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Behaviour of a Thermoplastic Charged Surface in the Vicinity of the Softening Point

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Summary

Conditions of formation and stability of „frost effect" on layer of polystyrene with a very thin surface film prepared by crosslinking in an electric discharge were studied for different starting electric potentials of the surface. It was found that during the rise of the temperature of the sample the surface potential falls and a stable frost exists in a certain temperature interval. The explanation of the observed phenomena is based on Cressman's expression for electrocapillar effect and on effects connected with dilatation of the basic layer and artificial film on its surface.

Introduction

CRESSMAN (1963) described a new surface phenomenon, known as the „frost effect". It depends in the formation of a wrinkling structure on the surface of electrically charged thermoplastic dielectrics after heating to the softening point. NICOLL (1964) came to the conclusion, that it is advantageous to form the surface layer artificially, e.g. by crosslinking caused by ionizing radiation. The layer formed in this way shows an increased surface tension as a consequence of strongly different dielectric and mechanical properties of the basic and surface layer. CRESSMANN (1963), BUDD (1965) and VINOKUROVA and CHERKASOV (1979) explain the frost effect as an analogy to the electrocapillary effect (BIKERMAN, 1958) and propose therefore the following expression to describe it

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$$\gamma = \gamma_0 - \frac{1}{2} \sigma_s U_s \qquad (1)$$

where γ is the resulting surface tension, γ_0 is the surface tension in the vicinity of the softening point, σ_s is the density of the electric surface charge and U_s is the electric surface potential. The condition for the frost effect to appear is $\gamma = 0$. Setting for σ_s we get

$$U^2_{sf} = \frac{2 \gamma_0 d_p}{\varepsilon_p} \qquad (2)$$

where U_{sf} is the threshold surface potential in the moment when frost exists, d_p is the thickness of the layer and ε_p is its permitivity. The relation between U^2_{sf} and d_p was determined, the experimental plot having a little different slope from the theoretical value and starting not from the beginning of the coordinates.

In this paper we describe experiments with specially prepared surface film on the surface of thermoplastic material, as, in accord with NICOLL (1964) we have obtained evidence, that simple materials gave very unreliable results in forming frost. On this material we have studied the change of the surface potentials having different starting values U_s with temperature (i.e. during development of the frost). This question, in spite of its fundamental character, stood till now aside.

Experimental

In our experiments we used a low-molecular polystyrene with softening point of about 334 K. Polystyrene was dissolved in toluene and the resulting lacquer was distributed over the surface of an aluminium disk using a glass rod. After drying for 24 h on air, protected against dust, they were transfered to a bell jar and dried for 1 h under the vacuum of about 50 Pa. The thickness of the layer was 10 μm. Samples were then charged with a corona discharge from a needle to a potential in the limits +200 to +1200 V. Shortly after charging the change of their surface potential was measured with a special electrometer which allowed the simultaneous heating of the samples and measuring of their temperature. This type of measurement simulates the conditions in the preparation of a practical frost image, i.e. charging of the surface, leaving a certain time for the preparation of the latent charge image and heat treatment resulting in the frost image.

For the purpose of forming crosslinked layer further samples were treated in the electrodeless discharge 6 kV, 10 kHz, in the vacuum of about 50 Pa, for 5 s. Our measurements of the wetting angle proved that under influence of the discharge the surface became crosslinked. During discharge treatment the polymer bonds are broken and simultaneous attaching of OH groups and crosslinking occur. Probably also some degradation, oxydation and water sorption play a role. In any case defined wetting angles gave defined properties in relation to frost effect.

Results

Typical plots of U_s vs. temperature T are shown in Fig. 1. The plot with the lowest value of surface potential (Fig. 1, curve a) shows a breaking point at 334 K, while the plots of samples with higher surface potentials (Fig. 1, curve b) show a transition region, instead of the point, which is centred round the point 334 K. In this region frost exists, beyond it, in the linear fall part of the curve, it disappears. With these samples, the frost was feable. After treatment we found plots, one of which is shown in Fig. 1, curve c. The shape and slope of individual parts of the curve differ from corresponding parts of previous curves, however, the existence of the region centre round 334 K is preserved. The observed frost effect was intensive.

We found that during slow quasi-continuous increasing of the temperature, frost appears at a certain value of surface potential U_{sf1} and at certain value of temperature T_{f1}.

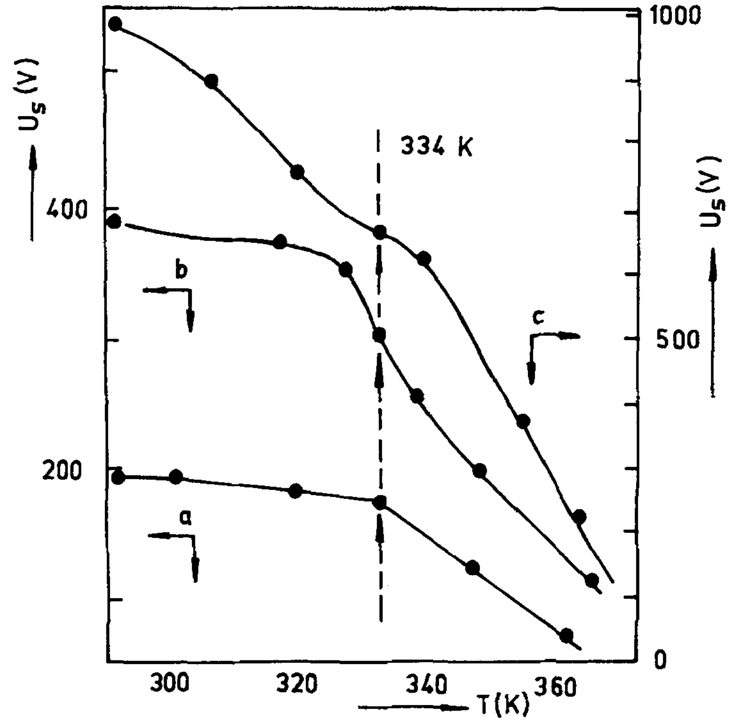

Fig. 1. Typical plots of surface potential vs. temperature

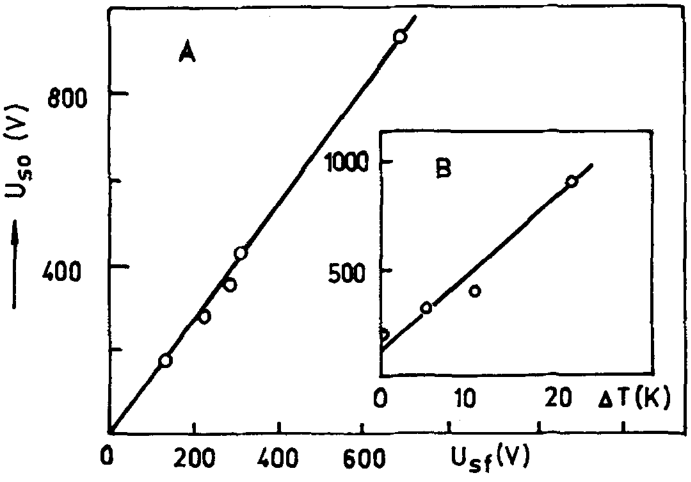

Fig. 2. A) Dependence of surface potential for frost appearance U_{sf} on starting surface potential U_{so}

B) Dependence of the frost temperature region ΔT on U_{so}

If the temperature was further increased the frost was preserved to the temperature T_{f2} and the surface potential U_{sf2}. Figure 2 shows the plots $U_{sf} = (U_{sf1} + U_{sf2}) / 2$ and $\Delta T = T_{f2} - T_{f1}$ versus the value of the starting surface potential U_{so}. Both plots are linear.

Discussion

As it was mentioned, we used materials with a special crosslinked film on the surface of the basic layer, prepared by electrical discharge. A further improved reproducibility of frost formation may be achieved by a short high temperature shock of the crosslinked layer, resulting in a slight degradation of the surface. This operation is strongly dependent on complex properties of the layer and substrate and is therefore not described here in detail (it has a supporting effect only).

We will try now to estimate the differences in the behaviour of the simple system and of the system with the artificially treated surface. If we suppose that the surface film has very different mechanical and electrical properties, the frost may be formed, basically, in two ways:

1) due to cracking caused by differing coefficients of dilatation, supported by high concentration of dislocations and other fault centres,

2) due to lowering of the tension of the surface film by a strong local electric field.

The occurence of thermal cracking without the assistance of the electric field is a well known phenomenon (some lacquers, e.g.). For the purpose of imaging, however, we are interested in systems, which can be influenced by electrostatics, i.e. in systems, where the mechanical effects are either of secondary nature, or support the electrical frost formation. In the first approximation, therefore, the behaviour may be described by the equation (1).

The surface potential is in principle strongly influenced by the electrical permitivity (3) resulting from the values of ε of the basic layer and the crosslinked layer. The result-resulting ε may be measured or calculated using Lichteneckers mixing rule

$$\varepsilon_1^{p_1} - \varepsilon_2^{p_2} = \varepsilon \qquad (3)$$

where $p_1 + p_2 = 1$ and p_1, p_2 are volume proportions of the components, if we know the thickness and ε of the surface layer. This value may be determined on a specially prepared thick film.

If we now charge our system to a starting value of U_{so} and heat it gradually, we observe that

(i) at a constant starting temperature the potential falls due to the conductivity of the material,

(ii) the heating results in accelerating the fall,

(iii) from a certain value of temperature frost appears and remains stable for an interval of temperatures. In this interval the speed of the fall changes,

(iv) after passing this interval another change of the speed of the potential fall occurs.

The centre of the temperature interval agrees with the break point in the plot of surface conductivity vs. temperature, which has the value 334 K for our material. The author (NEŠPŮREK, private communication) attributed this break to a phase transition.

For the elucidation of the behaviour characterized by the plots in Figs. 1 and 2, the complete Cressman expression (2) may be used. If we increase the temperature, the surface tension γ_0 decreases, ε decreases and, owing to the dilatation, d increases. The resulting γ therefore decreases due to γ_0, but this decrease may be to a certain degree compensated by the subtracted diminished value ε / d. The influence of U_s, which is in square, is therefore decisive. As a result, frost appears at higher U_s(what was observed). Because some uncompensated influence of γ_o exists some temperature shift may be attributed to it.

To explain, why the frost is preserved the longer, the higher is U_{so}, we must suppose, that deeper ripples or cracks in the structure of the surface need higher thermal energy to smooth. It is also not possible to exclude the forming of frost in the interval by the influence of heat only, extending the stable region. After disapearing of the frost, the new surface is formed, having rather the simple, Cressman type, character.

We noted that the formation of frost was influenced by the speed of heating. This indicates, that both mechanisms of frost formation imply relaxation effects. All experiments were done on virgin samples, as we eliminated in this way the $U_s(T)$ effects due to the thermal and electric history of the material.

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