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Influence of High Peroxide Concentration on the Mechanical Properties of Cross-Linked Low Density Polyethylene

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ABSTRACT

In this paper are presented the static and dynamic mechanical investigation of chemically cross-linked low density polyethylene (XLPE) prepared in our laboratory. This polymer has been tested mechanically at different frequencies, amplitudes, and temperatures as a function of cross-link density which is indicated to some extent by the amount of peroxide used in the cross-linking. The main findings can be described as follows: mechanical damping in XLPE at the α-relaxation point as a function of peroxide concentration is different for shear and compression modes of deformation. Moreover, the dynamic investigation at very small amplitudes indicated two relatively rigid structures. One structure at low concentration of peroxide is attributed to excessive crystallinity; the other one at the high peroxide concentration is probably due to the very regular and perfect polyethylene network. These two interesting structures are not detected by dynamical testing with large amplitudes. As far as Young's modulus as a function of peroxide concentration is concerned, we conclude that in this polymer this factor does not depend on the crystallinity but on changes of the so-called hard amorphous phase. These findings are consistent with our previous structural investigation.

INTRODUCTION

Some ultrasonic and structural investigations were presented in Refs. 1-4. The former and present studies are concerned with testing the changes in structure of cross-linked polyethylene (XLPE) as a function of peroxide concentration. In these studies we also estimated the usefulness of different physical methods for determination of structures in this polymer.

The methods employed for the preparation of XLPE have been described in Ref. 2. We recall in Ref. 2 that three peroxides, 1-Di-Cup R, 2-Luperox 130, and Luperox 101, were used for cross-linking of the polyethylene Petrolen WJF-47 (molecular weight $\overline{M}_n = 32{,}000$). Peroxides were used in the following concentrations: a 0.5, b 1.0, c 1.5, d 2.0, and e 2.5 weight percentage.

Some mechanical properties of low cross-linked PE have been presented in Ref. 5. There also exist a large number of investigations on irradiated PE. However, the nature of cross-linking of this polymer is still not well understood, especially the process of chemically cross-linked low density PE.

EXPERIMENTAL

1. A torsional pendulum was used to test the dynamic properties of XLPE as a function of temperature. The range of the testing temperatures was from 17 to 105°C, and the range of frequency was from 0.3 to 1.5 Hz. The storage modulus G' and the logarithmic damping decrement were calculated on the basis of the well-known formulas given in Ref. 6. The maximum torsional amplitude was 2.5° (approximately 468 μm).
2. The Weissenberg rheogoniometer type R-17 was used to test the XLPE as a function of frequency in the range 0.005 to 5 Hz at room temperature. The torsional amplitude was 1.2 degree (approximately 225 μm). The detailed evaluation of the storage modulus from these measurements is given in Ref. (6).
3. To confirm the results from a Weissenberg rheogoniometer, we have used a vibration table and a resonance method in the frequency range 100 to 900 Hz. The resonance method was applied in shear and compression. From these measurements the storage modulus and loss factor were evaluated according to Ref. 6. Samples from this test were separately prepared (i.e., cross-linked). The effective amplitude of deformation was in shear 50 μm and in compression 20-30 μm [7].
4. The static mechanical investigations were carried out on a TT-CM Instron Machine at room temperature [3]. The strain rate was 0.5 cm/min. From these tests we evaluated Young's modulus E_r, yield point R_{plr}, percentage of elongation at the yield point ϵ_{plr},

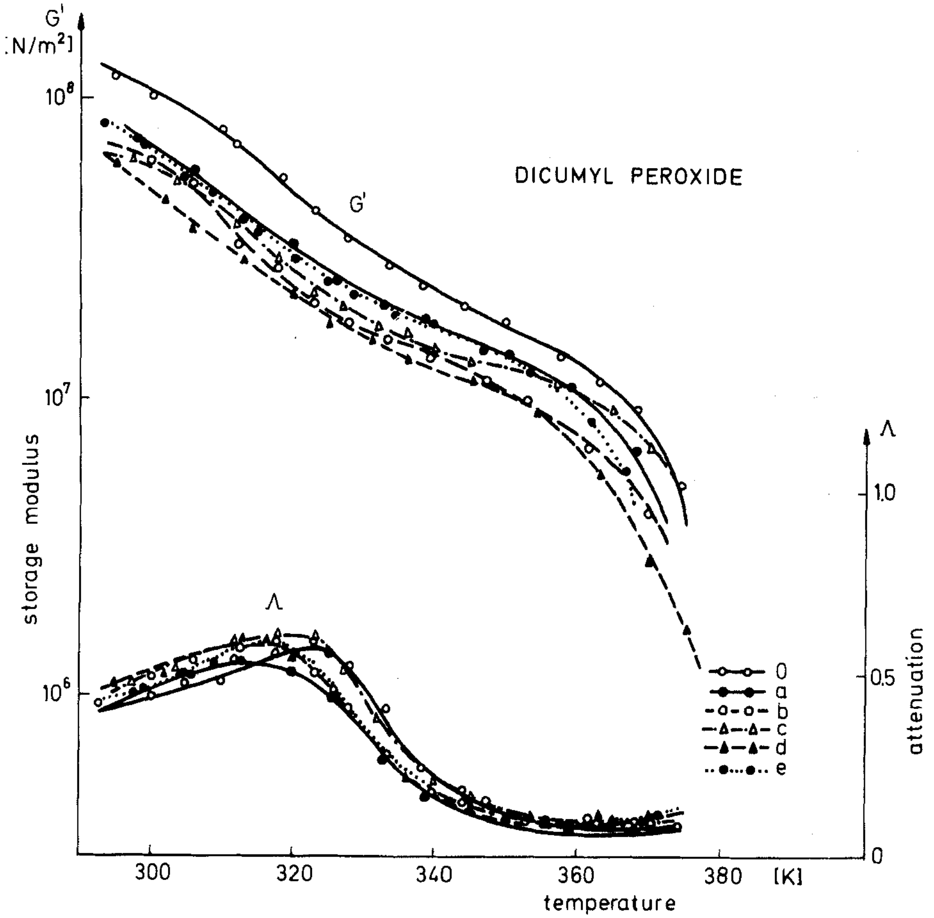

FIG. 1. The storage modulus G' and the logarithmic decrement of attenuation of XLPE as a function of temperature.

tensile strength σ_r, and percentage of relative elongation at the breaking point ϵ_r [8].

5. In addition, the thermal expansion coefficient was determined within the temperature range 30-60° C.

We present here the results for only one peroxide because all the peroxides used in this study gave similar results. Only the mechanical results which are of particular interest from the scientific point of view are presented here. Others can be found in Refs. 1-4, 6, and 7.

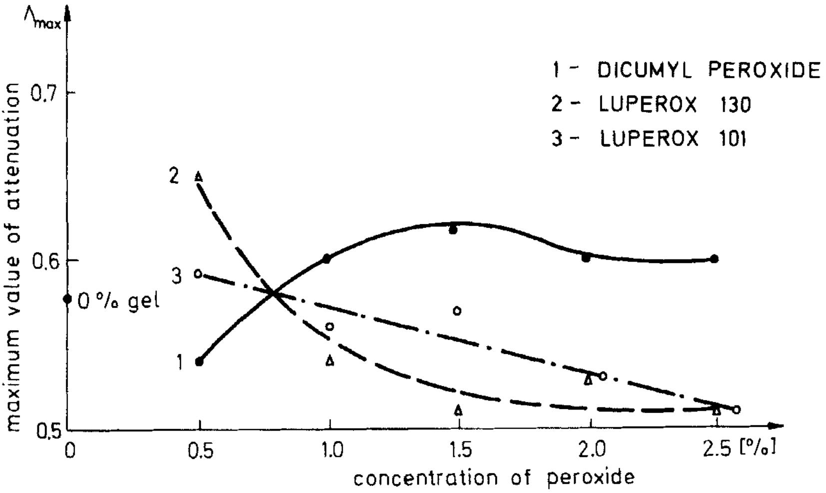

FIG. 2. The maximum value of attenuation of XLPE as a function of peroxide concentration.

RESULTS

In Fig. 1 it can be noted that the maximum of $\Lambda = f(T)$ in the vicinity of 320 K represents the so-called α-relaxation in the uncross-linked PE and cross-linked PE. The maximum value of the logarithmic decrement (the relaxation point) as a function of the peroxide concentration is shown in Fig. 2, In general, the maximum value of Λ gradually diminishes as the concentration of the peroxide used for cross-linking increases. Figure 3 shows how the temperature of the maximum of the logarithmic depends upon the peroxide concentration used. It is clearly seen in Fig. 3 that the temperature maximum falls for higher peroxide concentrations. We have found the same phenomenon in cross-linked polypropylene [9].

From Fig. 1 we have obtained data to draw the plot of G' versus peroxide concentration at 27°C (Fig. 4). It can be seen in this figure that the values of G' for the XLPE are below the values for the uncross-linked PE, and no extrema appear on these curves. The same situation occurs if the temperature is increased to 80°C [6]. At 87°C (Fig. 5) the values of G' for XLPE are higher than for the uncross-linked PE. It was found that G' typically behaves as a function of frequency as shown in Fig. 6 (v = frequency). Relationships of this type were used to draw the plot of G' versus the peroxide concentration for cross-linking (Figs. 7 and 8). It is seen in these figures that the characteristic feature of those plots is the appearance of a maximum for G' = f (% peroxide) at peroxide concentrations of 0.5 and 2%. The resonance investigation yielded relations equal to the above described curves.

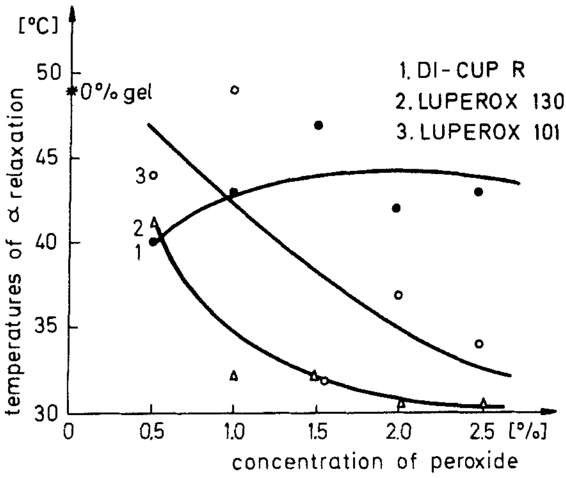

FIG. 3. The temperature of the maximum of attenuation of XLPE as a function of peroxide concentration.

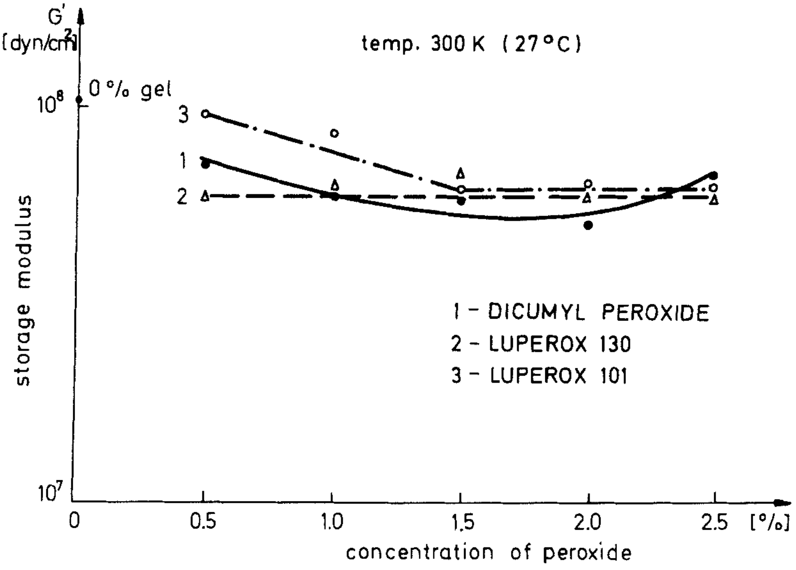

FIG. 4. The storage modulus G' at 27°C of XLPE as a function of peroxide concentration.

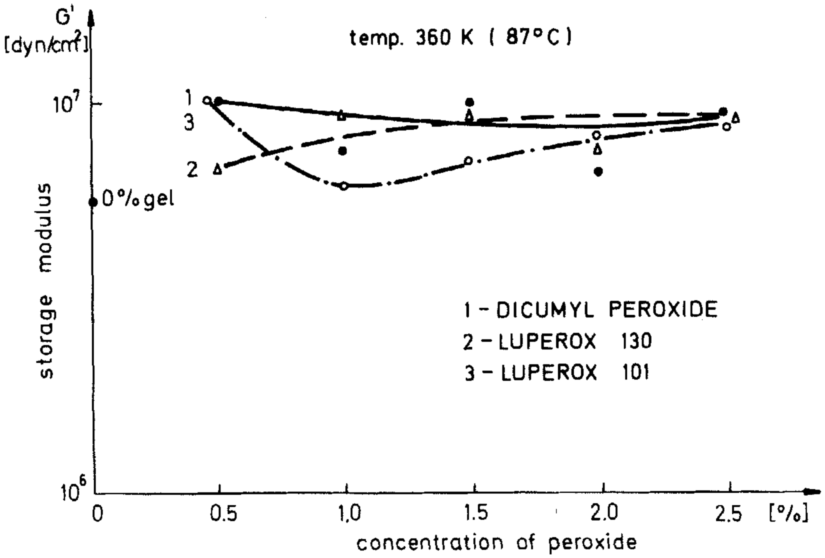

FIG. 5. The storage modulus G' at 87°C of XLPE as a function of peroxide concentration.

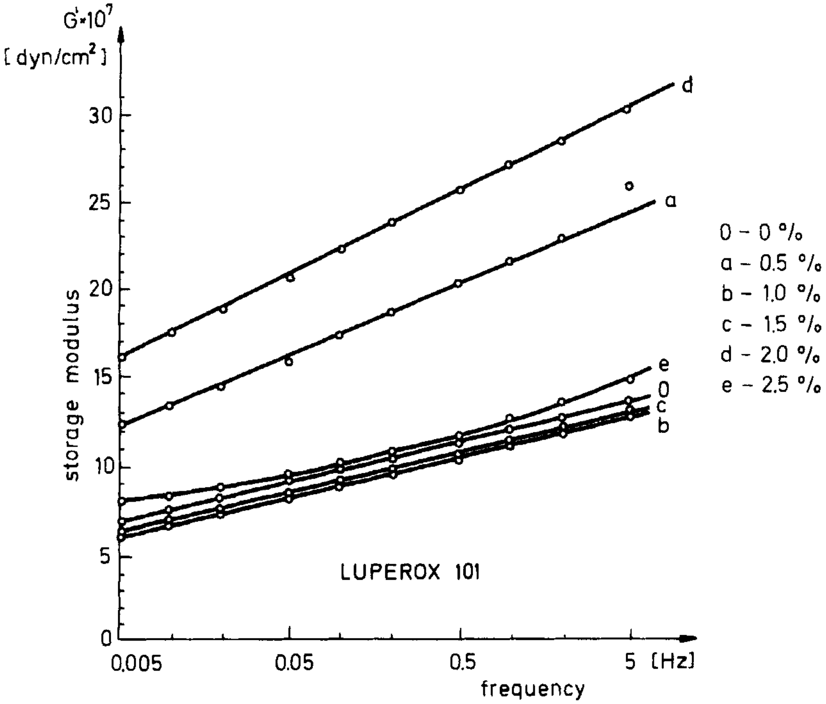

FIG. 6. The storage modulus G' of XLPE as a function of frequency (Hz) measured in a Weissenberg rheogoniometer.

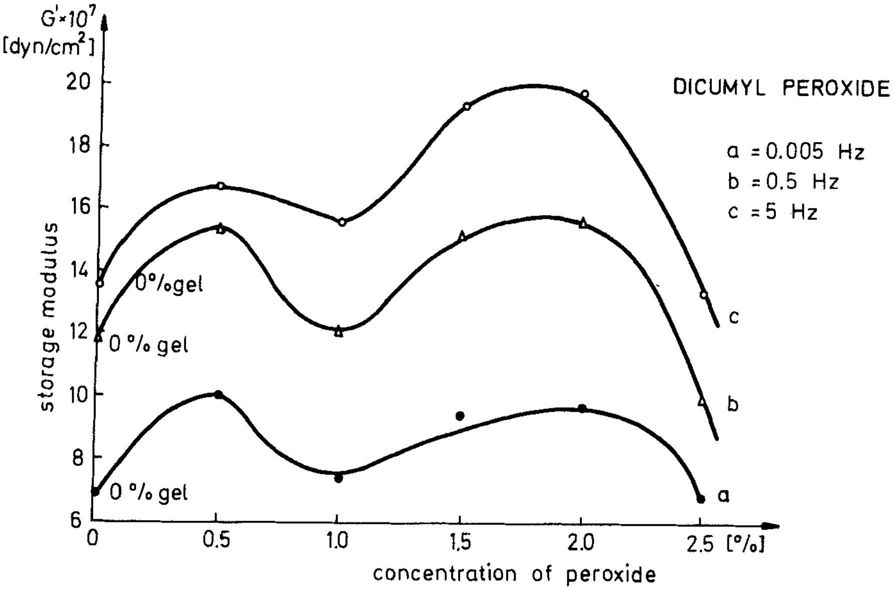

FIG. 7. The storage modulus G' of XLPE as a function of dicumyl peroxide concentration measured in a Weissenberg rheogoniometer.

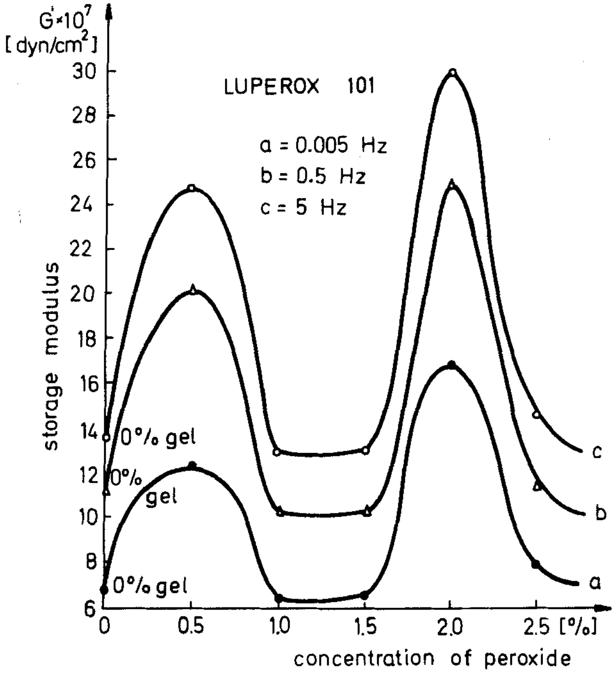

FIG. 8. The storage modulus G' of XLPE as a function of Luperox 101 peroxide measured in a Weissenberg rheogoniometer.

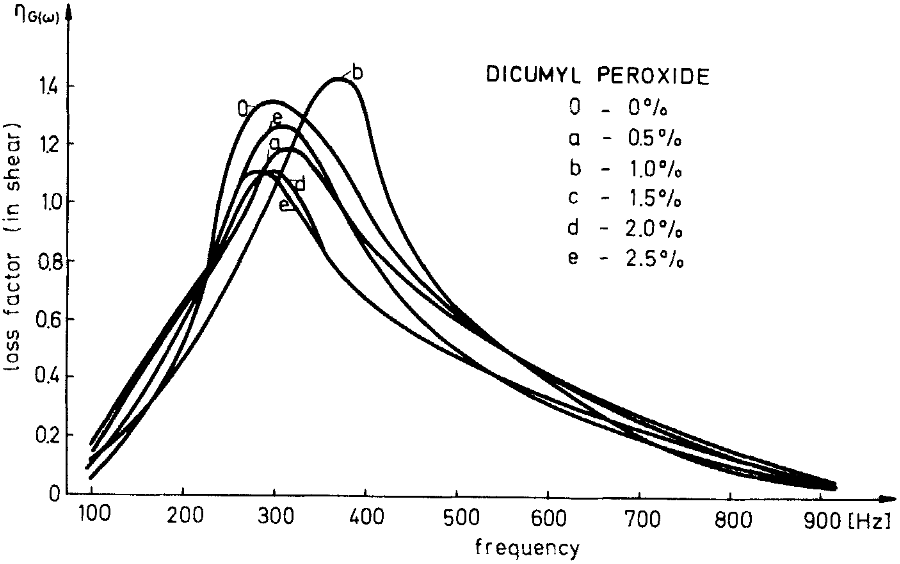

FIG. 9. The loss factor (in shear) of XLPE cross-linked with dicumyl peroxide as a function of frequency (resonance measurements).

In Fig. 9 we see the relationship between the loss factor and frequency obtained for shear strain. For the remaining peroxides and for compression, the curves are similar [9]. It is seen in Fig. 9 that in the vicinity of 300 Hz there is a loss factor maximum. This damping maximum is presumably due to the so-called α-relaxation. Figures 10 and 11 show the loss factor maximum value in shear and compression, respectively, as a function of peroxide concentration. The differences between these curves are that for shear the damping diminishes with increasing peroxide concentration and for compression the situation is reversed. On the other hand, the frequency corresponding to the loss factor maximum as a function of concentration (Fig. 12) is the same for compression.

Plots of G' for shear and K' for compression as a function of peroxide concentration are shown in Figs. 13 and 14. It is easily seen that these curves are similar to those given in Figs. 7 and 8.

Young's modulus as a function of peroxide concentration is shown in Fig. 15 [10, 13]. The modulus has a smaller value for higher concentrations of peroxide, as in the case of cross-linked polypropylene [9]. The yield point gradually decreases as the peroxide concentration increases (Fig. 16). On the other hand, the elongation at the yield point has larger values as the peroxide concentration increases (Fig. 17). As we found out, there is a similarity between Young's modulus of XLPE and XLPP as a function of the cross-linking agent

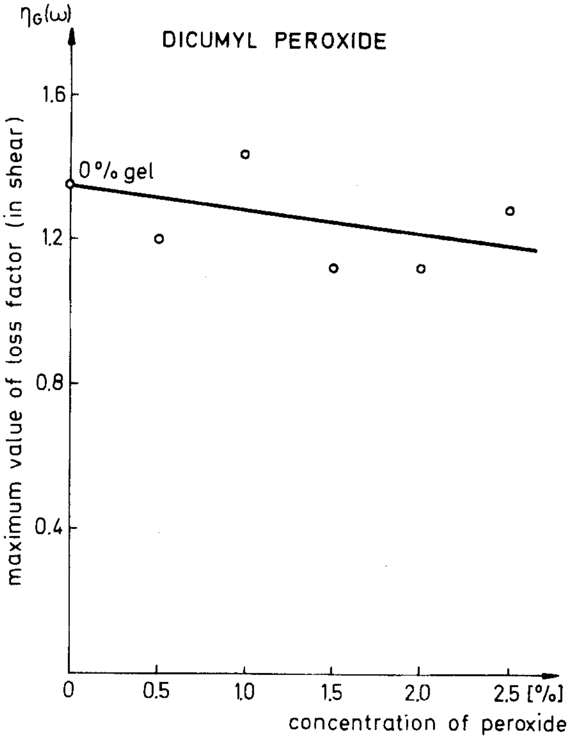

FIG. 10. The maximum values of loss factor (in shear) of XLPE as a function of dicumyl peroxide concentration.

[9, 10]. The plot of tensile strength as a function of peroxide concentration has a very interesting form. In the vicinity of 0.5% peroxide concentration there appears a maximum of $\sigma = f$ (% peroxide) (Fig. 18). Figure 19, which is the last one in this series of static mechanical tests, illustrates the relative elongation at break as a function of the peroxide concentration. This factor decreases for higher concentrations of peroxide.

Plots of the coefficient of thermal expansion as a function of peroxide concentration (Fig. 20) show maxima similar to some dynamic tests (Figs. 7, 8, 13, and 14).

DISCUSSION

Comparing Fig. 2 with Fig. 10, we conclude that damping at the α-relaxation point associated with shear and torsional stresses

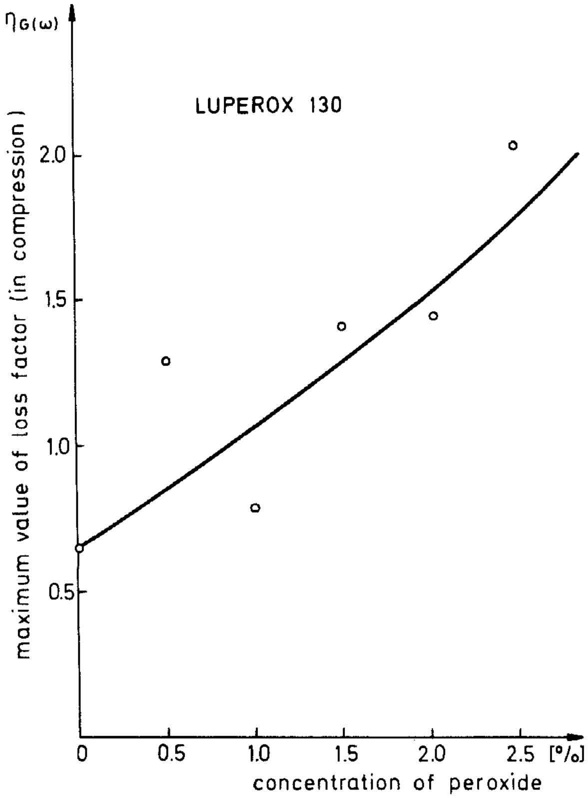

FIG. 11. The maximum values of loss factor of XLPE cross-linked by Luperox 130 as a function of peroxide concentration.

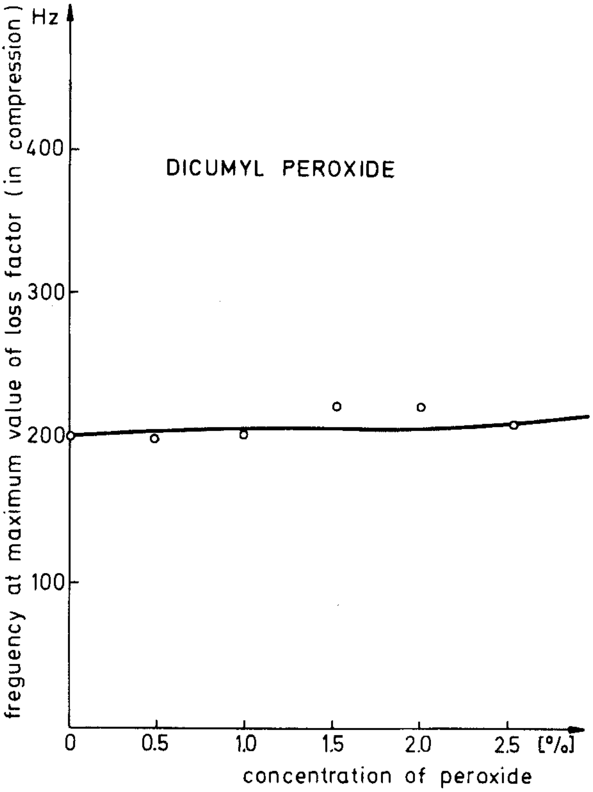

FIG. 12. The frequency of maximum values of loss factor (in compression) of XLPE as a function of dicumyl peroxide concentration.

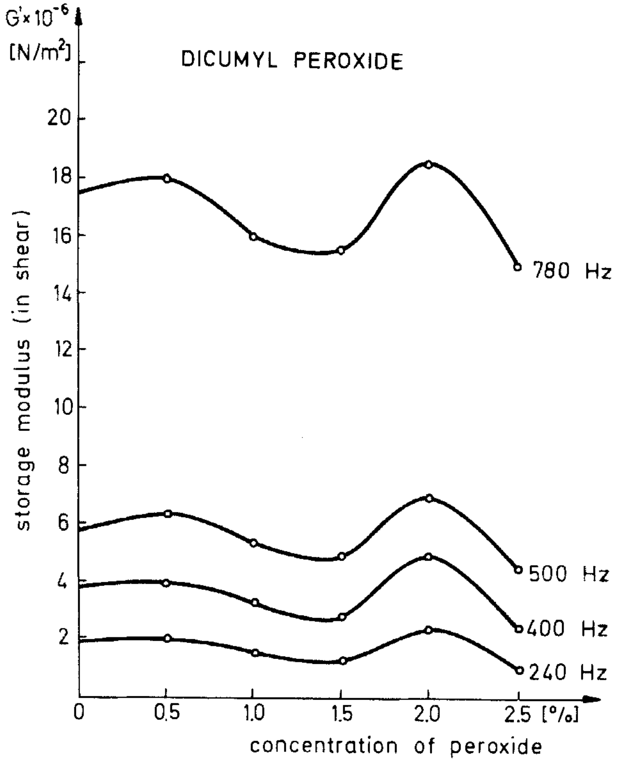

FIG. 13. The storage modulus G' (in shear) of XLPE as a function of dicumyl peroxide concentration measured by the Weissenberg method.

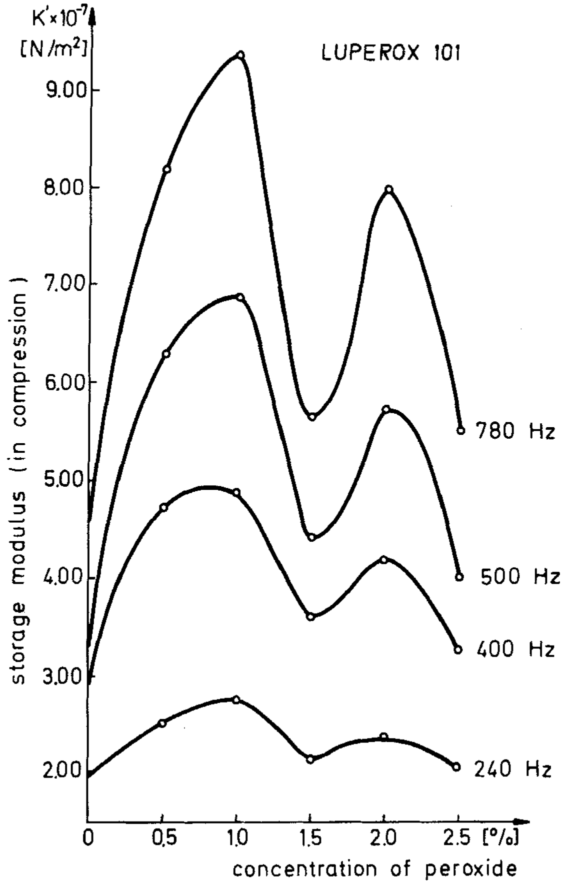

FIG. 14. The storage modulus K' (in compression) of XLPE as a function of Luperox 101 peroxide concentration measured by resonance method.

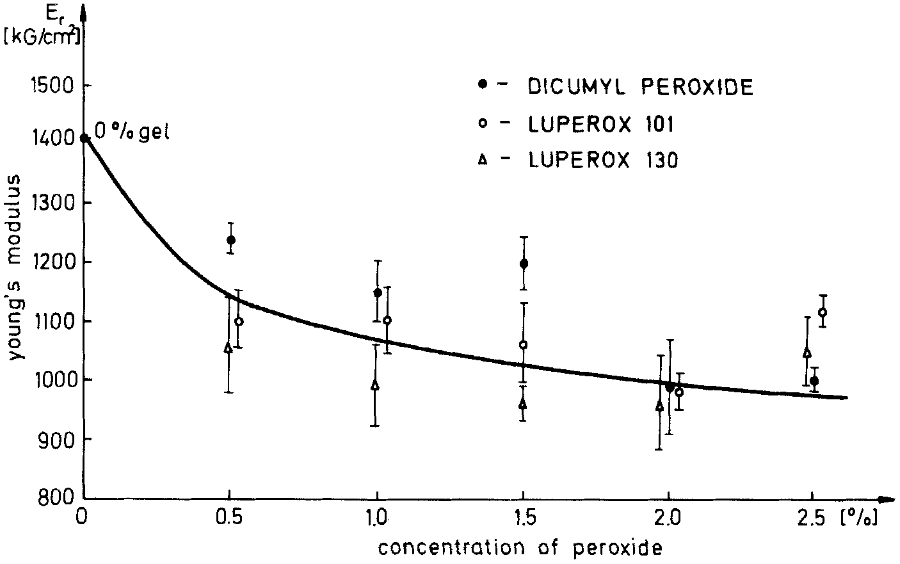

FIG. 15. Young's modulus E_r of XLPE as a function of peroxide concentration.

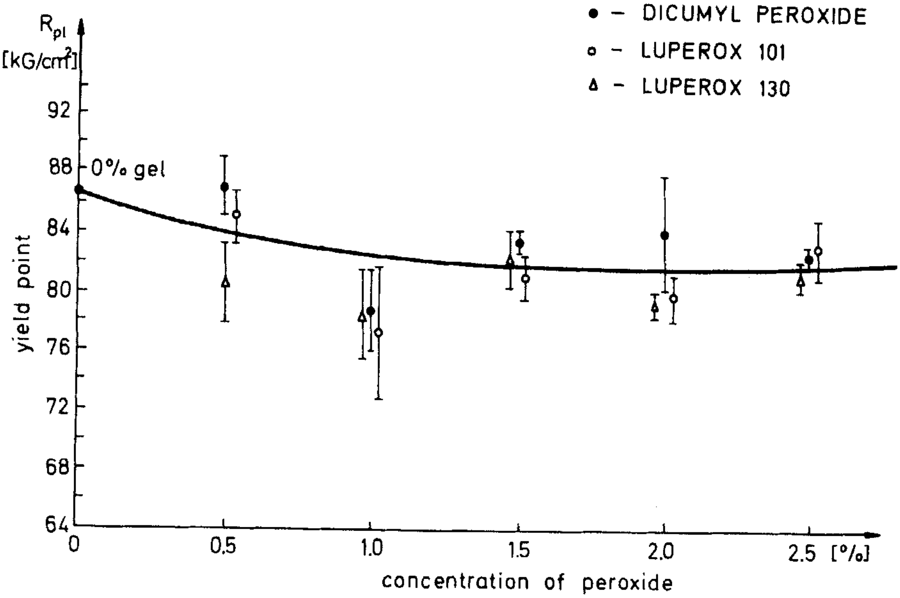

FIG. 16. The yield point R_{pl} of XLPE as a function of peroxide concentration.

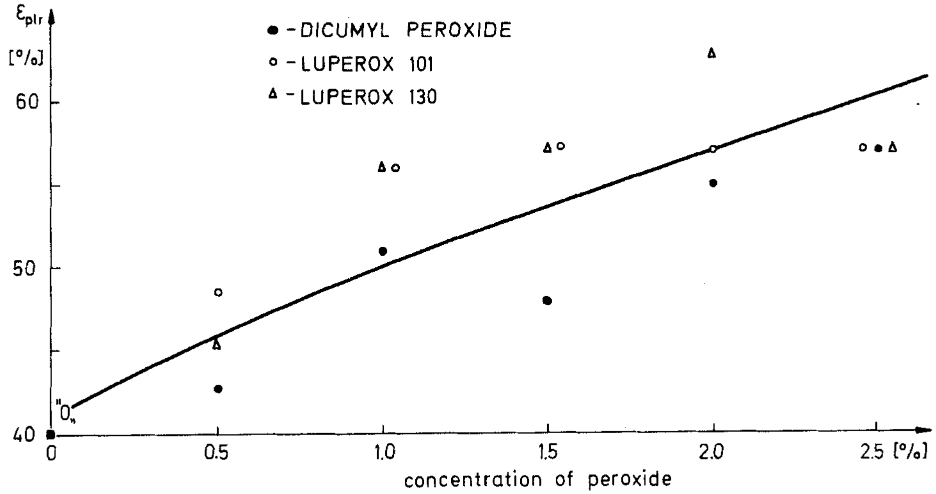

FIG. 17. The percentage elongation at the yield point of XLPE as a function of peroxide concentration.

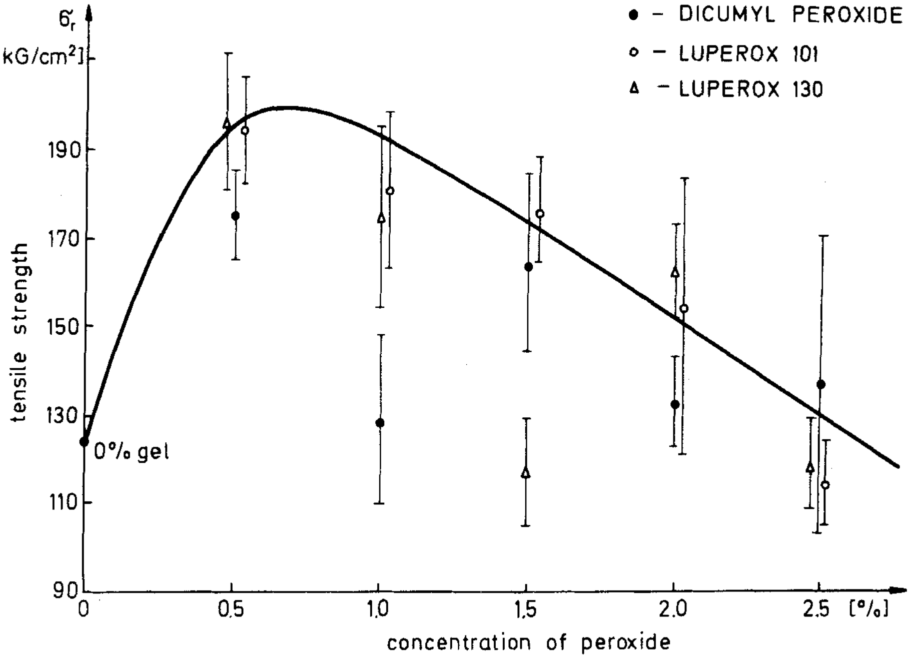

FIG. 18. The tensile strength σ_r of XLPE as a function of peroxide concentration.

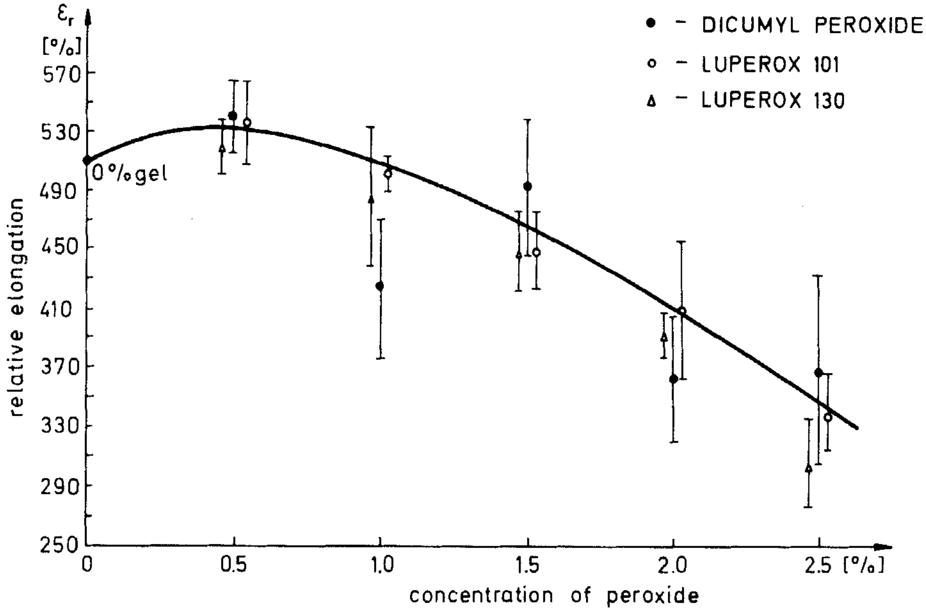

FIG. 19. The percentage of relative elongation at the breaking point of XLPE as a function of peroxide concentration.

decreases with increasing peroxide concentration, but increases with compressional stress with increasing peroxide concentration. These effects can probably be explained as follows: compression is produced by normal forces while shear is produced only by tangential forces. The so-called simple shear is the sum of pure shear and rotation. The experimental data [11] indicate that a viscoelastic body subjected to shear becomes less viscous; that is, the polymer damping decreases, presumably due to the rotation of the polymer chains. If the body is affected by axial forces, it becomes more rigid, which means that the damping increases. It is assumed that these effects have taken place in our experiments. Additionally, from an NMR test [12] we know that the amount of soft phase (short chains, network defects in XLPE) increases with increasing peroxide concentration. This probably produces diminishing of damping in shear and an increase of damping with axial forces.

It is difficult to explain the relation between T_{max} and the concentration of peroxide (Fig. 3) because there are different views about the effect of crystallinity on α-relaxation. However, it can be assumed that the increasing density of cross-links shortens the length of chains in the folds on the surface of lamellae, and it could be that such a chain length reduction will produce a temperature drop. A similar explanation

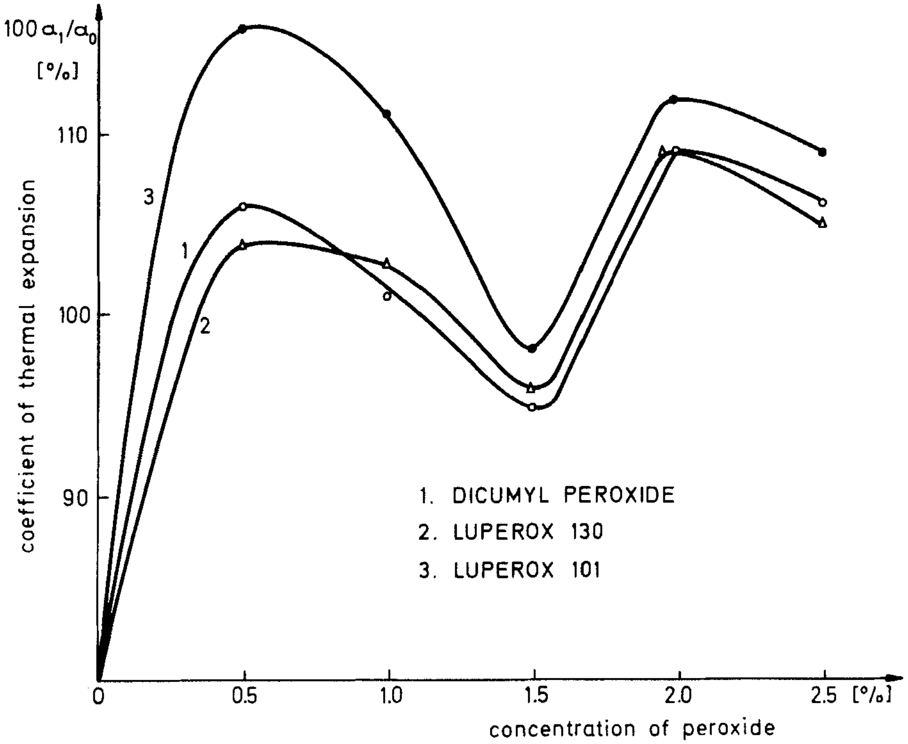

FIG. 20. The coefficient of thermal expansion of XLPE as a function of peroxide concentration.

has been given by Wunderlich [13] for the relation between the length of the fold and the temperature.

From Fig. 4 it is clearly seen that the storage modulus at 27 °C is probably affected mainly by crystallinity since this modulus takes higher values for the uncross-linked PE than for the XLPE. However, at 87° C (Fig. 5), which is near the melting point of PE crystallites [8, 10], the storage modulus of uncross-linked PE shows lower values than the XLPE. This is mainly due to an increase in stiffness of the PE network at this temperature.

The absence of any maximum of storage modulus plotted against the peroxide concentration shown in Figs. 4 and 5 and the appearance of some maxima on these curves shown in Figs. 7 and 8 and in Figs. 13 and 14 is, in our opinion, due to the following effects. The torsional pendulum produces so large a deformation (488 μm), that it probably exceeds the range of linear viscoelasticity of this material. Thus the storage modulus represents the averaged resultant properties of different phases in the XLPE specimen. In the Weissenberg and resonance methods the deformations are at least half those of the torsional method and are probably within the range of linear viscoelasticity. Thus the mechanical properties of different phases are not averaged.

The first maximum is presumably related to the appearance of excessive crystallinity and the second maximum is probably caused by a uniform, rigid PE network (Figs. 13 and 14). This last interpretation is based on our calculation [14], from which it follows that at 2% peroxide concentration one bond links two chains of the PE used by us. The sharp drop in value of storage modulus at a peroxide concentration higher than 2% is probably due to the degradation effect.

The fall in the value of Young's modulus plotted against peroxide concentration (Fig. 15) is not produced, in our opinion, by the drop of crystallinity because in that case we would face a maximum of the Young's modulus at about 0.5% peroxide concentration.

From our NMR tests [12] we can say that Young's modulus depends on the amount of rigid amorphous phase in XLPE. The same explanation for relaxation moduli in PE has been given elsewhere [15]. Our investigation has shown that the amount of this phase gradually diminishes with increasing concentration of peroxide [12].

It is difficult to interpret the dependence of the yield point on the peroxide concentration, because the yield point phenomenon is not well understood (Fig. 16). The increase of elongation at the yield point (Fig. 17) for the higher peroxide concentration can be explained by the facts found by NMR tests [12]. The NMR tests show that with an increase in peroxide concentration, the amount of the soft phase increases. The phase acts as a plasticizer and presumably contains network defects and degraded PE chains. The appearance of this phase produces the reduction of the stress necessary for yield. The plot of tensile strength as a function of peroxide concentration (Fig. 18) is similar to that produced by cross-linked natural rubber [17]. In our opinion this strength depends on the amount of crystallinities in XLPE because this dependence is similar to the relation between degree of crystallinity and peroxide concentration [2]. In this respect it could be that the crystallite but not the amorphous phase transfers the stress. We have faced the same phenomenon in XLPP [9]. As far as decreasing elongation at the breaking point is concerned (Fig. 19), we can say that it depends mainly on the degree of cross-linking in XLPE, not the crystallinity. Probably the increase of the degree of cross-linking, which is reflected to some extent by the increase of the gel fraction [1-3], produces restraint of the chain movement that could be manifested if elongation is plotted against peroxide concentration.

The relationship between the coefficient of thermal expansion and the peroxide concentration has been presented to show the correlation between the thermal and mechanical properties of this polymer. Thermal expansion (Fig. 20) shows maxima in precisely the same range of peroxide concentrations as does storage modulus tested in the viscoelastic range of strain. However, it is thus far impossible to explain the correlation between these two relationships based on the previously assumed XLPE structure.

Summarizing our investigations we can conclude the following: the mechanical damping of XLPE as a function of peroxide concentration at the α-relaxation point is different for shear and compression modes of deformation. Different structures of XLPE prepared by us can be distinguished by dynamic interaction only in the linear viscoelastic range of deformation. Based on the use of dynamic interaction in the linear viscoelastic range, we propose two rigid structures in XLPE. In our opinion, one may be ascribed to the crystallities and the other to the uniform XLPE network.

The static mechanical investigation shows that chemical cross-linking of PE causes changes of this material, even at room temperature, and that Young's modulus in this polymer is probably not dependent on crystallinity but on the so-called hard amorphous phase as in cross-linked polypropylene [9, 15].

These mechanical investigations are confirmed by our previous ultrasonic [2, 3], structural [1-3] and NMR findings [4, 12].

We conclude from these investigations that in practice we may sometimes come across unusual structural and dynamic mechanical properties of this material that is used, for example, in the preparation of cable coatings.

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REFERENCES

[1] K. A. Kunert, "Structure and Properties of Polymers Networks," in 9th Europhysics Conference on Macromolecular Physics, April 23-28, 1979, Jabłonna, Poland, No IV-2, p. 151.

[2] K. A. Kunert, J. Polym. Sci., Polym. Lett. Ed. 17, 363-367 (1979).

[3] K. A. Kunert and J. Ranachowski, Acoust. Lett. 4(2), 23-32 (1980).

[4] K. A. Kunert and J. Ranachowski, 7th Discussion Conference, Polymer Networks, September 15-19, 1980, Carlsbad, Czechoslovakia, C-27.

[5] T. R. Manley and M. M. Qayyum, Polymer, 12, 176 (1971); 13, 123 (1972); 14, 156 (1973).

[6] K. A. Kunert, Rep. Inst. Fundam. Technol. Res., Polish Acad. Sci., 8 (1979).

[7] K. A. Kunert, Ibid., 138 (1979).

[8] K. A. Kunert, M. Jakubowska, and J. Bojarski, Ibid., 51 (1977).

[9] K. A. Kunert, I. Chodak, H. Soszyńska, N. Piślewski, and J. Ranachowski, Ibid., 20 (1980).

[10] K. A. Kunert, I. Chodak, H. Soszyńska, N. Piślewski, and J. Ranachowski, Polymer (U.K.), In Press.

[11] R. H. Haward, The Physics of Glassy Polymers, Applied Science Publishers, London, 1973, p. 283.

[12] K. A. Kunert, I. Chodak, J. Ranachowski, and N. Piślewski, Polym. Bull. 3, 449-455 (1980).

[13] B. Wunderlich, Macromolecular Physics, Vol. 1, Academic, New York, 1973.

[14] K. A. Kunert, A. Wasiak, and H. Soszyńska, Rep. Inst. Fundam. Technol. Res., Polish Acad. Sci., 23 (1978).

[15] K. A. Kunert, H. Soszyńska, and N. Piślewski, Polymer (U.K.), In Press.

[16] S. Onogi, T. Sato, T. Asuda, and Y. Fukai, J. Polym. Sci., Part A-2, 8, 1211 (1970).

[17] A. E. Nielson, Mechanical Properties of Polymer and Composition, Dekker, New York, 1974.

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