Void Formation in a Filled SBR Rubber Determined by Small-Angle X-Ray Scattering

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Synopsis

Two commercial styrene–butadiene (SBR) latexes were used to prepare a model filled material consisting of glassy SBR filler particles about 1000 Å in diameter embedded in a rubbery SBR matrix crosslinked by γ-radiation. When transparent specimens of this material were extended, voiding occurred, as evidenced by stress whitening and greatly enhanced X-ray scattering intensity. More voids were formed at higher rates of extension, but voids disappeared when specimens were relaxed. The effects of filler content and cure time of the matrix on the size and number of voids formed were determined by low-angle X-ray scattering for a constant extension rate and a constant extension ratio $\lambda = 1.6$. The number of voids measured by X-ray scattering intensity decreased rapidly with time over the 3-h period of measurement. The number of voids remaining 1 h after extension increased about 40 times as filler content was increased from 15% to 50%. Increasing the cure time from 24 to 96 h increased the number of voids about four times. In contrast, the radius of gyration of the voids formed (250–350 Å) did not depend strongly on time, nor did it depend strongly on the filler content or the cure time of the matrix. Stress relaxation measurements made under the same conditions as X-ray scattering measurements showed effects typical of filled materials. However, the relaxation of stress (which followed a power law decay) was much slower than the decay of the number of voids as measured by X-ray scattering intensity.

INTRODUCTION

Application of stress causes void formation and consequent stress whitening in a variety of homogeneous and heterogeneous polymeric materials. A well-known homogeneous system is the polymeric glass, which often undergoes extensive voiding and crazing when strained to a few percent or less. The process is usually irreversible in glasses, and the opacity resulting from an applied stress remains indefinitely upon release of the stress. Void and craze formation in glassy polymers has been studied by a vareity of techniques, including electron microscopy,[1–4] small-angle X-ray scattering,[5–9] and light scattering.[10]

This work considers a heterogeneous system which may stress-whiten, namely, a filled rubbery polymer in which relatively hard filler particles are dispersed in a rubbery matrix. Many such polymers show a small volume increase when stress is applied[11–15] if the filler particles are not too small,[16,17] indicating that voids are formed throughout the sample. This void formation is observed as stress whitening only if the sample is initially transparent and the voids are sufficient in size and number to cause appreciable scattering of visible radiation. The amount of whitening depends on the rate of strain, and may or may not appear to be reversible, depending on the time scale of observation.

Stress whitening in filled rubbery systems is of considerable interest. The

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formation of small voids responsible for the whitening at relatively low strains may be the first step of the failure process which occurs at much higher strains. More importantly, detailed information about voids formed under stress may help elucidate the mechanism of rubber reinforcement by filler particles. The study of stress whitening and void formation seemed ideally suited to radiation scattering measurement. However, scattering studies of readily available systems are often difficult or impossible to make. Either the samples are opaque to the radiation, as is the case of carbon black filled systems to light irradiation, or the samples are so heterogeneous that radiation is scattered even in the unstressed state. The latter difficulty leads to measurement of the void scattering as a small difference measurement and subsequently to a very equivocal interpretation.

This work is a preliminary study by small-angle X-ray scattering (SAXS) of void formation in a filled system in which these difficulties have been circumvented. The filler is a polymeric latex, similar to those reported earlier.[18-20] Although the morphology of such systems had been studied earlier by SAXS,[21] stress whitening has not been studied. The particular system used for this study consists of a rubbery styrene–butadiene (SBR) matrix having a low styrene content in which glassy latex filler particles of an SBR with high styrene content are dispersed. The filled material is nearly optically transparent at zero strain, and it stress whitens remarkably at strains as low as 5%. It is well suited to studies of void formation by either SAXS or light scattering because the filler and matrix have very nearly the same electron density or refractive index. The samples appear homogeneous by SAXS or light scattering at zero strain. The greatly increased scattering intensity observed upon application of stress can only be due to void formation in the material, since SBR does not crystallize.

In these materials stress whitening and therefore scattering is time dependent. Rapid application of a tensile strain produces a large amount of stress whitening, whereas gradual strains produce less stress whitening. When a specimen is strained and held at constant strain, the whiteness decreases with time. Although visible whiteness and excess scattering disappear upon release of strain, the rate of return to the initial optical transparency varies according to the chemical composition and temperature of the sample.

This work relates the effect of these mechanical, chemical, and thermal variables on void formation as measured by SAXS. In particular, the effects of total percent filler, cure time of the matrix, extension rate, and repeated stretching are examined. Independent measurements of tensile stress relaxation were also made, and the time dependence of the tensile stress was compared to the time dependence of the X-ray scattering intensities.

EXPERIMENTAL

Materials

Two latexes were used to prepare the films from which X-ray scattering and stress relaxation data were obtained. The SBR latex used as filler contained 85% styrene and was obtained from the B.F. Goodrich Chemical Co. (Goodrite 2507). The particle size given by Goodrich for this latex was about 1000 Å. The glass transition was about 53°C. A second latex containing about 50% styrene was used for the preparation of the rubbery matrix. This latex was obtained from the Goodyear Tire and Rubber Co. (Pliolite 2000). It has a glass transition temperature of about −25°C.

Film Preparation

Films were prepared by mixing the two latexes at a predetermined composition ratio, casting the mixture on a glass plate, and evaporating the water. The resulting film was further dried *in vacuo.* Films having a thickness of approximately 0.8 mm were used. The films were cured at room temperature under a nitrogen atmosphere with ^{60}Co λ-radiation. The source had a radiation rate of approximately 1.2×10^6 rad/h, and the irradiation of the samples usually lasted 1–4 days.

Electron Microscopy

Electron micrographs were taken with a JEOL model 120U transmission electron microscope. Microtomed sections of the filled samples were stained with osmium tetraoxide. A representative micrograph of a specimen containing 30% filler taken at 20,000 magnification is shown in Figure 1. Since the butadiene in both the matrix and the filler can be stained, it is necessary to look for a contrast in grey areas. However, the filler (light-colored) can be seen to have a range of particle sizes between 500 and 1000 Å, and the preparation is not monodisperse. The spatial dispersion in the matrix, which is much more important in these

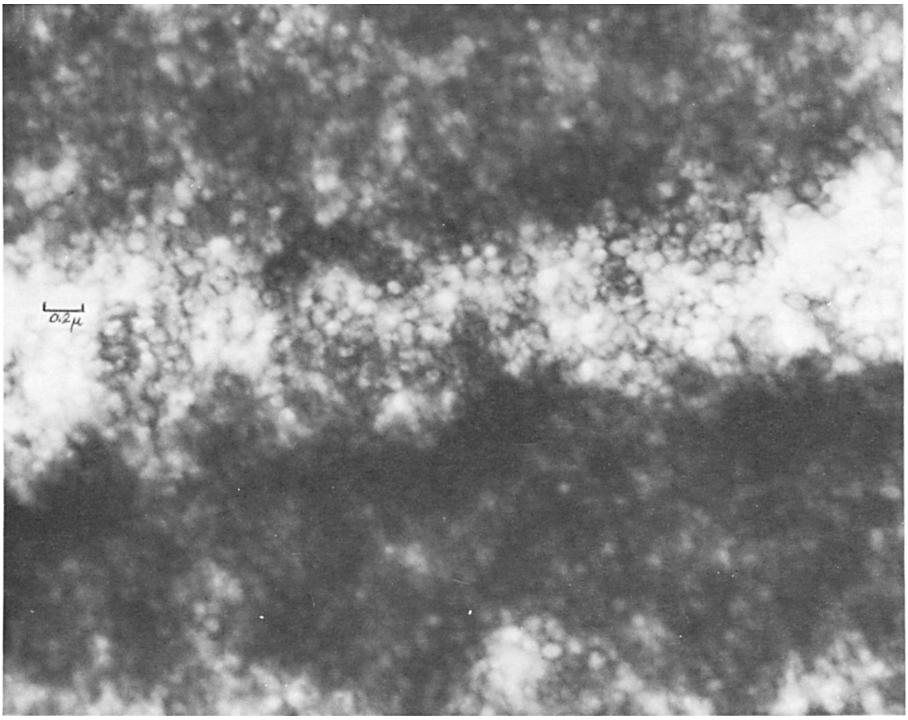

Fig. 1. Electron micrograph of sample containing 30% filler (20,000 ×). The marker is 0.2 μm.

preliminary experiments with commercial latexes, appears rather uniform with occasional clusters, particularly along the central band. Other pictures do not show the light central band but do show occasional clusters of about the same magnitude.

Small-Angle X-ray Scattering

Room temperature measurements of scattered intensity were made with a Kratky diffractometer mounted on a Philips PW1310 X-ray generator. Nearly all measurements were made using a 60-μ entrance slit. The intensity at angle 2θ was counted with a Norelco proportional counter coupled to a Norelco data control and processor. Counting was done at a series of angles, usually in increments of 1.19×10^{-4} rad.

Specimens of the cast films having dimensions 6 mm × 50 mm were cut for X-ray measurements. Four specimens were stacked together to obtain higher scattering intensity. The specimens were extended in a stretching device mounted in the diffractometer, and the intensities were measured at fixed extension ratio λ. The same measurements were also made on unstretched specimens. Corrections to the scattering intensities were required to compensate for the different thicknesses of the stretched and unstretched specimens. The corrected intensity difference between the stretched and unstretched specimen is due to the scattering by voids formed when the specimen is stretched. An example of the increase in intensity on stretching is shown in Figure 2 for a typical sample about 1 h after stretching to $\lambda = 1.6$.

Guinier plots of the data were made, and the radius of gyration was determined from the slopes of these plots. The number of voids is proportional to the intensity at zero angle $I_{2\theta=0}$, which was obtained by extrapolation of the Guinier plots from higher angles to zero angle.

Scattering intensities were time dependent, and, although data were obtained as soon as possible after samples were stretched, the "zero time" data are not

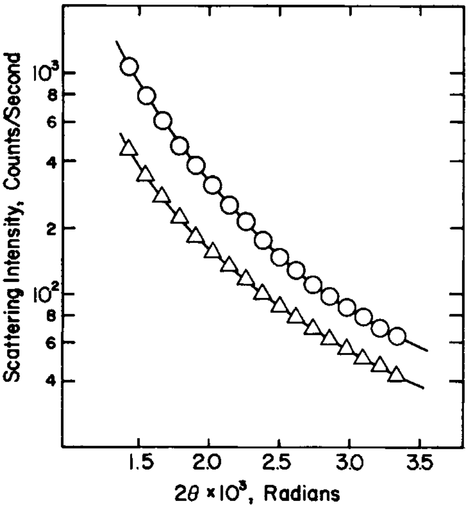

Fig. 2. Comparison of scattering intensities of extended ($\lambda = 1.6$) and unextended cured samples containing 50% filler: (△) unextended; (○) extended to $\lambda = 1.6$.

considered to be very reliable. The rate of strain could not be strictly controlled with the stretching device used, and the X-ray measurements required at least 10 min. Consequently, the first results at "zero time" are only included in plots of scattering results to give an indication of early intensities, but they are not used to correlate scattering intensities with other properties.

Stress Relaxation Measurements

The tensile stress relaxation modulus of each sample was measured at room temperature with a Statham Model UC3 transducer and a Statham SC1001 transducer readout. The applied strain was determined by measuring the distance between two benchmarks on the specimen with a cathetometer. The specimens used for stress relaxation measurements were approximately 8 mm × 40 mm.

RESULTS

Effect of Filler Content on Stress Whitening

The filled samples showed stress whitening over a wide range of filler content. The occurrence of whitening depended on the strain rate as well as on the strain to which a specimen was subjected. At constant strain rate, the minimum strain required for whitening increased as the proportion of filler decreased. For samples with moderate filler content (15–30%), stress whitening was easily seen at strains of about 30% or more. Stress whitening could be seen for samples with filler content as low as 5%, but the strain had to be increased above 30% to obtain whiteness comparable to that seen in samples having higher filler content. For a sample having 50% filler, less than 30% strain caused a large amount of whitening. No stress whitening was observed at any strain when a transparent film of the matrix alone was stretched.

The effect of filler content on the extrapolated zero-angle X-ray scattering intensity $I_{2\theta=0}$ is shown in Figure 3. Here $I_{2\theta=0}$ is plotted against time for samples with 15%, 30%, and 50% filler. Each sample was cured for the same length of time, 72 h, then extended at about 1300 mm/min to an extension ratio of $\lambda = 1.6$. The scattering increases remarkably with filler content. Figure 3 also shows a significant time dependence of the X-ray scattering intensity for these samples. $I_{2\theta=0}$ decreases more rapidly in the first hour than in succeeding periods, but the rate of decrease does not seem to vary markedly with filler content. As the decrease in $I_{2\theta=0}$ may be attributed primarily to a decrease in the number of voids, assuming the same distribution of hole sizes, this indicates that the rate of disappearance of voids does not depend appreciably on the filler content.

Effect of Cure Time

Increasing the time of cure increases the degree of crosslinking of the matrix and hence would be expected to affect the time dependence of both the stress whitening and the mechanical properties of the material. Scattering measurements were made on a series of samples having a constant filler content of 30% and varying times of cure, that is, exposure to γ-irradiation. Each sample was

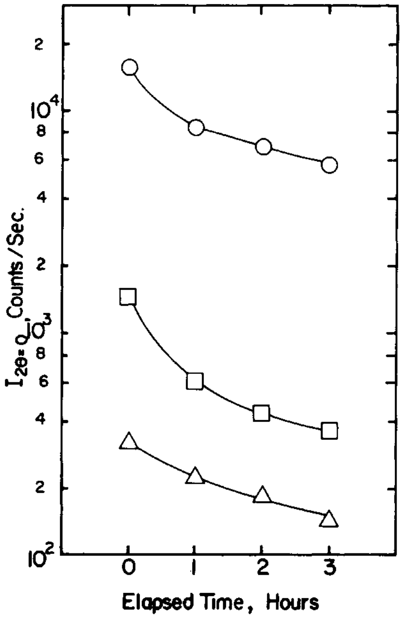

Fig. 3. Decrease of scattering intensity with time for samples cured 72 h having different filler contents: (△) 15% filler; (□) 30% filler; (○) 50% filler.

extended at about 1300 mm/min to an extension ratio of λ = 1.6. The results are shown in Figure 4. Although the decay of intensity $I_{2\theta=0}$ with time for different times of cure is roughly the same form, there is a clear correlation with cure time only at an elapsed time of 1 h or more. For times greater than 1 h the scattering intensity roughly correlates linearly with the cure time. This in effect correlates the scattering intensity with increased stress, since the samples were rapidly elongated to constant strain. In a first approximation the crosslink density increases linearly with cure time so that the stress increases linearly with cure time. However, no simple relationship exists between $I_{2\theta=0}$ and cure time

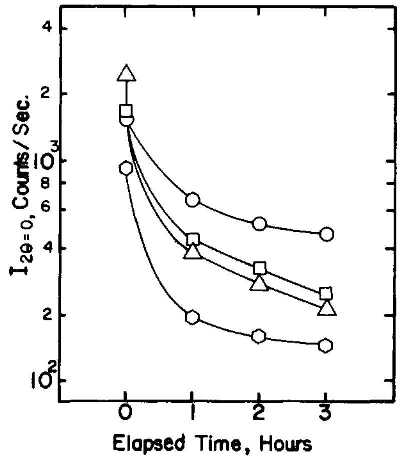

Fig. 4. Decrease of scattering intensity with time for samples containing 30% filler cured for different times: (○) 24 h; (△) 48 h; (□) 72 h; (○) 96 h.

for the initial measurements taken just after the samples were stretched, probably because of the difficulty discussed earlier in obtaining accurate data at short times. Of course, the initial decrease of intensity with time is greater for all of the samples.

These results demonstrate clearly that the void scattering depends strongly on the viscoelastic properties of the matrix as they are influenced by the degree of crosslinking.

Reversibility of Stress Whitening

Stress whitening in this system appears to be entirely reversible, although the time scale for returning to the initial state varies with cure time. Whiteness disappeared almost immediately upon removal of stress for samples cured from 24 to 96 h, and these samples stress whitened again when stretched a second time. Reversibility is also shown by X-ray scattering, as shown in Figure 5 for a specimen containing 30% filler which had been cured 72 h. This specimen was stretched at 1300 mm/min to $\lambda = 1.6$, held 1 h, and then the stress was removed for 1 h before X-ray data were obtained on the relaxed sample. The scattering intensity is nearly identical to that of an unstretched virgin sample.

Stress whitening was also reversible for samples having longer cure times, but a longer time period was required for the return to the initial state. A sample having 30% filler and cured 192 h did not regain transparency at room temperature until several hours after the release of stress. The time for the disappearance of whiteness after the release of the stress was considerably decreased by heating to about 60°C.

These results show that the time for the disappearance of voids upon removal of stress is strongly influenced by the viscoelastic properties of the matrix, as is the appearance of voiding at constant strain rate. The process by which voids disappear is more strongly retarded by a tightly crosslinked matrix than by a

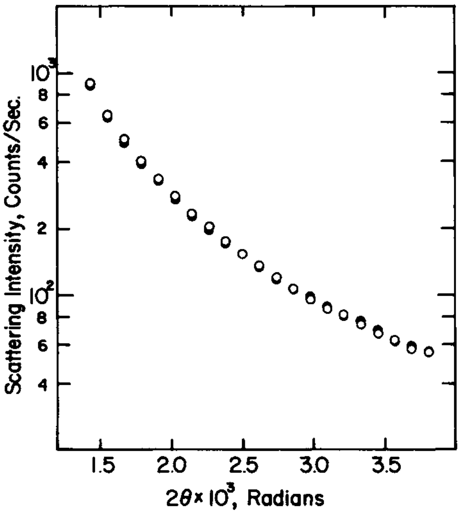

Fig. 5. Comparison of scattering intensity of a virgin sample with a sample stretched once. (Each contained 30% filler and was cured 72 h): (○) unextended virgin sample, (●) sample was extended 1 h, then stress was removed for 1 h.

lightly crosslinked matrix and hence occurs over a longer time scale. Thus for the latter case, stress whitening does not appear to be immediately reversible.

Effect of Extension Rate

Although the apparatus used did not allow precise control of the rate at which samples were extended for X-ray measurements, the effect of a large variation in initial extension rate was investigated for a few samples. A sample cured for 72 h with 30% filler did not show stress whitening when the extension rate was about 100 mm/min. When the cure time was increased to 96 h, whitening was observed, but the effect was too weak to be reliably detected by SAXS. For a cure time of 192 h, stress whitening was observed, and X-ray scattering data could be taken. Results are shown on Figure 6 for this sample at two extension rates, about 100 mm/min and about 1300 mm/min. Results of similar measurements at two extension rates are given for a sample with 50% filler which had been cured for 70 h.

As shown in Figure 6, samples having 50% filler showed high stress whitening even at a lower cure time of 70 h and at the lowest extension rate of 100 mm/min. The voiding of this very highly filled system is increased as if it were more tightly crosslinked.

Void Size

The aveage radius of gyration of the voids was obtained from the slope of the Guinier plots of the SAXS data. The radius of gyration was found to depend on the filler content, the cure time, and the time the samples were held in an extended state.

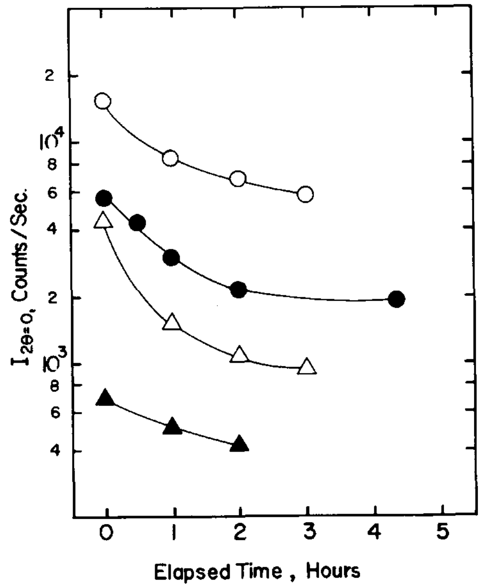

Fig. 6. Effects of extension rate on scattering intensities: (△) 30% filler, cured 192 h, stretched about 1300 mm/min; (▲) 30% filler, cured 192 h, stretched about 100 mm/min; (○) 50% filler, cured 70 h, stretched about 1300 mm/min; (●) 50% filler, cured 70 h, stretched about 100 mm/min.

The change in void size with filler content and elapsed time is shown in Figure 7 for a series of samples, each of which was cured for 70 h and extended to $\lambda = 1.6$ at about 1300 mm/min. The void size appears to increase somewhat with filler content. It is possible that this increase at the higher filler content is somewhat overestimated because an increased concentration of voids in the samples with higher filler content could cause increased interparticle scattering instead of pure intraparticle scattering.[22] In all samples except the one containing 50% filler, the average void size appeared to decrease slightly with time, although the decrease is not greater than 20%. The void size for the sample with 50% filler was almost constant during the period of time of the measurements.

Figure 8 shows the change of void size with time for samples with 30% filler and cured for different times. The extension ratio is again 1.6 in each case. There is a large apparent decrease in the void size during the first hour of measurement which is more pronounced for the more lightly cured samples. After

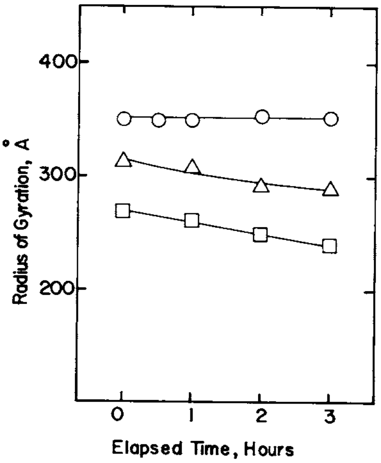

Fig. 7. Effect of filler content on void size for samples cured 70 h: (□) 15% filler; (△) 30% filler; (○) 50% filler.

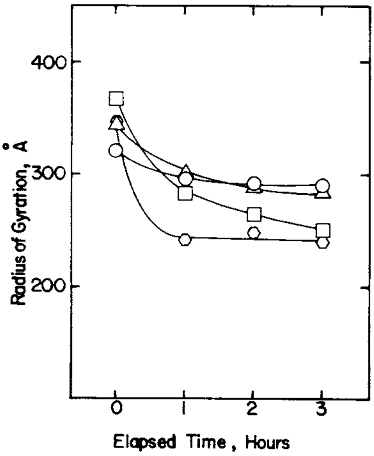

Fig. 8. Effect of cure time on void size for samples with 30% filler extended to $\lambda = 1.6$: (⬡) 24 h; (□) 48 h; (△) 72 h; (○) 96 h.

the first hour, there is a slower decrease with time. A comparison of Figures 7 and 8 shows the uncertainty in the "zero" time size determination for roughly the same cure time. At long times (3 h) the sizes are 285 and 288 Å, respectively. At "zero" time, the sizes are 314 and 345 Å, respectively.

Both the void size and the number of voids decrease with the time the sample is held in an extended state. However, the decrease in void size after 1 h (~5%) is not nearly so great as the decrease of the number of voids (as measured by the decrease in scattering intensity) after 1 h (~30%), as shown in Figure 4. For the more tightly crosslinked and more highly filled samples, change of void size after 1 h is almost negligible (<5%).

Effect of Repeated Stretching

The effect of repeated stretching was investigated to see if signs of filler agglomeration could be seen after repeated stretching and relaxing.[23] Samples containing 30% filler and cured for varying lengths of time were used. A sample cured 72 h did not show whitening after being stretched and relaxed five times up to the strain where stress whitening was known to occur on the first stretch. If filler agglomeration were the cause of the decreased whitening, the process might be impeded by a stiffer matrix; consequently, there would be a decrease in whitening after prestretching highly cured samples. Accordingly, cure times were extended to 164 and 192 h in additional samples containing 30% filler. These samples still showed stress whitening after being repeatedly stretched 5, 10, or 20 times, although the whitening was less than for virgin samples.

SAXS data for the sample having a cure time of 192 h, stretched 10 times to $\lambda = 1.6$, are shown in Figure 9, along with data for a virgin sample having the same cure time and same extension ratio. The intensity of scattering going from short to long times decreases approximately one-half. Data are also shown in Figure 10 for a similar sample with 30% filler cured 164 h and repeatedly stretched to $\lambda = 1.6$. The decrease is greater than one-half for 10 repetitions of the stretching as well as for 20 repetitions. The interesting feature is that intensities for the samples stretched 20 times almost immediately come to the asymtotic limit of the sample stretched 10 times. It is as though the number of "unstable" voids

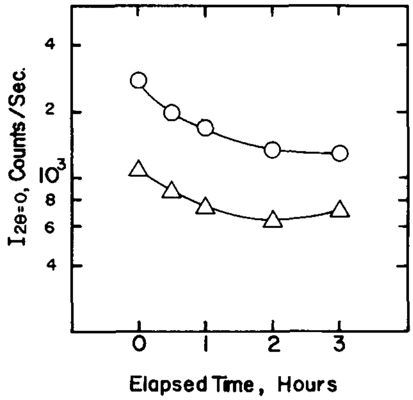

Fig. 9. Effects of repeated stretching on scattering intensities for samples with 30% filler, cured 192 h, and extended to $\lambda = 1.6$: (○) virgin sample; (△) sample extended and relaxed 10 times.

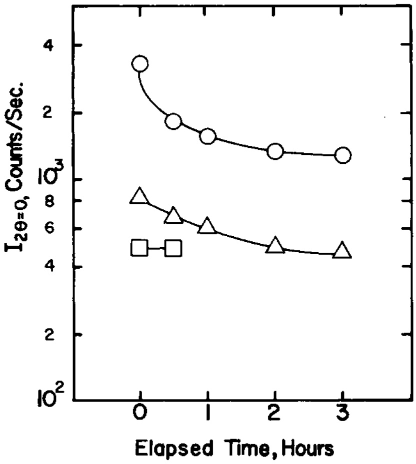

Fig. 10. Effect of repeated stretching on scattering intensities for a sample with 30% filler, cured 164 h, and extended to $\lambda = 1.6$: (○) virgin sample; (△) sample extended and relaxed 10 times; (□) sample extended and relaxed 20 times.

(that is, those capable of rapid decay) is decreased on repeated stretching. Alternatively, any agglomeration of filler particles at fixed strain has probably occurred by the 20th stretch.

Data from Figures 9 and 10 may be combined with those of Figure 4 to show the effect of cure time on scattering intensity over an extended range of cure. The intensities at 3 h given in Figures 9 and 10 for both samples cured for long times (164 and 192 h) is about 1300 counts/s. Therefore the number of voids approaches a limiting value at long cure times. The decrease in $I_{2\theta=0}$ with elapsed time also becomes smaller with increasing cure time.

Stress Relaxation Measurements

The decreases of scattering intensities and radii of gyration with time reflect the relaxation of size correlations of the order of hundreds of angstroms. There is also a concomitant decrease of the macroscopic stress in the specimen as it is held at constant strain. The latter decrease of stress is presumably achieved by molecular motions of the order of tens of angströms operating over the whole specimen, including the regions containing the voids. In order to compare these fundamentally different observations, two series of stress–relaxation measurements were made on specimens whose SAXS stress whitening behavior had been measured under similar conditions.

In the first series, filler content was varied while cure time was held constant at 96 h. These experiments were (excepting a small difference in cure time) identical to those reported in Figures 3 and 7 for cure times of 70 h. In the second series of stress relaxation experiments, cure time was varied for samples having a constant filler content of 30%. In these experiments the conditions were identical to those for the SAXS measurements reported in Figures 4 and 8. Plots of the logarithm of the tensile relaxation modulus $E(t)$ against the logarithm of time are shown in Figure 11 for various filler contents. In Figure 12 the variation of $E(t)$ with cure time at fixed filler content is shown. The extension ratio λ was 1.6 for all runs in both series.

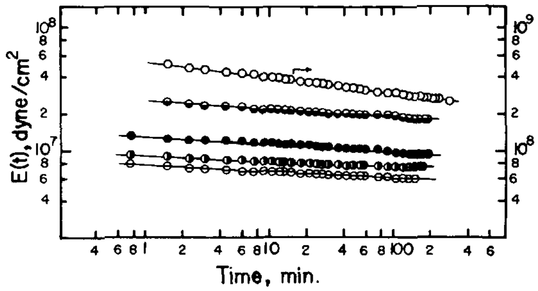

Fig. 11. Stress relaxation for samples cured 96 h having different filler content: (⊖) matrix only; (◑) 5% filler; (●) 15% filler; (◒) 30% filler; (○) 50% filler.

In every case the double logarithmic plots are linear over the two and one-half decades of time over which data were obtained, although the slopes systematically change in both figures. Accordingly, the data are well represented by the relationship

$$E(t) = E_i t^n,$$

where E_i is a value of $E(t)$ at an arbitrarily chosen time near the shortest time at which reliable measurements were obtained, and n is a constant. Power law relationships of this type have long been observed for the stress–relaxation of a variety of filled and unfilled elastomers.[24–26]

No attempt was made to obtain values of the equilibrium modulus by a more sophisticated graphical analysis of the stress–relaxation data.[27] However, the effect of increasing filler content can be illustrated by the trend in any isochronal set of values of $E(t)$ taken from Figure 11. The same trends would be observed for these isochronal moduli as would be observed for equilibrium moduli. The isochronal moduli are seen to increase with increasing filler content; this trend has been observed for a variety of filled and crosslinked systems.[14,28]

It is apparent from Figure 12 that any isochronal set of values of $E(t)$ for samples having different cure times can be used to show the effect of cure time on the modulus at constant filler content. The modulus, of course, increases with increasing cure time.

The variation of the rate of stress relaxation n with filler content at a constant cure time of 96 h is given in Figure 13. Here n is $-d\log E(t)/d\log t$, the negative slope of the plots of Figure 11. There is little dependence of n on filler content

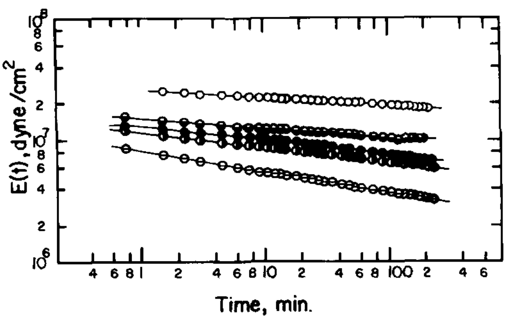

Fig. 12. Stress relaxation for samples having 30% filler cured for different times: (⊖) uncured; (◑) 24 h; (●) 48 h; (◒) 72 h; (○) 96 h.

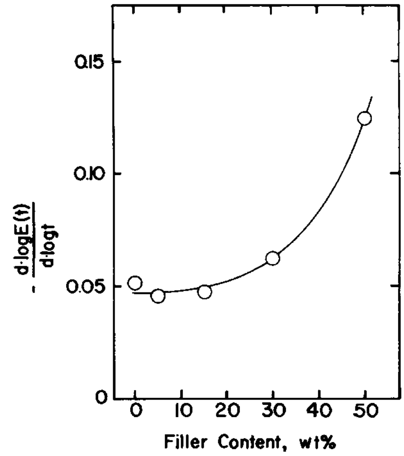

Fig. 13. Variation of stress relaxation rates with filler content for samples cured 96 h.

until about 30 wt % filler. At about this point, *n* increases sharply, and at 50 wt % filler content the rate is more than double its value at less than 30 wt % filler. This increase is similar semiquantitatively to the behavior of crosslinked rubbers containing conventional fillers.

Figure 14 shows the dependence of the rate of stress relaxation *n* taken from Figure 12 on the cure time at constant filler content of 30 wt %. The value of *n* decreases with increasing cure time (and degree of crosslinking). This trend also is the same as the trend in unfilled materials.[29]

The time dependence of stress–relaxation differs significantly from the time dependence of the scattering intensity. For a constant cure time of 72 h, the effect of filler content on the scattering intensity is given in Figure 3. Because individual X-ray intensity measurements require much more time than individual stress–relaxation measurements, only data points at 1 h and later are available at each filler content. Thus, although doubly logarithmic plots of intensity vs. time can be made, such plots (not shown) cannot establish (or dis-

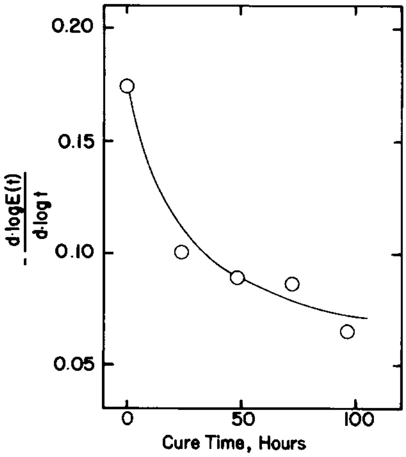

Fig. 14. Variation of stress relaxation rates with cure time for samples with 30% filler.

prove) a power law relationship between these variables. However, the slopes of these doubly logarithmic plots are in the vicinity of −0.35 to −0.5, and it is clear that the rates of decay of intensity are much higher than the comparably presented rates of stress relaxation shown in Figure 13.

The data of Figures 4 and 14 may be similarly compared to show the effect of cure time on the stress–relaxation rate and the rate of decay of intensity. It is evident from the semilogarithmic plot of Figure 4 that within experimental error (using intensities at 1 h and later) the rate of decay of intensity is independent of cure time at fixed composition, whereas the rate of stress relaxation decreases monotonically with increasing cure time. A doubly logarithmic plot (not shown) of the intensity data of Figure 4 vs. time has a slope of about −0.3, about three times higher than the rate of decay of stress.

DISCUSSION

Number of Voids as a Function of Filler Concentration, Cure Time, and Strain Rate

If $I_{2\theta=0}$ is assumed to be proportional to the number of voids, the data of Table I show how the number of voids changes with filler loading and cure time. Since "zero time" intensities are hard to measure due to unavoidable relaxations, intensities at 1 h have been compared in Table I. The data are collected from Figures 3, 4, 6, and 9.

It is immediately apparent that filler loading has the largest effect on the number of holes. For example, as the filler concentration increases threefold (15–50%), and the modulus increases threefold for the same experiment (1×10^7–3.2×10^7 dynes/cm^2 at 1 h, Fig. 11), the scattering intensity increases 37-fold (230–8500 counts/s^{-1}).

In contrast the scattering intensities are only linearly correlated with cure time. That is, as the cure time increases eightfold (24–192 hrs), the scattering intensity increases ninefold (180–1700 counts/s). (For cure times below 96 h the moduli at 1 h in Figure 12 are also available for comparison and discussion later.)

Table II below combines the 1 h scattering intensities from Figure 6 at different strain rates and from Figure 9 at different initial conditions of prestretching.

TABLE I
Zero Angle Intensities (counts/s) at 1 h as a Function of Filler Concentration and Cure Time at 1300 mm/min Strain Rate and $\lambda = 1.6$

	Filler concentration/		
Cure time (hr)	15%	30%	50%
24		180[a]	
48		380[a]	
72	230	600,[b] 440[a]	8500,[b] 8800[c]
96		680[a]	
164		1500,[d] 1500[c]	
192		1700[e]	

[a] Figure 4.
[b] Figure 3.
[c] Figure 6.
[d] Figure 9.
[e] Figure 10.

TABLE II

Zero Angle Intensities (counts/s) at 1 h as a Function of Strain Rate and Initial Conditions of Strain with $\lambda = 1.6$

	Initial conditions Strain rate (mm/min)	Stretched once	Stretched 10 times	Stretched 20 times
30% filler	100	500[a]		
	1300	1500[a]	600[b]	480[b]
		1500[b]		
		1700[c]	730[c]	
50% filler	100	3000[a]		
	1300	8500[a]		

[a] Figure 6, 70-h cure.

[b] Figure 10, 164-h cure.

[c] Figure 9, 192-hr cure.

There was insufficient scattering at a strain rate of 100 mm/min to make meaningful SAXS meaurements on samples containing 15% filler. Similarly there was insufficient scattering at 1300 mm/min to make meaningful SAXS measurement on samples containing 5% filler. Thus, there is a threshold strain rate for this particle size filler, using the present equipment; furthermore, the threshold rate decreases as the filler concentration increases. After the threshold is passed, however, the influence of strain rate is not a major effect compared to filler composition. For example, a 10-fold increase of strain rate causes only a three-fold increase in scattering (at 1 h) for both 30% and 50% filler loadings.

The stress softening effect is well known in filled rubbers. The effective stress after a few repeated stretchings of a filled rubber to a constant strain of $\lambda = 1.6$ would be decreased to ⅓ of its original value at these particular filler loadings. Many further stretchings to a fixed strain do not significantly lower the stress. As expected, the scattering intensities parallel the effective stress in decreasing to ⅓ of their initial values after 10 stretches and decreasing only slightly thereafter.

Thus the dominant variable in the production of holes is the effective stress at or near the filler particles. The cure time affects the matrix crosslink density and therefore linearly influences the stress at constant strain. The scattering intensity parallels the expected increase in stress. Similarly, in the stress-softening experiments the scattering intensity follows linearly the expected stress on the matrix. Strain rate thresholds have been shown to exist, although the filler loading is the dominant factor in determining the threshold.

Since the dominant feature appears to be the filler loading, the data of Figure 3 are replotted in Figure 15 to relate scattering intensity to filler composition at a fixed time of 1 h. On the basis of three points an exponential relation appears to exist between the scattering intensity and the filler loading. Such a strong dependence on filler concentration over the range of 15–50% strongly suggests the importance of the effective stress near a filler particle rather than the simple loss of the volume fraction of rubber. The important consideration must be the geometric constraints put on the remaining rubber volume under stress.

The rubber molecules must untangle undirectionally to relieve the uniaxial applied stress. If the only source of relief is through the narrow interstices be-

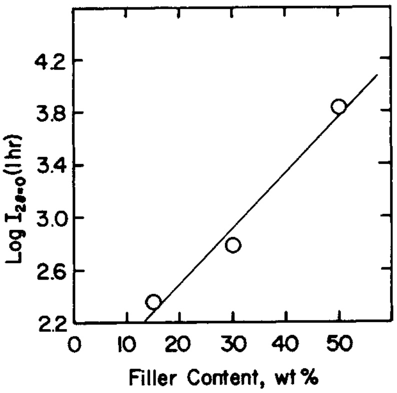

Fig. 15. Dependence of scattering intensity at 1 h on filler content for samples cured 72 h (data for Fig. 3).

tween filler particles along the stretching direction, there must be a tension on the rubber chains near the filler particles and perpendicular to the stress direction. Finally, the tension reaches a point such that a small anisotropic void appears, or if the stress becomes isotropic, the critical triaxial stress is achieved and a spherical void is formed.[30]

There are, of course, well-known relations between filler concentration and the macroscopic viscosity and modulus in filled rubbers. Consequently, the relationship between the scattering intensity and filler concentration may in reality only be a relationship between the number of voids and the stress field.

Size of Holes as a Function of Filler Concentration, Cure Time, and Strain Rate

In order to minimize the inaccuracies of the void sizes at "zero" time the 1-h void sizes are summarized in Table III. As can be readily seen, the void size changes very little with either filler composition or cure time.

The void size is about 300 Å and decreases slightly with decreased filler and short cures. Gent and Tompkins[30] have shown that the stress that can cause a void in the homogeneous (unfilled) rubber is the sum of a term due to surface energy required to form a bubble in a liquid plus a term due to the stored energy of an elastic substance. The stress therefore to form a bubble of radius r can

TABLE III

Radii of Gyration of Voids (Å) as a Function of Filler Concentration and Cure Time at 1 h after Extension at 1300 mm/min to $\lambda = 1.6$

	Filler (%)		
Cure time (h)	15	30	50
24	242[a]		
48	282[a]		
70	300,[b] 296[a]	300[b]	350[b]
96	304[a]		

[a] Figure 8.

[b] Figure 7.

be related to the mechanical work over a distance r. By the adaptation of eq. (1) in their paper to this situation the radius of the spherical void becomes

$$r = \frac{4}{5}\frac{\gamma}{G}$$

where γ is the surface tension and G is the shear modulus of the rubber. The radius r of the void therefore should have a size of 240 Å when reasonable values of the surface tension (30 ergs/cm^2) and modulus (10^7 dynes/cm^2) are assumed.

A radius of gyration of approximately 300 Å has been measured. This would correspond to a spherical radius of 375 Å. Of course, these sizes are weighted by the scattering method to emphasize the large sizes. Voids of this order of magnitude have been found in the crazing of plastics. For example, LeGrand, Kambour, and Haaf[31] have reported 100-Å craze voids in polystyrene by observing a single craze with SAXS. Kambour and Holik[32] reported 100–200-Å craze voids in phenylene oxide polymers by sulfur-impregnation of crazes followed by observation by electron microscopy. The surface energies of these materials would be comparable to rubber. If the material became rubbery before a void formed, the modulus would probably be higher than a conventional rubber. Consequently, the particle size would be smaller. At very low strains, less than 0.5%, the voids formed are not permanent and are much smaller.

Gent and Tompkins[17,30] have suggested that such small size holes cannot be formed even in an unstrained carbon black filled elastomer in which the external pressure has been released. The results reported here allow very little interpretation other than void formation. The location of the void in the filler–rubber geometry, however, cannot be determined with these simple measurements. The void could conceivably also occur either in the filler particle or at the filler–rubber interface (dewetting). Since the interfacial energy between filler and matrix is very similar to the cohesion energies of either the filler or matrix in this system, it appears likely that dewetting at the filler is a smaller effect than void formation in the stress-concentrated regions away from the filler particle. However, it is possible that trace amounts of soap from the latex polymerization could facilitate dewetting at the filler particle or even void formation at other sites. Effects of soap are currently being investigated.

Stress Relaxation

The filler does increase the isochronal modulus in a manner similar to other hard reinforcing fillers. That is, modulus is increased about 15–20% for a filler content of 5%. This in agreement with Morton and Healy's measurement[18] of the tensile modulus on a related system, namely, a butadiene rubber matrix with polystyrene latex fillers. From these earlier measurements of Morton[19] and co-workers this system could similarly be called a reinforcing filler.

Correlation of Stress Relaxation and Scattering Data

The data of Figures 11 and 12 were all taken with samples at a constant extension ratio $\lambda = 1.6$. In Figure 15 it was shown that scattering intensity depended exponentially on filler content. Since filler content and modulus are related, it seemed reasonable to determine whether the scattering intensity (at 1 h) would scale in some manner with the 1-h isochronal moduli obtained from Figures 11 and 12. Because the data were not taken with this analysis in mind, no quantitative presentation illustrating this is included. However, a cursory examination seems to indicate a nearly exponential dependence of the isochronal scattering intensity on the isochronal modulus over a fivefold range of modulus.

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