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Dielectric Constant of Rolled Polyvinylidene Fluoride

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The contribution of dipole orientation to dielectric constant is markedly affected by rolling. The intensity of the γ peak is increased and the maximum shifted slightly to higher temperatures and frequencies. The shift is much larger with the β peak. Its intensity, however, is reduced by rolling. Long before the maximum of the β peak is reached, annealing effects irreversibly change the sample. With annealing, the values of the dielectric constant gradually approach those of the unrolled material. The observed effects can be explained by a substantial orientation of chains in the roll plane, which is perpendicular to the applied electric field. Such an orientation increases the average contribution of dipoles in crystal defects to polarisation as observed in the γ peak. Stronger interaction between partially aligned chains in the amorphous matrix hampers the rotation of chain segments in the electric field, and hence reduces the β peak and shifts it to higher temperatures.

1. Introduction

In our studies of the physical properties of highly drawn polymers, we have found striking changes in the amorphous component of cold-drawn samples [1]. Particularly, the heat content [2], the sorption and diffusion [3, 4] are far below the values for a relaxed, supercooled liquid which one normally assigns to the amorphous component of a semicrystalline polymer sample. The reduction in sorption and diffusion is primarily a consequence of a closer packing of highly stretched and aligned tie molecules. Because both ends of the amorphous sections of these molecules are fixed in adjacent crystals, the molecules cannot assume conformations corresponding to thermodynamic equilibrium. The closer packing reduces the free volume so that the number of sites for sorption is decreased, and it also yields a higher cohesive energy density, thus increasing the energy requirement for the formation of a hole which would accommodate the sorbed molecule, and also increasing the energy barrier for the diffusion jump of such a molecule. The increase in cohesive energy density and the prevalence of more-extended conformations of the tie molecules explain the experimentally observed reduction of enthalpy and entropy.

Measuring the dielectric constant is a promising method for studying the physical properties of amorphous chains possessing a finite dipole moment. Both the electronic displacement and dipole orientation polarisability are affected by crystallinity and by the special conditions of the amorphous component. Such effects are much more conspicuous in the temperature- and frequency-dependent dipole contribution, which is a function of chain mobility and orientation. Sufficiently below the melting point, chain mobility in the crystal lattice is so small that one may neglect the contribution of dipoles bound in the crystal lattice. The complex dielectric constant therefore depends primarily on dipole orientation in the amorphous regions of the sample and in crystal defects caused by free chain ends and chain folds.

The alignment and closer packing of polymer chains certainly must affect the orientational component of dielectric polarisation. In a rolled film, chain orientation is in the roll direction and the electric field perpendicular to it. If the dipole moment μ is perpendicular to the chain axis, there is an increase in polarisation by dipole rotation, such that the term $\mu^2/3kT$ for random distribution of dipole axes (space orientation) is replaced by $\mu^2/2kT$ (planar orientation). Closer packing increases the forces between adjacent chains, thus hampering the orientation. This may produce a shift in the maximum absorption at constant temperature to lower frequency or at constant frequency to higher temperature, with a reduction in magnitude. In addition, one must expect that, of the two absorption mechanisms normally observed with polymer samples, the one corresponding to the orientation of a larger chain section, and therefore occurring at higher temperatures, will be affected more than the one corresponding to a smaller grouping.

A particularly suitable polymer for dielectric investigation is polyvinylidene fluoride (PVF_2). It is partly crystalline, and in many respects very similar to polyethylene, so that one expects a similar influence of drawing on chain orientation and on the thermodynamic properties of the amorphous component. In addition, the chain has two different dipole moments CH_2 and CF_2, which in a trans conformation (zigzag) have the same orientation (fig. 1) as long as the chain is positionally tactic, i.e. all the monomers have the head-tail sequence. It has been shown by high-resolution NMR [5] that there is a nearly 5% exception to that, i.e. 5% of all monomers are in the inverse position, as shown by underlining ht.$\underline{\text{th}}$.ht.ht. In such a double inversion, the two adjacent CF_2 and CH_2 pairs have their dipole moments in opposite directions, so that in the first approximation their contribution to the orientational dielectric polarisation cancels. The situation in such a group is identical to that in polyethylene, which, owing to antiparallelism of the CH_2 groups, does not show any dipole contribution to the dielectric constant.

2. Experimental

The PVF_2 used was Kynar L1875G – a Pennsalt Chemicals Corporation general-purpose, high-molecular-weight resin. The material is supposedly neither branched nor cross-linked. PVF_2 of the same type was investigated in the undrawn state by Ishida, Watanabe, and Yamafuji [6], Wentink [7], Peterlin and Holbrook [8].

The sample was prepared by compression molding of PVF_2 pellets into sheets of 1.2 mm thickness which were slowly cooled to room temperature, and then rolled at room temperature to a thickness of 0.4 mm. From a similarly rolled sample, we calculated the increase in length to be about 165%, and the increase in width to be about 8%. Discs of 50 mm were cut from the rolled sheets and coated with silver paint to insure good electrical contact with the condenser plates. A General Radio Co capacitance-measuring assembly, type 1610, with a frequency range of 20 to 100000 c/sec, and dielectric sample holder, type 1690A, were used. The condenser and sample were sealed in a thermostated air-bath containing dry nitrogen gas. This arrangement permitted measurements from −60 to 150° C.

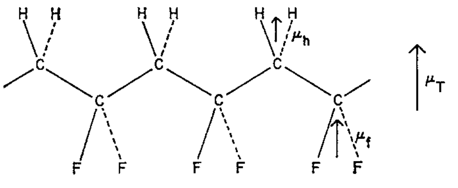

Figure 1 Extended PVF_2 chain with head-tail (ht) sequences. The dipole moments are 0.5×10^{-18} esu for CH_2 and 1.6×10^{-18} esu for CF_2.

From wide-angle X-ray scattering, one concludes that the crystal lattice is rather well oriented with the *c*-axis in the roll direction. Within experimental error, rolling did not increase the density of our sample.

3. Results and Discussion

The isofrequency curves of ϵ' and ϵ'' as functions of temperature for the rolled and unrolled samples are plotted in figs. 2 and 3. The plots resemble the ideal example for the influence of chain orientation and hampered rotation due to closer chain packing. At all temperatures and frequencies, the dielectric constant of the rolled sample is larger than that of the original isotropic material. We believe that the increase is a consequence of chain orientation which, at constant number and unchanged dipole mobility, would produce up to a 50% increase in polarisability. The increase in our sample is between 10 and 25%, as a consequence of incomplete chain orientation and hampered rotation due to closer chain packing. The changes are smallest at −50° C, so that one may surmise that the lower temperature values will hardly be affected by rolling.

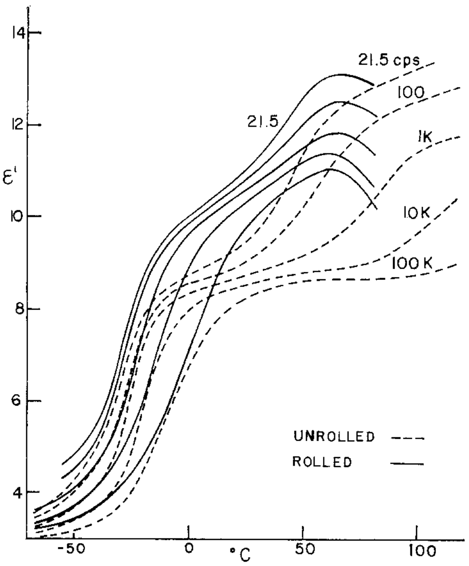

Figure 2 Isofrequency curves of the dielectric constant ϵ' of rolled and unrolled PVF_2 versus temperature.

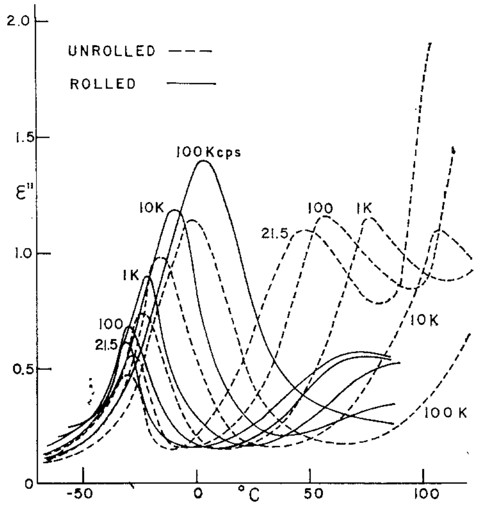

Figure 3 Isofrequency curves of the dielectric loss coefficient ϵ'' of rolled and unrolled PVF_2 versus temperature.

The contribution to dielectric polarisation in the low temperature range below the γ peak is mainly due to electronic displacement, which would only be affected by rolling in so far as the electronic polarisability is anisotropic, i.e. having a value along the chain direction different from that perpendicular to it. Because we were only able to measure the dielectric constant with the electric vector perpendicular to the roll direction, we cannot determine whether such an effect exists. An estimate could be obtained by measuring the rolled and unrolled samples at a sufficiently low temperature, e.g. – 100° C, where the dipole contribution is negligible. At equal crystallinity, any difference observed would be a consequence of the anisotropy of the electronic polarisability of the PVF_2 chain. The condition of equal crystallinity is important because the conformation of PVF_2 in the crystal lattice is markedly different from that in the amorphous regions.

The γ peak of the dielectric loss ϵ'' conforms rather well to the data of the dielectric constant. The curves for all temperatures and frequencies are higher for the rolled than for the unrolled sample. The maxima are sharper, higher, and shifted to slightly higher temperatures. The existence of the shift is much more evident if, instead of the maxima, one observes the shapes of the isofrequency curves. They are slightly displaced at the low- and noticeably displaced at the high-temperature side of the maxima. The shift is greatest at higher frequencies, i.e. with the peaks which are at higher temperatures. The activation energy for the γ process is hardly changed by rolling, as may be seen in fig. 6. With increasing temperature, either more dipoles may be mobilised or, the number of dipoles remaining constant, the mobility of each dipole may be increased, as can be seen from the increase in the area of the absorption curves of the rolled and unrolled samples. The shift to higher temperatures by rolling means an increase in binding, which may be either a consequence of closer packing or of additional strain imposed on the molecules in crystal defects. The higher contribution to ϵ' and ϵ'' is just the consequence of crystal orientation by rolling, which aligns perpendicular to the field the chains in the crystal lattice and hence also in the defects caused by free chain ends.

In the unrolled sample, the transition between the γ and β region in the dielectric constant ϵ' yields a plateau which becomes wider with increasing frequency. It is well developed at 100, 10, and 1 kc in the temperature range 0 to 100° C, and only indicated at 100 and 21.5 c/sec. Such a plateau is characteristic for the glass transition which according to dilatometric measurements [9] occurs at about 27° C. Rolling completely removes this plateau, so that the γ peak immediately joins the β peak. Such a change may be caused by the slight shift of the absorption maxima to higher temperatures and even more by a stronger assymmetry of the γ peak, as shown in the absorption curves (fig. 3). The long tail extending to higher temperatures shifts the minimum between the γ and β peaks to temperatures higher than those the γ maxima are shifted to, increasing the absorption at the minimum. Consequently, the dielectric constant of the rolled sample does not remain constant over any temperature range.

The β peak in rolled PVF_2 is not fully developed, in that only the low-temperature side is present in both the ϵ' and ϵ'' plots. In the ϵ'' plot, the most striking feature is its drastic reduction in intensity in sharp contrast to the γ peak. This fact means that either the number of dipoles involved in the β process is reduced by rolling or that the orientation of their rotational axes is less favourable. With the incomplete peak, it is hard to distinguish between these two possibilities. The shift of the absorption maxima to higher temperatures and lower frequencies is a consequence of the stronger interchain interaction due to alignment and closer packing.

At 60° C and above, the β peak is distorted by annealing effects. Not only ϵ'' but also ϵ' exhibits a smaller rate of increase with temperature which turns over in a drop. The changes are irreversible. Annealing destroys the structure imposed on the sample by rolling and transforms it into that of the relaxed, unrolled material. Fig. 4 shows ϵ' at room temperature for the unrolled and rolled samples before and after heating for 4 h at 80° C. The latter treatment reduces ϵ' and brings it closer to the value of the undeformed material. Complete identity is not obtained because some crystallisation occurs during annealing.

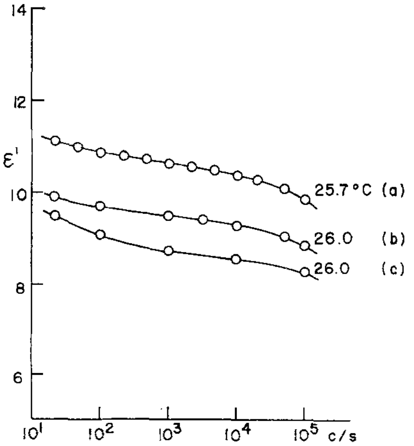

Figure 4 Dielectric constant ϵ' isotherms as a function of frequency: (a) rolled sample at 25.7° C; (b) rolled sample at 26.0° C, after annealing at 80° C for 4 h; (c) unrolled sample at 26.0° C.

Despite the fact that, owing to annealing, one cannot observe the β peak of the rolled material, one can deduce from ϵ'' and a little less conveniently from ϵ' that rolling affects the β peak much more than the γ peak. The molecular mechanism of dielectric polarisation offers a good qualitative explanation. The two maxima observable with most dipolar solid polymers are due to two orientational mechanisms. At the low-temperature γ peak, the dipoles of chain sections in crystal defects are rotated in the field direction, whereas at the higher-temperature β peak, larger chain sections in the amorphous regions are involved. Closer packing and chain strain as consequence of rolling impose more severe limitations on the β mechanism, which requires the motion of relatively large groups, and much less on the γ mechanism, i.e. the rotation in a crystal defect. Therefore, the absorption in the β peak at the low-temperature side is greatly reduced, and the maximum shifted to such high temperatures that, in PVF_2, it cannot be observed, because, far below the temperature of the maximum, annealing starts to change the sample irreversibly.

A very good comparison of the rolled and unrolled sample can be obtained from a Cole-Cole plot (fig. 5). To show the changes with temperature more clearly, the ordinates, ϵ'', have been enlarged five times, thus deforming the circular isotherms into ellipses. The plot is similar for both samples at the lower temperature limit between −62.7 and −41.3° C. As soon as the upper section of the circular arc, corresponding to the γ peak, is well developed, the differences are conspicuous. The absorption and dielectric constant of the rolled sample are far above those of the unrolled material. In the Cole-Cole plot, the curves are higher and shifted to the right, to higher ϵ'. The centre of the corresponding circles is rapidly moving to higher ϵ', as a consequence of the higher contribution of every dipole due to the alignment of its rotational axis in the roll direction, i.e. perpendicular to the electric field. In both the rolled and unrolled sample, the β peak is rather unsymmetric. The β peak, however, is poorly developed in the rolled sample. One sees only the ascending, low, ϵ' side, and perhaps an indication of a maximum at the 60° C isotherm. The latter, how-

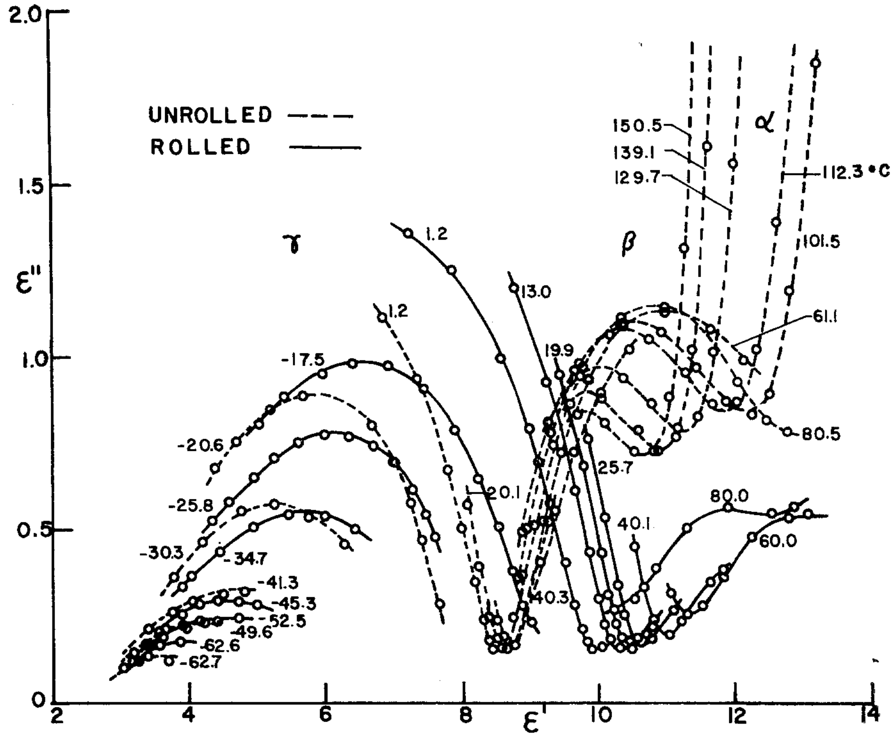

Figure 5 Cole-Cole plot for rolled and unrolled PVF_2.

ever, is much smaller than in the unrolled material.

The 80° C isotherm is already markedly shifted to smaller ϵ' as a consequence of annealing during measurement. But it is still far from that of the unrolled sample. The γ and β peaks suggest that rolling strongly increases the contribution of dipoles in crystal defects as a consequence of chain alignment perpendicular to the electric field but, at the same time, markedly reduces the contribution of chain sections in amorphous regions.

In the unrolled PVF_2, one sees quite well the effect of incipient premelting. Above 80° C, the β peak is no longer fully developed. The absorption starts to drop long before the expected maximum, reaches a minimum, and then goes up rapidly yielding the α peak, characteristic of melting, with high mobility and high absorption. In this peak, the loss is increased much more than the number of mobilised dipoles, giving a greater loss for each dipole than before.

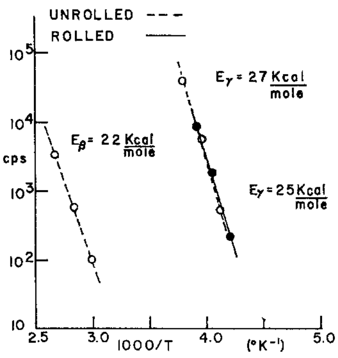

Figure 6 Arrhenius plot of the maximum absorption frequencies for rolled and unrolled PVF_2. The activation energies for the γ peak are 25 kcal/mole and 27 kcal/mole, and for the β peak 22 kcal/mole.

From the Arrhenius plot (fig. 6) of the logarithm of the maximum absorption frequency versus $1/T$, one obtains the activation energies for the γ and β processes for the rolled (γ) and unrolled samples (γ and β). Within the error limits, E_γ is the same (25 and 27 kcal/mole) for both samples. One concludes that the rotation mechanism for the γ-process, i.e. for the rotation in crystal defects, is not significantly changed by rolling. The observed increases in ϵ' and ϵ'' are only due to the more favourable positioning of chain axes. In the case of the β peak, one has data for only the unrolled sample, yielding $E_\beta = 22$ kcal/mole, which is less than E_γ. That means that the potential barrier is less in the β than in the γ mechanism.

4. Conclusion

Rolling orients the crystalline lattice so that the macromolecular chain axis is in the roll direction, as shown by wide-angle X-ray scattering. The latter method, however, does not yield much information about the orientation of chains in the amorphous component. Dielectric measurements prove to be more valuable in this respect because the main contribution to the frequency- and temperature-dependent orientational polarisation at sufficiently low temperatures comes from the dipoles outside the crystalline lattice, i.e. from dipoles in crystal defects and in amorphous regions.

In the case of PVF_2, the low-temperature γ peak is due to the rotation of dipoles of the chains in crystal defects. The increase in the dielectric constant and dielectric loss in this peak as a consequence of rolling can be explained by a more favourable orientation of the macromolecular chains. Every single dipole with a rotational axis perpendicular to the field contributes, to ϵ' and ϵ'', 50% more than is the average for a random orientation of the axis. Since the increase in our data is about 20%, one may conclude that there is a significant, but certainly not a complete, orientation of chain axes in the roll plane perpendicular to the applied electric field. If the angle between the field and the rotational axis of the dipole is ϕ, one obtains for the average square of the sine

$$< \sin^2 \phi > = 0.8$$

which compares to 0.67 for random and 1.0 for perpendicular orientation. The small shift of the absorption maxima at constant frequency to higher temperatures indicates a small increase in friction, i.e. stronger forces as a consequence of closer packing and strain imposed on the chains in defects. But the effect is small and, within experimental error, does not show up in the activation energy.

The β peak relates to the rotation of chain sections in the amorphous regions outside the lattice. It is strongly reduced by rolling. This seems very reasonable because the stronger interaction between adjacent chains hampers the mobility of large chain sections in the amorphous matrix. No such effect is to be expected in crystal defects. Incipient annealing effects, however, drastically limit the observation of the peak. At 80° C, the sample is already changed irreversibly. The dielectric constant and loss rather rapidly approach the values of the unrolled sample with random chain orientation.

Acknowledgements

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