

Dielectric Loss Behavior of Cross-linked Polyethylene and Analog Materials

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Synopsis

The dielectric loss behavior of crosslinked polyethylene has been determined over the frequency range 10–5 kHz and over the temperature range -150 to 100°C . Major loss effects occur at the lower temperatures and are caused by libration of the organic byproducts of the crosslinking agent, dicumyl peroxide. Analog materials prepared from linear low density polyethylene by blending in of either acetophenone or 2-phenyl-2-propanol confirm the hypothesis. The effects of concentration of by-products and of orientation of the polymer have been studied. Activation energy analyses suggest that room temperature losses will occur in the microwave region. The behavior is significantly affected by curing with steam, typical loss peaks being an order of magnitude lower than for dry cured specimens. A new loss region appears close to but below, 0°C .

INTRODUCTION

Crosslinked polyethylene is now widely used as insulation for underground electric cable and is also gaining acceptance in foamed form as microwave insulation. When dry-cured, the polyethylene contains approximately equal amounts of the byproducts of the dicumyl peroxide initiator, namely acetophenone and 2-phenyl-2-propanol. Both of these molecules are polar and would be expected to give rise to dielectric losses in particular regions of the frequency–temperature plane. The acetophenone is simply dipolar due to the carbonyl group, whereas the phenylisopropanol is capable of hydrogen bonding.

Although the dielectric loss spectra of polyethylenes have been well known for many years,¹ there have been relatively few studies of polyethylenes containing polar solutes. Polyethylene shows three regions of dielectric loss centered around 60°C , 0°C , and -100°C , which are labeled α -, β -, and γ -loss regions, respectively. These regions essentially result from carbonyl dipoles produced by adventitious or deliberate oxidation, whereas both the β and γ losses originate from the amorphous phase,² the α region is associated with the crystalline phase. Studies of ethylene–carbon monoxide copolymers³ showed that carbonyl groups enter the crystal provided they exist only as carbonyl groups, whereas, in oxidized materials,¹ carboxylic acid groups may be formed which are excluded from the crystals, resulting in low magnitude loss from the crystalline regions.

Polar solutes would be expected to be located in the amorphous phase and hence to give rise to β or γ losses but with activation energies different from those of oxidized polyethylene. Kumler and Boyer^{4,5} have studied the temperature of onset of libration of triplet free radicals in various polymers. Some correlation would be expected between their data and those for the studies being reported here.

In order to understand the basic behavior of each solute molecule, analog materials have been prepared by soaking the solute molecules into thin films of polyethylene. These specimens have been studied and the individual behaviors compared to those of the crosslinked polyethylene in order to see if a synergistic effect occurred between the two solute molecules.

EXPERIMENTAL

Crosslinkable polyethylene (Union Carbide PT4703) was compression-molded into a sheet and then crosslinked under pressure by heating the mold to 200°C and holding the temperature for 5 min before slow cooling. The time and temperature combination was more than adequate for a 99% cure.⁶ A specimen was also steam-cured, as in industry using 200°C and 200 psi in a small pressure bomb. It was taken from a compression molded film produced at 130°C.

Linear low density polyethylene (Dow Chemical 530) was compression-molded using a template at a temperature of 150°C with an initial time of 4 min at 500 psi to permit complete melting. The press was then allowed to cool to room temperature in air. Solute molecules were added to the film by soaking in the individual liquids. Sections of steam-cured XLPE were also studied. Several steam-cured cables were studied and were supplied by Dr. Dexter Seymour of John Royle and Sons and by EPRI. Those supplied by EPRI were a standard Waltz Mill transmission cable and a specimen produced by Pirelli.

Dielectric relaxation data were obtained using a General Radio Bridge over the frequency range 10–5 kHz and the temperature range –150 to 100°C.

RESULTS

Dry-Cured Crosslinked Polyethylene

Dielectric constant and loss spectra of the crosslinked polyethylene cured in

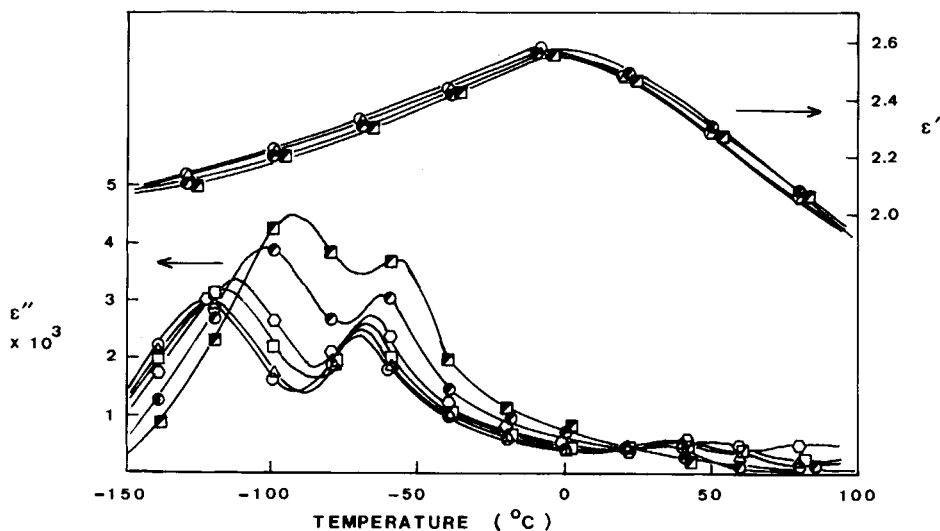


Fig. 1. Dielectric constant and loss of dry-cured crosslinked polyethylene: (○) 10 Hz; (Δ) 20 Hz; (□) 50 Hz; (○) 100 Hz; (●) 1 kHz; (■) 5 kHz.

the compression mold, as described, are presented in Figure 1. There is a faint α -loss process in the region of 50°C , which is of a magnitude normally encountered in polyethylenes ($\epsilon''_{\text{max}} \sim 5 \times 10^{-4}$) and usually ascribed to adventitious oxidation. There does not appear to be a β -process, although there could be a small peak submerged at the high temperature end of the dominant γ process. Two major loss processes occur in the region of -70°C and -110°C , and they overlap. It is clear from the data that the lower temperature peak is shifted to higher temperatures by increasing frequency at a much faster rate than is the high temperature peak of the two. The activation energies of the two processes therefore must be considerably different. A reasonable hypothesis would be that each peak is caused by a different solute molecule. Additionally, 2-phenyl-2-propanol might be expected to relax at higher temperatures due to its larger size and its ability to hydrogen bond. In order to test this hypothesis, aceto-

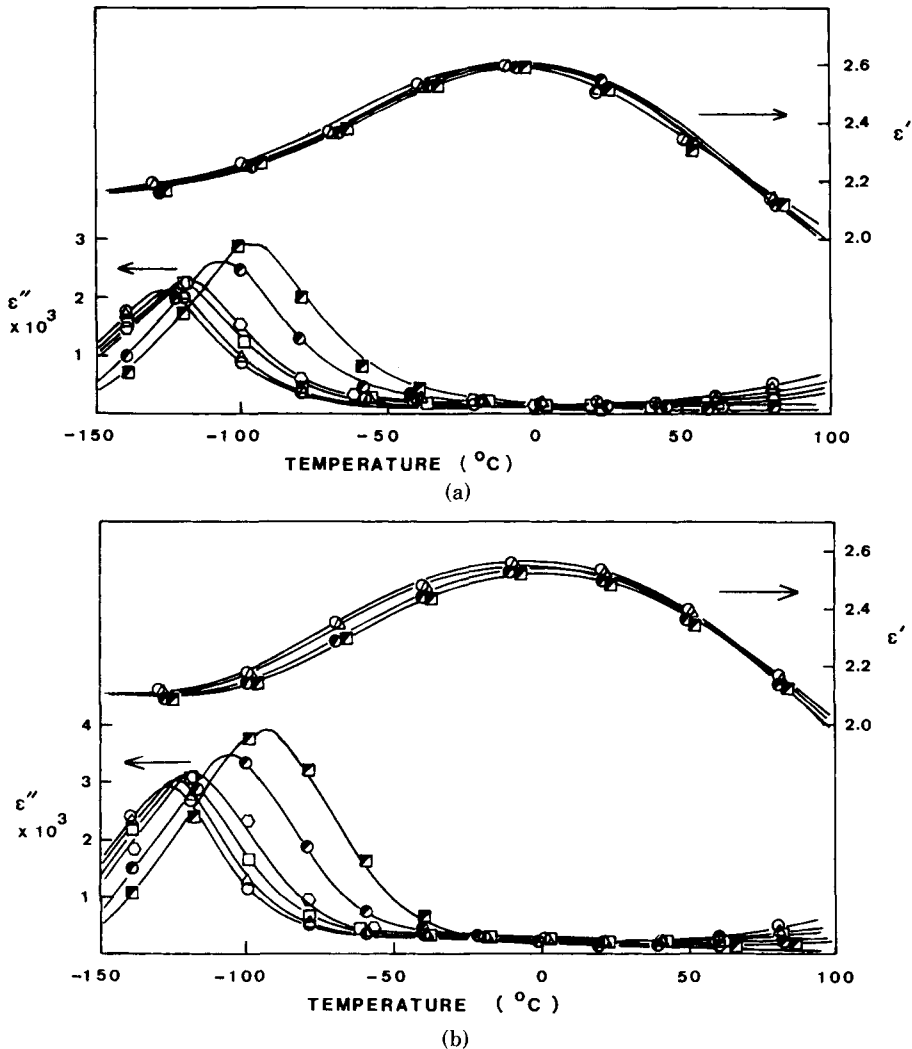
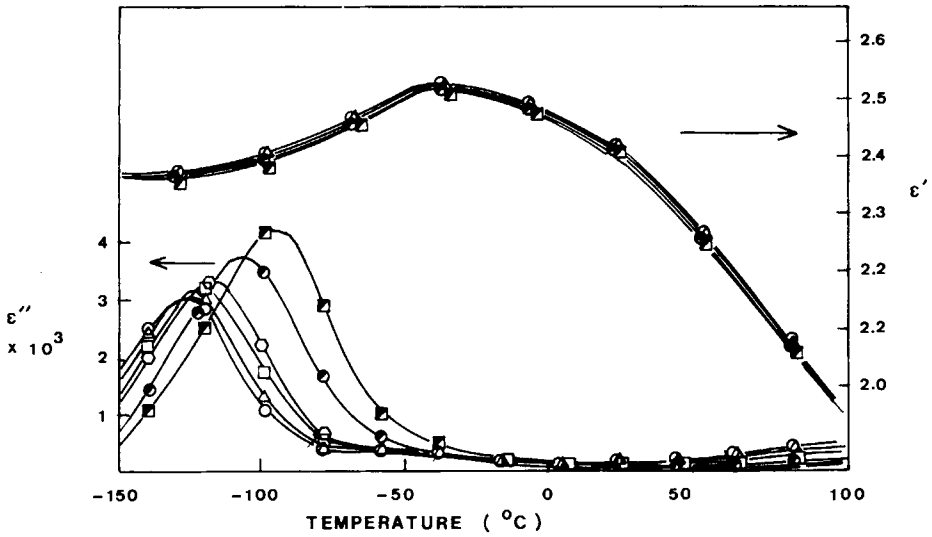
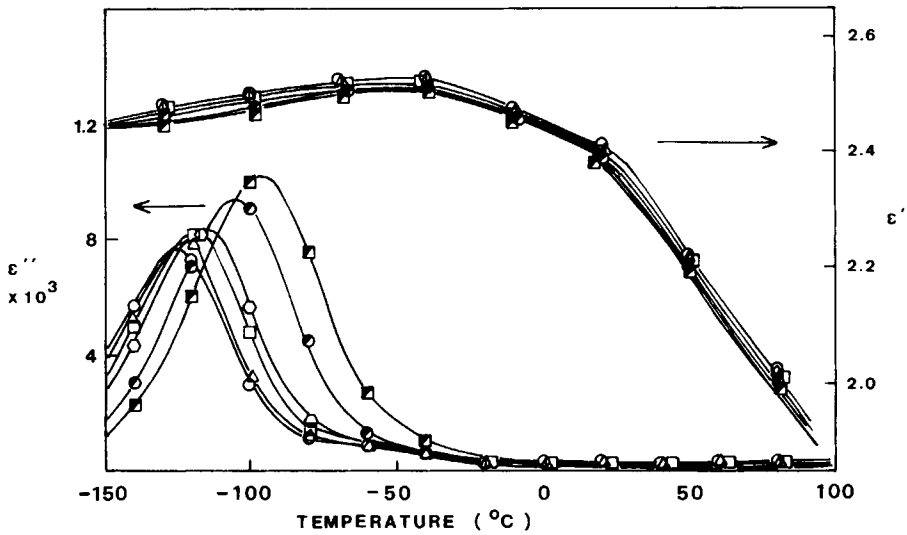


Fig. 2. Dielectric constant and loss spectra of linear low density polyethylene containing acetophenone (symbols as in Fig. 1): (a) 0.3 wt % and stretched to 450%; (b) 0.56 wt % and stretched to 450%; (c) 0.59 wt %; (d) 1.0 wt %.



(c)



(d)

Fig. 2 (Continued from the previous page.)

phenone and 2-phenyl-2-propanol have been separately soaked into films of linear low-density polyethylene and the analog materials then studied.

Analog Materials

The first such material to be studied contained acetophenone. Several specimens were prepared, each with a different acetophenone content. Many of these specimens were stretched to 450% (i.e., well beyond the yield point) prior

to study to find out if the dielectric behavior might change with orientation of the polymer molecules produced by extrusion during cable manufacture. It was found that the behavior was essentially unaffected by orientation. In Figure 2 are shown the dielectric constant and loss spectra for contents of 0.3% stretched, 0.56% stretched, 0.59% unstretched, and 1.0% unstretched (all % are wt %). The behavior of all specimens was similar phenomenologically. As expected, the magnitude of the loss increased with acetophenone content. These curves clearly correspond to the lowest temperature loss peak observed in dry-cured crosslinked polyethylene (Fig. 1). There is a slight shift in loss peak towards higher temperatures as acetophenone content is increased. However, the shift observed over the concentration range studied was only 1°C.

One specimen was prepared containing 2-phenyl-2-propanol with a concentration of 0.56% by weight. The dielectric constant and loss spectra are presented in Figure 3. One relatively sharp peak is present centered around -60°C and clearly corresponds to the higher temperature peak observed in dry-cured crosslinked polyethylene (Fig. 1).

For comparative purposes, the data reported at 1 kHz in the preceding figures are presented in Figure 4, where it can clearly be seen that the two peaks present in dry-cured crosslinked polyethylene correspond quite closely to the peaks observed in the analog materials.

Another important comparative method is to make Arrhenius plots of the logarithm of frequency against the reciprocal of the temperature of maximum loss. Such plots are shown in Figure 5, where it can be seen that these plots are also very similar to the two sets of peaks, confirming the validity of the hypothesis that the two impurity molecules contribute separately. Activation energies obtained from the slopes of the plots were 10.1 kcal/mol for the acetophenone and 48.2 kcal/mol for the 2-phenyl-2-propanol.

The temperature regions in which the molecules relax correspond fairly well with those corresponding to the onset of libration of free radicals^{4,5} and tend to confirm the hypothesis that sufficient motion is already present at temperatures above the γ -relaxation but below the β -relaxation for moderately sized molecules to move around.

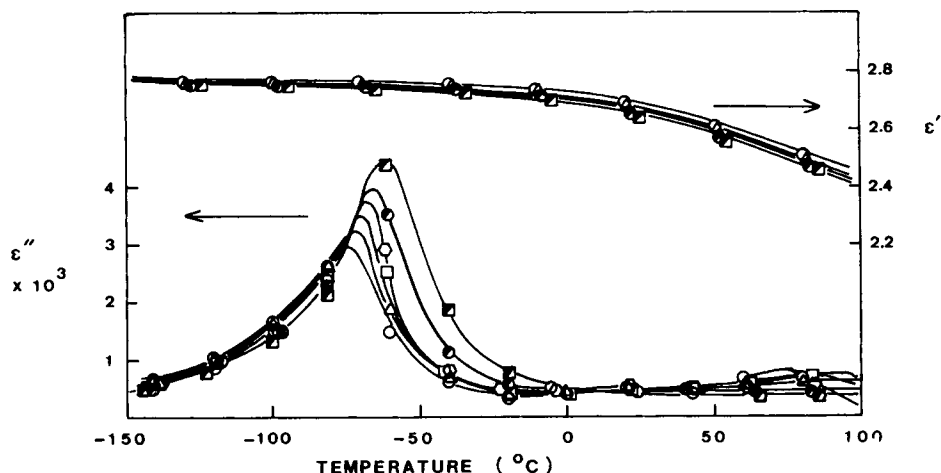


Fig. 3. Dielectric constant and loss spectra of linear low-density polyethylene containing 0.56% 2-phenyl-2-propanol (symbols as in Figure 1).

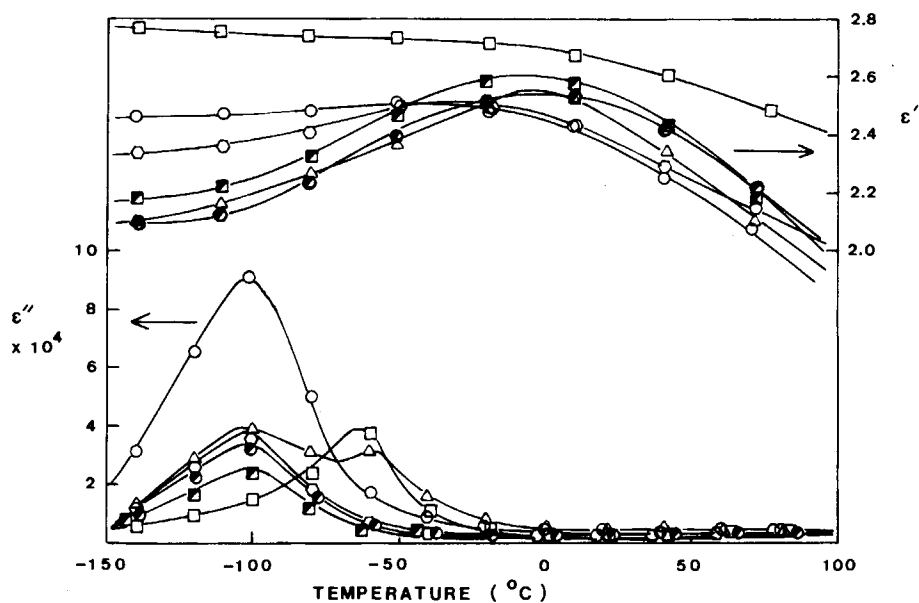


Fig. 4. Dielectric loss spectra at 1 kHz for the specimens reported in Figures 1-3: (Δ) XLPE; polyethylenes containing acetophenone; (\blacksquare) 0.3% stretched; (\bullet) 0.56% stretched; (\circ) 0.59% unstretched; (\circ) 1.0% unstretched; (\square) polyethylene containing 0.56% 2-phenyl-2-isopropanol.

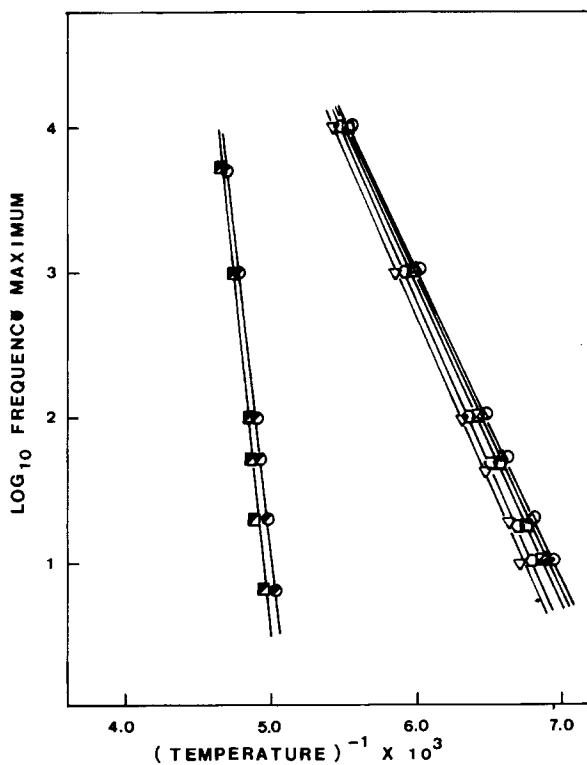


Fig. 5. Arrhenius plots of the data presented in Figures 1-3: (∇, \blacksquare) XLPE; polyethylenes containing acetophenone; (\circ) 0.3% stretched; (Δ) 0.56% stretched; (\square) 0.59% unstretched; (\circ) 1.0% unstretched; (\bullet) polyethylene containing 0.56% 2-phenyl-2-isopropanol.

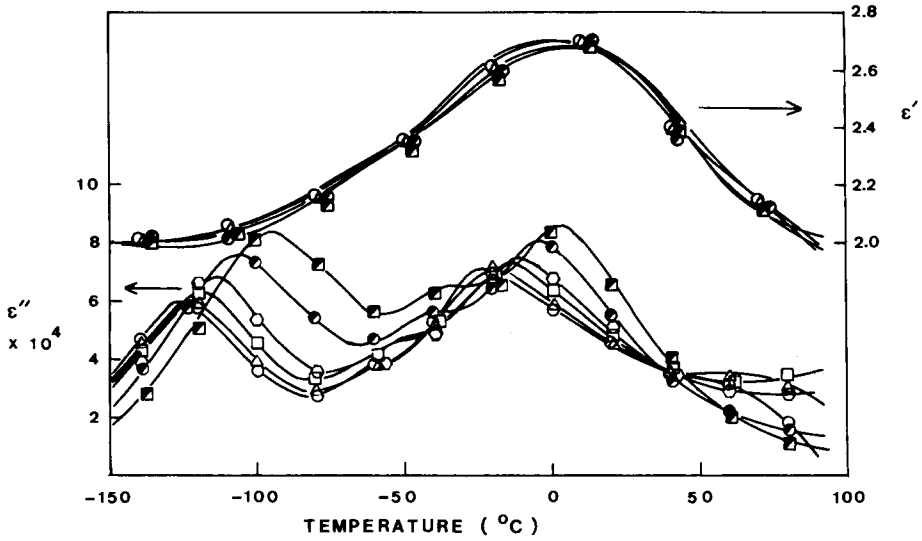


Fig. 6. Dielectric constant and loss spectra for steam cured transmission cable (symbols as in Fig. 1).

Steam-Cured Crosslinked Polyethylene

Several specimens of steam-cured transmission cable have been investigated. They give somewhat similar results, but with dielectric losses almost an order of magnitude lower than would be expected on the basis of the studies of dry-cured crosslinked polyethylene and the analog materials. Typical dielectric constant and loss data are presented in Figure 6. The lowest temperature loss peak, now known to be caused by acetophenone, is only slightly modified, oc-

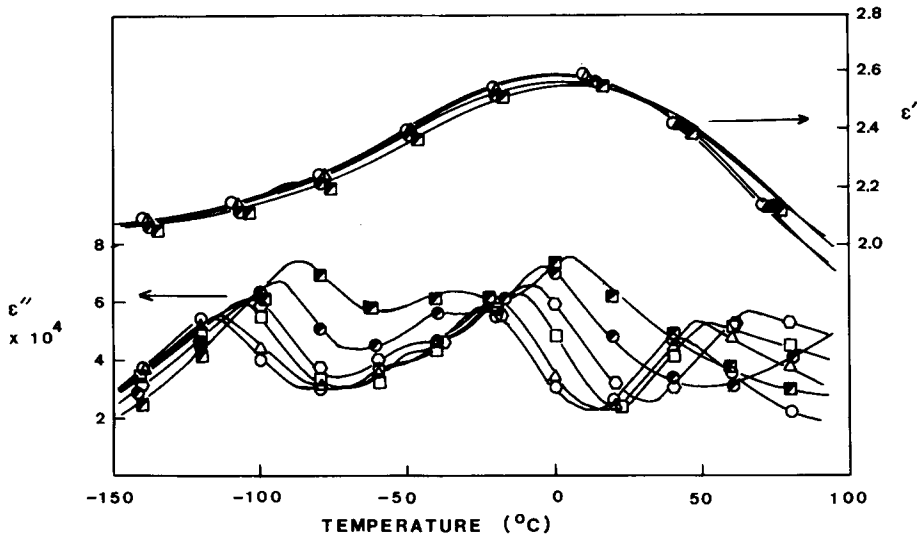


Fig. 7. Dielectric constant and loss spectra for specimen steam cured at 200°C and 400 psi in a bomb (symbols as in Fig. 1).

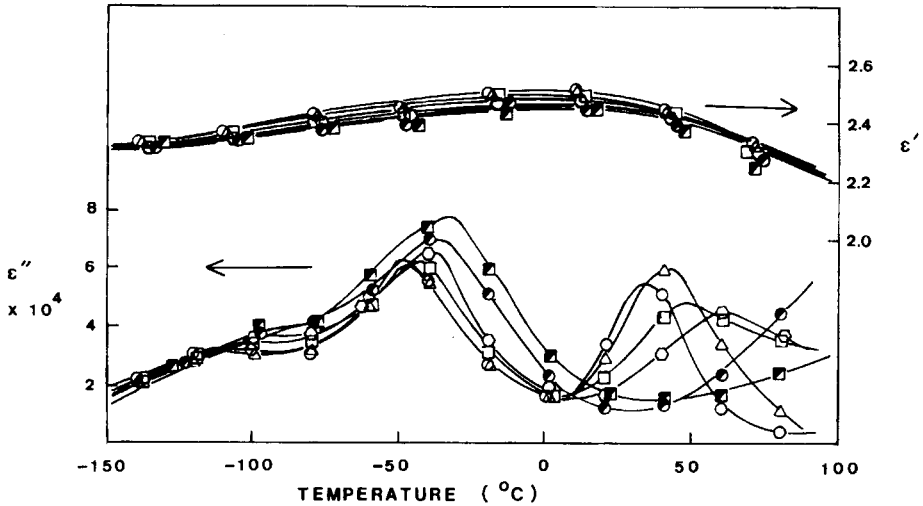


Fig. 8. Dielectric constant and loss spectra for uncured crosslinkable polyethylene (symbols as in Fig. 1).

curing 2°C lower at 1 kHz. However, the activation energy of 10.5 kcal/mol is not changed. The peak due to 2-phenyl-2-propanol has been significantly affected. It may be the shoulder or small peak at -55°C for 20 Hz and -35°C for 5 kHz, which is overwhelmed by a new peak which appears between -20°C and 0°C . It seems likely that this peak is caused by absorbed water. All steam-cured cables studied showed similar behavior, i.e., the losses were much lower than for dry-cured specimens and the additional peak sited around 0°C was present.

A specimen of compression-molded crosslinkable polyethylene was crosslinked in a bomb at 200°C using an amount of water calculated to produce 400 psi

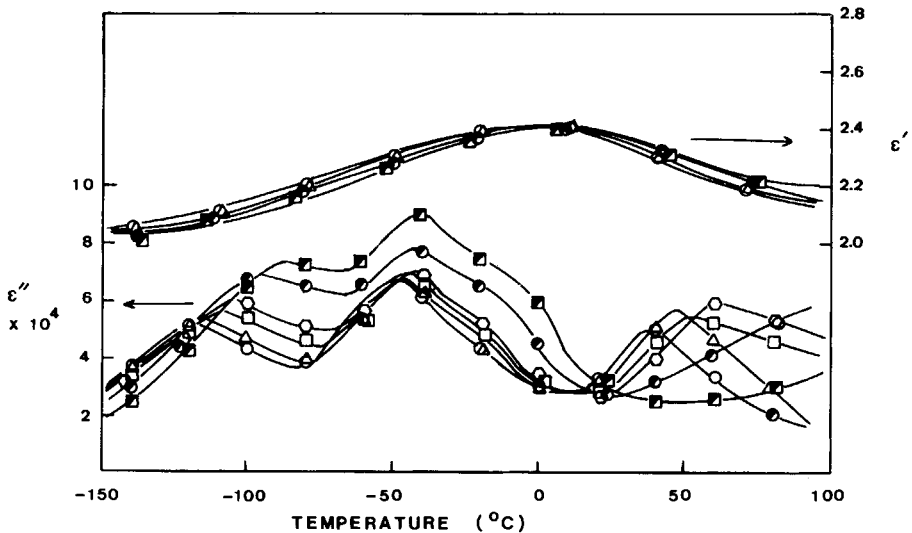


Fig. 9. Dielectric constant and loss spectra for specimen undercured in a bomb at 200°C and 200 psi (symbols as in Fig. 1).

pressure at 200°C. The dielectric spectra are shown in Figure 7, where a comparison with Figure 6 will show that similar behavior results. There are slight differences in the spectra, largely related to a small change in the magnitude of the peak at -50°C and a larger loss in the region of 50–100°C.

Since it was possible that the specimens might not be completely cured, the dielectric spectra of a compression molded but uncured specimen were obtained and can be seen in Figure 8. Here the observable peaks are caused by the dicumyl peroxide present and can be seen in the vicinity of -50°C and +50°C. They do correspond fairly well with the small peak or shoulder at -50°C and the loss noted near +50°C in the laboratory specimen cured using steam. Studies of a specimen undercured through use of too little water confirmed this hypothesis (Fig. 9). Clearly both the -50°C and +50°C peaks are intensified relative to the previous specimen (Fig. 7).

DISCUSSION

The behavior of the dry-cured specimen is relatively straightforward and can be understood simply in terms of the behavior of the analog materials. Essentially two separate but overlapping regions of dielectric loss occur in the region -150 to -50°C, which can be attributed to the individual loss peaks of the two major byproducts of the crosslinking agent, namely acetophenone and 2-phenyl-2-propanol. These loss peaks have magnitudes $2\text{--}4 \times 10^{-3}$ (ϵ'' values), the room temperature losses in transmission frequency ranges being background levels of ca. 5×10^{-4} . The activation energies of the two peaks are quite different, being 10.1 kcal/mol for the acetophenone and 48.2 kcal/mol for the 2-phenyl-2-propanol. Extrapolation of these two loss peaks to 20°C using Arrhenius plots produces loss maxima at 3×10^5 Hz for acetophenone and 9×10^{11} Hz for 2-phenyl-2-propanol. Using the data for the analog materials as a standard, the dry-cured specimens contained 0.58% by weight of acetophenone and 0.45% by weight of 2-phenyl-2-propanol. Amounts closer to 1% would have been expected. One possible reason for this might be that different amounts of these organic chemicals are present as condensed phases. The magnitudes and locations in the temperature-frequency plane of the loss peaks are barely affected by solute concentrations and specimen deformation.

The steam-cured specimens show major discrepancies when compared to the analog materials. First, the loss levels are very much lower than would be predicted if the water molecules absorbed by the polymer during curing played only a passive role. Similar behavior was manifest both in laboratory-cured materials and manufactured cables. The acetophenone loss peak, which remains essentially the same as for dry cured specimens, has a magnitude consistent with ca. 0.2% concentration. Since the much smaller loss peak at -50°C could be caused by either residual dicumyl peroxide or 2-phenyl-2-propanol, it is not possible to make a similar estimate for the second byproduct molecule. All we can be sure about is that the magnitude of its loss peak is at most $1/10$ that of an analog material.

There are two possible explanations for the behavior. First, the water could enter actively into the mechanism of the crosslinking reaction. Second, the 2-phenyl-2-propanol and some of the acetophenone could dissolve in the micro-

droplets of water⁷ known to be present in steam-cured cable. The loss process observed around 0°C could be a Maxwell–Wagner process resulting from conduction in water droplets. Many of the lower frequency loss curves peak below the conventional freezing point of water (the activation energy of the process is 29 kcal/mol). However, when in the form of microdroplets, water exhibits freezing points of as low as -40°C⁸ consistent with the data. Clearly, much more work is needed on this particular point before the nature of this loss peak can be understood.

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