Effect of Orientation on Electrical Properties of Polymers

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Synopsis

This article deals with the effect of orientation on the electrical properties (tangent of the angle of dielectric losses tan δ, electric strength E, and lifetime τ) of polymer films.

It is shown that the orientational stretching of PVC and PC films leads to the change of the temperature position of dipole segmental losses and reduces the value of tan δ in the maximum of this region. Under the orientation the electric strength of PE and PVC films increases considerably, and the lifetime τ increases under the high strengths of the field, and reduces under the low ones.

The mechanical loads causing no orientation only reduce the lifetime of the polymer films.

INTRODUCTION

It is known that the orientation of polymer chains leads to a change in the physical properties of polymers.[1-4]

We have studied the effect of orientation on the electrical properties of polymer films, namely, on the tangent of the angle of dielectric losses tan δ, the short-time electric strength E, and the lifetime τ (the time interval between the moment when voltage is applied and the breakdown of the specimen).

The investigation also covered the effect of a mechanical load causing no orientational stretching of specimens on the lifetime of polymer films.

EXPERIMENTAL

Commercial dielectric films of polyethylene (PE), poly(vinyl chloride) (PVC), and polycaprolactam (PC-4) of 50, 100, and 200 micron thickness, respectively, were investigated. Low-density PE of 35000 average molecular weight with 30 branches per 1000 carbon atoms was tested. PVC was plasticized with dibutyl phthalate of 0.5% concentration. PC-4 film was prepared by sharping melt method, and polycaprolactam was obtained from caprolactam at a polymerization temperature of 250°C in nitrogen.

In order to orient polymer chains, the specimens were stretched out in a special device at a temperature of 20°C. The orientation of the specimens is evidenced by the extent of stretching $\lambda = l/l_0$, where l_0 is the distance be-

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tween two points of the specimen (in the middle region) before its stretching, and l is the same distance after the stretching. As the initial film specimens were thin (50–200 microns), the electrical characteristics were measured in a single direction, namely, perpendicular to the axis of orientation stretching.

The capacity and tan δ of the specimens was measured in the frequency range of 0.4 to 10 Kcps and within the temperature range of 20–180°C by means of a dielectric bridge of MLE-I type. The silver disk coatings with diameter of 20 mm, sprayed under vacuum, were used as electrodes.

The electric strength was determined in air in the field close to uniform with a 50-cps frequency voltage being applied for a short time.

When determining the lifetime, the specimens were placed on a steel plate that served as the lower (grounded) electrode. Ten cylindrical high-voltage steel electrodes having diameters of 8 mm were pressed against the specimen surface. These electrodes were connected with a high-voltage source via fuses. When a specimen broke down under one of the electrodes, its fuse burnt out, and this electrode was disconnected from the high-voltage supply. The time till the breakdown, τ, was recorded by means of an electric potentiometer. For this purpose, resistance, the voltage drop of which was recorded by means of an electric potentiometer, was switched on in a series with tested cells. The moment of the specimen breakdown under one of the electrodes was registered with the pen jump on the belt of the potentiometer. The time before the breakdown was determined as $\tau = L/v$, where v is the motion speed of the belt of the potentiometer and L is the distance on the belt between the moment of the voltage application to the pen jump. The tests were carried out in air at a 50-cps frequency voltage. For each set of testing conditions, the value of log τ was taken as the arithmetic mean of all the log τ values under individual electrodes, and in each test the value of log τ was placed between 80% (log τ) average and 120% (log τ) average at a 0.95 probability.

Along with the investigation of the change in lifetime when orienting polymer chains, the lifetime was studied for comparison as a function of mechanical load causing no orientational stretching of the specimen. In so doing, the lifetime was measured in a unit allowing to subject polymer films to constant mechanical stress during the whole testing period.[5]

RESULTS AND DISCUSSION

In the temperature and frequency ranges studied by us, for poly(vinyl chloride) (PVC) two regions are observed of dielectric losses: losses with a sharply defined maximum of tan δ, and losses the tan δ of which grows monotonically with temperature (Fig. 1). The first region of losses may be classed with the losses of relaxational nature, since with growing measurement frequency, the maximum for this region shifts toward higher temperatures. Under orientation, the maximum of these losses changes its temperature position (shifts toward lower temperatures). A temperature shift of the maximum losses under orientation indicates that these losses are due to the movement of the kinetic segments of macromolecules[6] and belong to dipole-segmental losses (the α-process). The speedy growth of tan δ at high temperatures is likely to be due to the losses at the cost of electric conductivity.
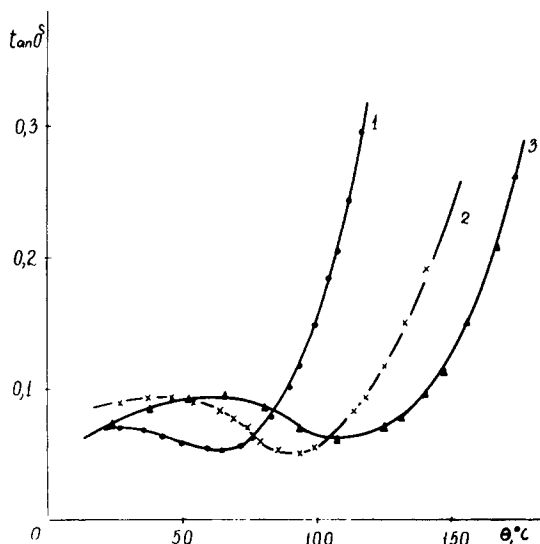
Fig. 1. Effect of orientational stretching on the temperature dependence of tan δ for a PVC film: (1) initial specimen, f = 1 kHz; (2) initial specimen, f = 10 kHz; (3) specimen stretched out threefold, f = 10 kHz.

For a polycaprolactam (PC) film in the range from 20° to 180°C, tan δ passes twice through the maximum at measurement frequencies starting with 5 Kcps (Fig. 2). At lower frequencies, the second maximum is unnoticeable, probably due to the fact that at low frequencies, losses at the cost of electric conductivity which grow rapidly with temperature are very considerable. As the frequency is increased, the two maxima of losses are shifted toward higher temperatures, i.e., these losses are also of a relaxation nature.
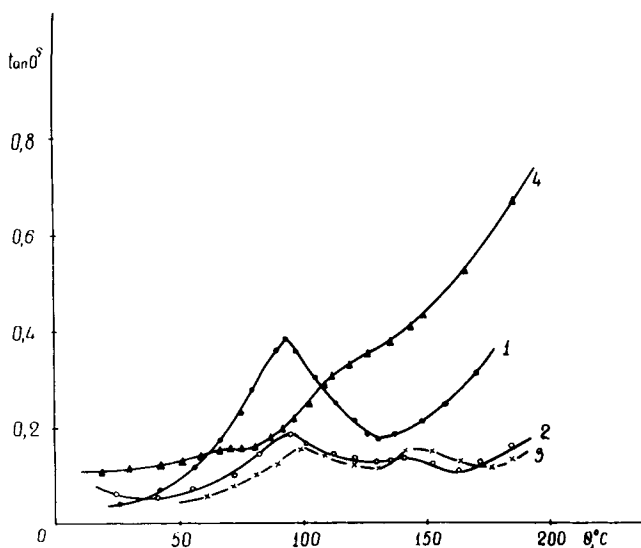

Fig. 2. Effect of orientational stretching on the temperature dependence of tan δ for a PC film: (1–4) tan δ; (1–3) initial specimen; (1) f = 1 Kcps; (2) f = 5 Kcps; (3) f = 10 Kcps; (4) specimen stretched out twofold, f = 10 Kcps.
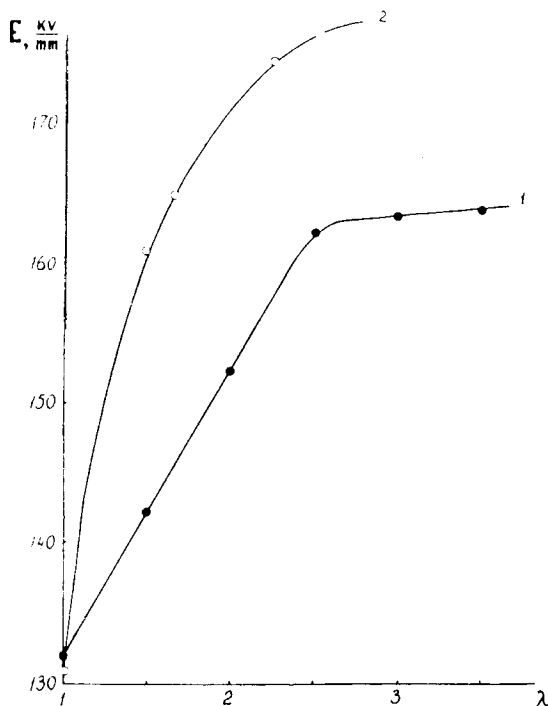
Fig. 3. Electric strength of a PE (1) and PVC (2) film as a function of the degree of stretching (at a temperature of $\theta = 20°C$).

In stretching a PC film specimen, the maxima of losses are shifted toward lower temperatures, and there is a growth of the value of tan δ within the maxima of these regions of losses (especially for the second region of losses).

Figure 3 shows the increase of the polymer film electrical strength with the increase of the extent of stretching. At first, the electrical strength is seen to grow sharply, then more and more smoothly. The specimen thickness is observed to drop with stretching, and this can make a definite contribution into the increase of E.

For the purpose of division of contribution of the thickness reduction and orientation of macromolecules in the increasing of E of the polymer films under their uniaxial stretching, the following experiment was carried out. The dependence of $E = f(h)$ for the PVC film was determined under constant degree of orientation H ($\lambda = 1$). Then, specimens of the same thickness (115±5 microns) were selected and stretched out to various λ values. After determining the specimen thickness with the respective λ, the increment of strength caused only by thickness reduction of the specimen under the stretching $\Delta E(h)$ was determined from the dependence of $E = f(h)$. By substracting from the increment of E, caused by the stretching (Fig. 3, curve 2) the increment of E, connected only with the thickness reduction (Fig. 4, curve 1), one can find the increase of E is caused only by the orientation of macromolecules.

As is seen from Figure 4, the increase in E at the expense of orientation occurs only in case of low E then depending on further stretching E increases only at the cost of the decrease of thickness.
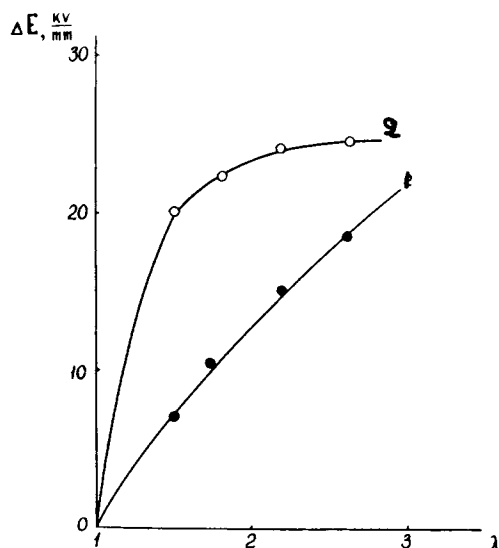
Fig. 4. Increase in electrical strength of PVC film with extent of stretching due to decrease in thickness (1) and orientation of macromolecules (2).

The dependence log τ versus E for the initial PE film (Fig. 5, straight line 1) is a straight line, i.e. the following formula is met

$$\tau = B \exp(-\beta E)$$

where B and β are parameters depending on the properties of the material studied.

In orientational stretching of a specimen, a break in the dependence log τ versus E is observed at a certain value of $E^*(\tau^*)$; at high field strength, the lifetime of the stretched-out specimen grows as compared to that of the initial specimen, whereas at low field strength, it decreased.
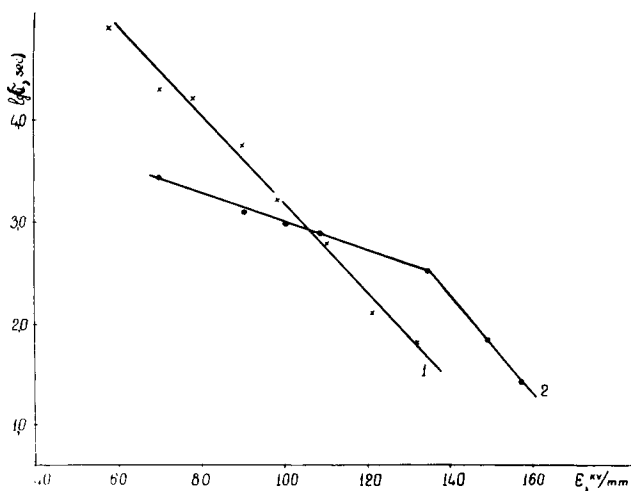

Fig. 5. Effect of orientational stretching on the lifetimes of a PE film: (1) initial specimen; (2) specimen stretched out fivefold.
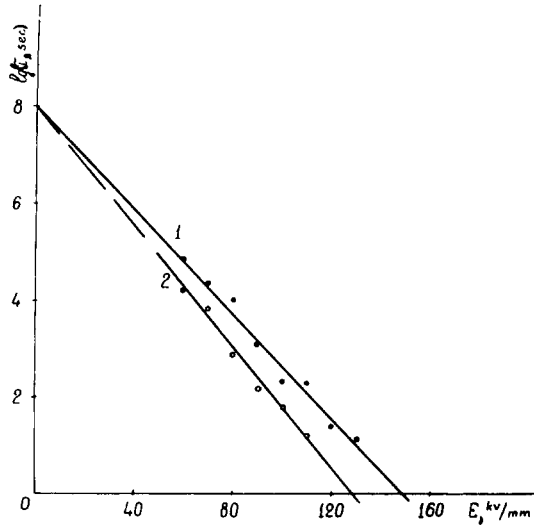
Fig. 6. Effect of mechanical load on the lifetime of a PE film: (1) initial specimen; (2) specimen subjected to a mechanical stress of $\sigma = 0.5$ kg/mm^2.

Such variations in the lifetime curve at orientation may be explained in the following way: at $E > E^*$, when the τ value is low the breakdown mechanism is close to that in the case when a voltage is applied for a short time. It is natural that the growth of intrinsic electric strength in the course of stretching (Fig. 3) entails an increase in the lifetime at high electric field strengths.

Specifically, an increase of the packing density of polymer chains and the growth of the degree of crystallinity will raise the oxidation of macromolecules as the increasing packing density impedes the diffusion of ozone (oxygen) molecules into the polymer, and a crystalline phase is much more difficult to oxidize than an amorphous phase.

At low electric field strengths when the τ value is high, the mechanical stresses developed in the specimen in the course of its stretching lead to a growth of microcracks and to an increase in inhomogeneity which speeds up the breakdown. As a result, the lifetime decreases at low electric field strengths when stretching a specimen.

Figure 6 shows the effect of constant mechanical load that causes no stretching of the specimen on the dependence log τ versus E for a PE film. (Similar results were also obtained for polystyrene and poly(ethylene terephthalate) films.) In this case, the straight-line nature of the dependence log τ of E is not violated, but the lifetime is decreased as compared to the initial specimen. This is likely to be associated with the fact that for polymer films in a mechanically stressed state, the breakdown process is speeded up because of nonuniform distribution of mechanical stresses in the inhomogeneities of the specimen.

CONCLUSIONS

1. Orientational stretching of poly(vinyl chloride) and polycaprolactam film specimens leads to a shift of the dipole-segmental losses and to a change in the value of the maximum tan δ for these regions.

2. When orienting polymer films, the electrical strength of a polyethylene and poly(vinyl chloride) film grows and the lifetime curve varies: at high field strengths, the lifetime increases, whereas at low field strengths, it diminishes. Mechanical loads causing no orientational stretching only reduce the lifetime of a polyethylene film.

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