnSt and ionomer microstructures. Time-resolved SAXS measurements following thermal quenching of the ZnSt-filled ionomers from above the melting point of the ZnSt were used to characterize the development of the two microphases.

**EXPERIMENTAL DETAILS**

SEPDM and ZnSt filled SEPDM samples were kindly supplied by Dr. Ilan Duvdevani of Exxon Research and Engineering Co. (Annandale, NJ). The composition of the starting EPDM was 55% ethylene, 40% propylene, and 5% ethylidene norbornene. The ionomer was prepared by sulfonating the EPDM with acetyl sulfate and converting the product to the zinc salt Zn-SEPDM by neutralization of the sulfonated polymer with zinc acetate. The ionomer contained 30 meq phr of zinc sulfonate groups. ZnSt-filled SEPDM samples were prepared by first dispersing ZnSt in a solution of the ionomer in a toluene/methanol mixture, followed by precipitation of the mixture in methanol. The samples were dried under vacuum at 50°C, and films were compression molded at approximately 200°C.

SAXS experiments were done on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory (SSRL). The wavelength (\(\lambda\)) of the incident radiation was 0.143 nm, and sample-to-detector distances of 22.14 and 22.75 cm were used. The sample temperature was controlled with a Mettler FP80 (Hightstown, NJ) hot stage used in conjunction with a Mettler FP82 temperature controller. Sample cells were fabricated from aluminum differential scanning calorimetry (DSC) pans modified with Kapton windows in the top and bottom. Beam monitors placed before and after the sample cell allowed for the calculation of absorption coefficients and normalization of the intensities with respect to sample thickness and incident beam intensity. Additional details of the experimental setup at SSRL may be found elsewhere.

Two types of experiments were performed: (1) temperature-resolved dynamic heating experiments where the sample was heated at 20°C/min and (2) time-resolved quenching experiments where the sample was cooled rapidly from a high temperature to a lower temperature. The SAXS data were corrected for parasitic scattering, incident beam decay, sample absorption, and thermal background. Scattering intensity from a calibrated polyethylene standard was used to convert the SAXS data to absolute intensity.
RESULTS AND DISCUSSION

Temperature-Resolved Dynamic Heating Experiments

In Figure 1, the SAXS intensity for the neat Zn-SEPDM ionomer is plotted against the scattering vector \( q \) (where \( q = 4\pi \sin \theta / \lambda \) and \( \theta = \frac{1}{2} \) of the scattering angle) for temperatures between 40 and 294°C. The diffuse maximum between approximately \( q = 0.5 \) and 2.8 nm\(^{-1}\), which corresponds to a characteristic size \( d \) in real space (\( d = 2\pi / q \)) of 2.2 to 12.6 nm, is due to microphase separation of an ion-rich phase. Similar ionic peaks with \( d \approx 1 \) to 5 nm are observed in most ionomers.\(^1,2\) A second significant feature of the scattering pattern, which is also seen in the SAXS results of other ionomers, is a large upturn at low \( q \), in this case for \( q < 0.4 \) nm\(^{-1}\). Although the origin of this scattering upturn is uncertain, in the past it has been attributed to a heterogeneous distribution of the ionic species in the polymer.\(^8,9\) Agarwal and Prestidge\(^10\) observed large ionic domains, \( \sim 500 \) to 1000 nm, by transmission electron microscopy (TEM) studies of Zn-SEPDM, which could contribute to the intense zero-angle scattering seen in Figure 1. However, TEM evaluation of Zn-SEPDM ionomers by Handlin et al.\(^11\) only detected ionic domains with diameters of 2 to 3 nm.

The low intensity of the ionic peak in the Zn-SEPDM is due to the relatively low sulfonation level of the polymer and the low volume fraction of ionic domains. The intensity of the ionic peak decreased as the temperature increased, and the peak disappeared by approximately 190°C. The disappearance of the ionic peak at elevated temperature suggests that the ionic aggregates dissolve into the rubber matrix, that is, an order-disorder transition. This notion may be supported by the dynamic mechanical results of Agarwal et al.,\(^12\) who attributed the melt relaxation to motion in the ionic domains. The results of Galambos et al.\(^8\) for sulfonated polystyrene ionomers suggest that the intensity of the low-angle scattering upturn shown in Figure 1 should increase as the ionic peak disappears, that is, as the ionic groups are dispersed into the polymer continuous phase. The SAXS data for temperatures from 140 to 294°C show a monotonic increase in the zero-angle scattering as temperature increases. The increase of the low-angle scattering is small, which reflects the low volume fraction of ionic domains in this particular ionomer.

Whereas the SAXS data indicate that the ionic peak disappears by approximately 190°C, melt processability of the neat ionomer does not accompany the apparent dissolution of the ionic domains. Above 200°C, where no ionic peak is apparent, the melt viscosity of the ionomer is still exceedingly high, which indicates either that some ionic aggregation still exists but is unresolved by these SAXS measurements or that simple dipolar associations of homogeneously distributed sulfonate groups are still very effective at

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**Figure 1.** Temperature-resolved SAXS of Zn-SEPDM for a heating scan (20°C/min).

**Figure 2.** Temperature-resolved SAXS of 9 wt % ZnSt in Zn-SEPDM for a heating scan (20°C/min).
increasing the terminal relaxation time of the ionomer melt.

Temperature-resolved SAXS scattering data for the filled ionomers containing 9, 23, and 33 wt % ZnSt are given in Figures 2, 3, and 4. As with the neat Zn-SEPDM, an intense scattering upturn occurred at low $q$ for each material. The intensity of the low-angle scattering increased substantially with increasing ZnSt concentration, which indicates that the zero-angle scattering in the filled ionomers is due principally to the ZnSt. It may arise from large ZnSt domains, but resolution of features larger than about 20 nm is not possible from these data. Light-scattering experiments may be better able to characterize the origin of the low-angle X-ray scattering of the filled-ionomers, but those experiments were not done as part of this study.

A second feature in the lower temperature SAXS curves for the filled ionomers is a shoulder on the high-$q$ side of the low-angle upturn that increases in intensity with increasing ZnSt content. At the highest ZnSt concentration (33%), a shoulder and peak at approximately $q = 1.6 \text{ nm}^{-1}$ ($d = 3.9 \text{ nm}$) are visible in the scattering curve at the lower temperatures presented in Figure 4. Based on how these scattering features change with temperature, we attribute these scattering features to a poorly organized ZnSt microstructure. Any scattering that would arise from ionic domains is probably effectively masked in these SAXS data because of the much higher intensity of the ZnSt scattering.

The hypothesis of the existence of a poorly organized ZnSt microphase in these materials is supported by a previous thermal analysis study$^5$ of ZnSt-filled Zn-SEPDM ionomers that showed that at least some of the ZnSt was present as crystalline, phase-separated domains. The crystallization rate of ZnSt in the ionomer, however, was considerably suppressed compared with crystallization of pure ZnSt, which is a consequence of dipolar interactions between the metal carboxylate and sulfonate groups. As a result, multiple low-temperature melting peaks were observed in melt-pressed specimens of ZnSt-filled Zn-SEPDM, which indicated a poorly organized crystalline structure of very small crystallites. Those effects were more pronounced at lower ZnSt concentrations, which appears to be consistent with the SAXS data in Figures 2 to 4.

Another pertinent observation$^5$ is that when the ZnSt-filled Zn-SEPDM samples were aged at room temperature, which is about 75°C above $T_g$ of the ionomer and 100°C below the melting point of pure ZnSt, the melting point and the amount of crystallinity of the ZnSt in the filled ionomer increased. This observation is consistent with the heating experiments described in the following paragraph, because annealing the materials at a higher temperature should favor the formation of more perfect crystals of ZnSt.

When the ZnSt-filled ionomer samples were heated, the low-angle shoulder developed into a distinct peak at approximately $q = 1.6 \text{ nm}^{-1}$ ($d$...
= 3.9 nm), and the peak sharpened and increased in intensity as the temperature was increased up to 100°C (see Figs. 2–4). Above approximately 105°C, the peak began to decrease in intensity and eventually disappeared at a temperature between approximately 115 and 130°C, depending on the ZnSt concentration. For example, for the samples containing 9 and 33% ZnSt, the maximum peak intensity occurred at approximately 115 and 126°C, respectively. The q for the peak was independent of the ZnSt loading and temperature. The melting point of ZnSt in Zn-SEPDM also increases with increasing ZnSt concentration with roughly the same dependence as the temperature of maximum peak intensity shown in Figures 2 to 4, which supports the assignment of the SAXS peak to crystalline ZnSt. The decrease of the peak intensity above 100°C is due to melting of the ZnSt crystals.

During the heating scan, the low-q shoulder in the SAXS patterns for the lower temperatures disappeared at the expense of the higher-q peak as the temperature increased. This behavior was most noticeable in the samples containing 9 and 23% ZnSt, where no peak was observed until the temperature reached approximately 80°C. This suggests that the initial ZnSt added to the ionomer, which presumably complexes with the sulfonate groups, is present either as a disordered, noncrystalline phase or as small, imperfect crystals that are associated with the ionic domains that produce the broad scattering shoulder between q = 0.6 to 2.0 nm⁻¹. As more ZnSt is added, the ionic sites of the ionomer become saturated with associated ZnSt, and the excess ZnSt forms unhindered, better developed crystals. It is tempting to attribute the q = 1.6 nm⁻¹ peak that was observed below 80°C for only the material containing 33% ZnSt to unhindered crystals. The fact that only the 33% ZnSt filled ionomer exhibited a strong melting endotherm (by DSC) at the melting point of pure ZnSt is consistent with that assignment. For the samples with the two lower concentrations of ZnSt, the ZnSt and the sulfonate groups are probably contained within the same microstructure. When the temperature is increased, however, ZnSt crystals phase separate, which produces the higher q peak observed in the SAXS patterns. That result is also consistent with the prior DSC study that showed the melting endotherm of a pure ZnSt phase developed upon annealing the 9 and 23% ZnSt-filled ionomers. It is not clear whether the metal sulfonate groups of the ionomer form ionic aggregates at temperatures below the melting of ZnSt as characterized, for example, by the peak in the SAXS curve presented in Figure 1, because resolution of the ionic peak is not possible due to the much stronger scattering of the ZnSt crystals.

The changes in the intensity of the zero-angle scattering upturn with increasing temperature confirm that most of the scattering in the filled ionomers comes from a ZnSt phase. For the neat ionomer, there was only a very small increase of the intensity of the zero-angle scattering as temperature was increased from 40 to 300°C. In contrast, the intensity of the upturn for the ZnSt-filled ionomers decreased significantly as the melting point of the ZnSt crystals was approached. For the two lower concentrations of ZnSt, (Figs. 2 and 3), the decrease of the zero-angle scattering intensity was coincident with the development of the peak at q = 1.6 nm⁻¹, which indicates that some reorganization of the ZnSt structure occurred. This is consistent with the idea that annealing the samples below the melting point of ZnSt produced and improved the perfection of ZnSt crystals. For the 33% ZnSt concentration (Fig. 4), the upturn intensity also decreased as the peak developed, but there was also a clear increase in the upturn intensity between 70 and 90°C that is not as easy to explain. This may be due to premelting of imperfect ZnSt crystals that eventually are reincorporated into more perfect crystals while the material anneals during the heating scan, but that also might be expected to occur in the samples with lower ZnSt concentration. One explanation for the differences may be that the amount of ZnSt melting at lower temperatures for the samples with the two lower ZnSt concentrations is too small to resolve in the zero-angle scattering intensity; the earlier DSC experiments revealed that the percentage of ZnSt crystallinity in the 9 and 23% ZnSt samples was considerably lower than in the 33% ZnSt sample. Another explanation may be that the premelting only occurs for the unhindered ZnSt crystals, that is, the ZnSt in excess of what is associated with the metal sulfonate groups of the ionomer.

The q = 1.6 nm⁻¹ peak (d = 3.9 nm) in the scattering curves described previously corresponds to the long period of a ZnSt bilayer in which the chains are tilted about 27°. Vold and Hattiangdi reported a similar long spacing, 4.11 nm, for ZnSt crystals.

The zero-angle scattering of the filled ionomers decreased above the melting point of the ZnSt (T_m) as a consequence of the melting of the ZnSt, but it decreased to an intensity below that of the neat Zn-SEPDM (cf. Figs. 1–4). The electron density (Δρ_e) contrast between ZnSt crystals and the
ionomer is approximately 0.06 to 0.07 electrons/Å³ (contrast this with Δρ_e = 0.1 electrons/Å³ between the crystalline and amorphous phases in polyethylene), and this decreases to Δρ_e = 0.01 electrons/Å³ when the ZnSt melts. The decrease in the zero-angle scattering presented in Figures 1 to 4 above T_m is consistent with the calculated change in Δρ_e. Note that the Δρ_e values are relatively insensitive to whether one includes the zinc sulfonate groups in the calculation of the electron density of the SEPDM phase; the contribution of the zinc sulfonate to the electron density is relatively small, because of the very low concentration of these groups.

A broad, weak ionic peak was present above T_m in the SAXS patterns of the ionomer samples containing ZnSt (Figs. 2–4). That observation indicates that the ionic domains either coexisted with the ZnSt crystals below T_m or some other type of microdomain formed when the ZnSt melted. It was not possible to determine if this feature was present in the SAXS patterns below the melting point of the ZnSt because the scattering due to the ZnSt crystals masked the same q region. For the sample containing 9% ZnSt, the peak above T_m in the SAXS pattern was centered between approximately q = 1.2 to 3.2 nm⁻¹ (d = 2.0–5.2 nm), and, as the ZnSt concentration increased, the peak shifted slightly to higher q. For 33% ZnSt, the peak occurred between 1.4 and 3.8 nm⁻¹ (d = 1.6–4.5 nm). In all cases, the weak SAXS peak persisted to temperatures in excess of 280°C, although there was a definite weakening of the intensity and, perhaps, broadening of the peak at the elevated temperatures. The persistence of the weak SAXS peak above T_m indicates that either the ionic aggregates were not completely solvated by the molten ZnSt plasticizer or that new microphase-separated domains, probably containing molten ZnSt and the metal sulfonate groups from the ionomer, were formed. The addition of ZnSt to the ionomer significantly lowers the melt viscosity. Thus, whatever the microstructure associated with the weak SAXS peak above T_m in the ZnSt-filled ionomers, its influence on the viscoelastic behavior of the polymer is distinctly different than that of the ionic domains that occur in the neat ionomer. The relatively low viscosity of the melt compared with that of the neat ionomer is consistent with the conclusion that the molten ZnSt interacts with the metal sulfonate groups and effectively suppresses the ionic network at elevated temperatures.

The ZnSt-filled ionomer melts were relatively clear and homogenous, whereas melts of ZnSt-filled EPDM with even much lower ZnSt loadings were opaque and heterogeneous, that is, clearly macrophase separated. Those observations bolster the argument for a specific interaction between the metal stearate and the ionomer, which supports the conclusion that the molten ZnSt partially solvates the ionic or dipolar interactions in the ionomer microstructure and produces a more homogeneous melt.

The scattering invariant Q provides a measure of the extent of phase separation for a two-phase system that is independent of the size and shape of the dispersed phase. Q may be calculated from the scattering intensity, I(q) using eq. (1):

\[ Q = \int_0^\infty q^2 I(q) \, dq = \phi_1 \phi_2 (\Delta \rho)^2 \]

where the \( \phi_i \) are the volume fractions of the two phases and \( \Delta \rho \) is the electron density difference between the two phases. Because the scattering data only cover a finite q range, two approximations were made in applying eq. (1) to the experimental scattering data: (1) The I(q) data were
extrapolated to $q = 0$ and (2) it was assumed that $I(q) = 0$ for $q > 3.2$ nm$^{-1}$. These assumptions introduce relatively small error into the invariant calculation because $Iq^2$ rapidly goes to zero as $q \to 0$ and $I(q)$ is relatively constant and close to zero at high $q$. The error in the high-$q$ region is negligible, and, in the low-$q$ region, it is less than 10%.

The temperature dependence of the invariant for the neat Zn-SEPDM and the ZnSt-filled ionomers is shown in Figure 6. For Zn-SEPDM, $Q$ was relatively insensitive to temperature, although there was a small decrease in $Q$ between approximately 100 and 110°C that was probably due to the uncertainty in the $Q$ calculation but also may be indicative of some dissociation of the ionic aggregates. The nonzero value for $Q$ at temperatures up to 300°C indicates that the ionic phase did not completely disappear as was concluded previously from the failure to resolve an ionic peak in the SAXS curves (Fig. 1) for $T > 190^\circ$C. The discrepancy probably arises from the difficulty in resolving a weak and broad peak in the high temperature data presented in Figure 1. According to the invariant data shown in Figure 6, the ionic aggregates persisted to elevated temperatures in the neat ionomer, which is consistent with its extraordinarily high viscosity. The magnitude of the invariant for the Zn-SEPDM below 190°C and any changes that occur with changes in temperature are clearly much smaller than for the ZnSt-filled ionomers. As a result, $Q$ effectively provides a measure of the phase separation of the ZnSt, and any effects of ionic microphase separation are either minor or not clearly resolved. For the ZnSt-filled ionomers, $Q$ at the lower temperatures increased with increasing ZnSt, which is consistent with the notion that the ZnSt was phase-separated.

A sharp decrease in $Q$ coincided with the melting point of ZnSt in all the filled samples. The temperature at which this occurred increased with increasing ZnSt concentration, because the melting point of the ZnSt in the ionomer increased with increasing concentration. The magnitude of the change in the invariant at the melting point also increased with increasing ZnSt. Because the scattering invariant is related to the volume fractions of the two phases (see eq. 1), the decrease of $Q$ at $T_m$ (see Fig. 6) indicates that, when the crystalline ZnSt domains melt, the ZnSt mixes with the ionomer.

The invariant for the materials with the two lower ZnSt loadings falls below that of the neat ionomer above $T_m$ (see Fig. 6). Although the differences between the three samples may be within the uncertainty in the calculation of $Q$, that result may also indicate that molten ZnSt-swollen phase dissolves some of the ionic aggregates, which would be consistent with the improved melt flow of the ZnSt-filled materials. $Q$ for the ionomer containing 33% ZnSt remains higher than that for the neat ionomer above $T_m$, yet that material also exhibits the lowest melt viscosity. In this case, some of the ZnSt may remain phase separated; that is, perhaps 33% is above the solubility limit of ZnSt in the Zn-SEPDM.

The ionomer containing 9% ZnSt exhibited a small decrease in $Q$ below the ZnSt melting point as the temperature was increased. That was probably due to the melting of small, imperfect crystals that correspond to the lower temperature melting endotherms observed for that material by DSC. For the material containing 33% ZnSt, $Q$ increased just prior to melting of the ZnSt, which was probably due to some additional crystallization of ZnSt as the temperature was ramped. The difference between the premelting behavior of the 9 and 33% ZnSt samples may be that, in the latter material, the crystallization of the excess ZnSt, that is, the ZnSt not associated with the metal sulfonate groups of the Zn-SEPDM, is not perturbed by the presence of the ionomer. In contrast, all of the ZnSt in the 9% ZnSt sample is probably complexed with the ionomer (based on the DSC data), and the suppression of mobility hindered perfection of the crystals as the temperature increased below the melting point.

Thermal density fluctuations (TDFs) arising from short-range inhomogeneities due to changes in density with temperature produce increased
scattering intensity in the SAXS at high $q$. Although this contribution to the scattering is commonly subtracted from SAXS data, for multiphase systems the TDFs may contain significant contributions from short-range concentration fluctuations. For this reason, it is instructive to examine the magnitude of this correction for the ZnSt-filled ionomers.

The TDFs for the different samples considered in this investigation are plotted against temperature in Figure 7. For the neat ionomer, the TDF gradually increased with increasing temperature, and there appears to be a slope change near 100°C. That temperature closely matches the temperature at which the invariant also changed and probably corresponds to phase mixing of some of the ionic aggregates into the rubbery continuous phase.

The TDFs of the ZnSt-filled ionomers exhibited a much larger and sharper increase near 100°C, which is consistent with a first-order transition associated with the melting of ZnSt. The increase in the TDFs at $T_m$ suggests a model wherein the crystalline ZnSt microdomains melt and spontaneously mix into the ionomer-producing strong concentration fluctuations.

**Time-Resolved Quenching Experiments**

Above the melting point of the ZnSt, the SAXS patterns of the ZnSt-filled ionomers showed only a weak peak that we attributed to a microphase probably containing zinc sulfonate groups from the ionomer and some ZnSt. The importance of the ZnSt in the melt is that it significantly lowers the melt viscosity, presumably by solvating the ionic associations in the ionomer. When the melt is cooled to below $T_m$, the ZnSt phase separates and crystallizes, which is thought to be responsible, at least in part, for the development of the good mechanical properties of these elastomers. The phase-separated ZnSt crystalline phase must be associated with the ionic microstructure of the ionomer because the materials are relatively clear even at high levels of ZnSt loading and the crystallization kinetics of the ZnSt are significantly perturbed in the filled ionomers.

Time-resolved SAXS analyses provide a convenient way to follow the development of the ZnSt microstructure in real time. Although this topic was not exhaustively studied in this investigation, some preliminary time-resolved SAXS data are presented to illustrate the technique and preview future experiments. Figure 8 shows time-resolved SAXS patterns following a temperature quench from 120 to approximately 77°C for Zn-SEPDM containing 23% ZnSt. The 120°C melt exhibited a broad SAXS peak at approximately $q = 2.2 \text{ nm}^{-1}$ ($d = 2.9 \text{ nm}$). The first SAXS curve...
shown in Figure 8 was obtained 75 s after the cooling began, at which point the sample temperature was approximately 84°C and the SAXS peak was still clearly visible. The temperature equilibrated to 76.9 ± 1.1°C within approximately 120 s, and no ZnSt crystallization was observed up to that point. The SAXS curve at 165 s shows a peak at \( q = 1.6 \text{ nm}^{-1} \) \( (d = 3.9 \text{ nm}) \) that is due to the ZnSt bilayer (see Fig. 5). Once the ZnSt began to crystallize, its scattering obscured any other features that may have been present in the scattering curve between \( q = 0.6 \) to 3.6 nm\(^{-1}\), so it was not possible to determine whether the ZnSt crystals coexisted with an ionic microstructure. The intensity of the ZnSt SAXS peak increased as additional ZnSt crystallized, and the maximum intensity reached a relatively constant value after about 9 min.

Similar results as shown in Figure 8 were obtained at other crystallization temperatures. As a first approximation, the peak intensity was expected to be proportional to the amount of the ZnSt phase formed. The invariant \( Q \) would have been a better measure, but those calculations were not made because of the difficulty in extrapolating the low-\( q \) data to \( q = 0 \). Figure 9 shows the time evolution of the maximum peak intensity for time-resolved SAXS data following temperature jumps of the 23% ZnSt filled ionomer from 120 to 77 and 67°C. The dashed lines in Figure 9 represent the best fit of eq. (2) in which \( I_{max,\infty} \) is the asymptotic intensity of the scattering peak, which should be proportional to the final volume fraction of the crystalline ZnSt phase, and \( R \) is effectively the crystallization rate. \( I_o \) is a constant that corrects for the cooling transient and any retardation of the crystallization; no physical significance is attached to \( I_o \):

\[
I_{max} = I_o + I_{max,\infty}(1 - e^{-Rt})
\]  

The fitting parameters that produced the best fit of the data presented in Figure 9 are summarized in Table I. Crystallizing the ZnSt at the lower temperature produced a faster rate of crystallization, although crystallization at the higher temperature produced a greater degree of crystallinity of the ZnSt. Neither of those results is surprising, but they do demonstrate how the processing history of the filled ionomers may affect the microstructure of the materials, which also affects their mechanical properties.6

**CONCLUSIONS**

SAXS provided some insight into the origin of reinforcement and plasticization of the Zn-SEPDM by ZnSt. First, it is clear that the ZnSt is phase separated at temperatures below the melting point of ZnSt, although it is also compatible with the ionomer at concentrations of at least 33 wt %. The compatibility, which is not the case for ZnSt in unsulfonated EPDM, provides strong circumstantial evidence for a specific interaction between the metal stearate and the ionomer.

The crystallization kinetics of the ZnSt in the ionomer is perturbed by the interaction with the zinc sulfonate groups, so that, when the filled ionomer is cooled quickly from the melt, as occurs in a typical molding process, the resulting organization of the ZnSt is not well developed. Improved ordering occurs when the ZnSt-filled polymer is heated above 50°C and presumably with aging under ambient conditions, although the latter was not assessed in this investigation. In addition, the ZnSt crystals are organized as a bilayer that is tilted approximately 27° to the normal of the crystal surface. The relative clarity of ZnSt-filled Zn-SEPDM films indicates that the ZnSt crystal size is very

![Figure 9](image)

**Figure 9.** SAXS peak intensity vs. time for temperature-quench experiments from 120 to (C) 67 and (D) 77°C. The dashed lines represent the least-square fits of eq. (2).
small, which is supported by the low melting point and multiple melting endotherms observed for these materials and may be consistent with the bilayer crystal structure.

It is certainly conceivable that the ZnSt behaves as a reinforcing filler, although that contention has never been established unambiguously. An alternative explanation for the improvement of the mechanical properties of SEPDM by the addition of ZnSt is that the plasticizer promotes the preparation of better, imperfection-free films. However, one observation made here supports the reinforcing-filler concept. The mechanical properties of the ZnSt-filled ionomer usually improve with aging, and a substantial improvement is observed within 24 h of molding. The DSC results indicated that perfection of the ZnSt crystals improved under ambient conditions after molding, as evidenced by increases of the melting point and the degree of crystallinity. The SAXS results support the DSC results, although in both cases the changes in the ZnSt crystal structure occur at either higher temperatures or longer times when the sample is aged at room temperature rather than in the conditions in which the improved mechanical properties are observed.

SAXS data taken at elevated temperatures indicate that the ionic microphase that is responsible for the cross-linked characteristics of ZnSEPDM persists to at least 300°C, which explains the high melt viscosity and difficulty in melt processing the ionomer. Although microphase-separation is also observed above the melting point of the ZnSt in the ZnSt-filled ionomers by the SAXS measurements, the composition of that microphase is believed to be much different than that for the neat ionomer. For the filled polymers, the microphase at high temperatures is probably a mixed phase of the salt groups from the ionomer and molten ZnSt. In that case, the solvated ionic groups would be ineffective at providing physical cross-links, which is consistent with the considerably lower melt viscosity of the ZnSt-filled polymers.

The high temperature SAXS data also indicate that above its melting point, ZnSt is at least partially miscible with Zn-SEPDM. The dissolved ZnSt should effectively solvate any non-microphase-separated sulfonate groups and prevent their association with other sulfonate groups to form simple cross-links. When the ZnSt/ZnSEPDM melt is cooled to below the melting point of the ZnSt, however, ZnSt phase-separates and crystallizes, although, as stated earlier, the crystallization kinetics are significantly perturbed from those of neat ZnSt or ZnSt in EPDM.

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