Turk J Phys
25 (2001) , 575 – 581.
© TÜBİTAK

Influence of Above-Molecular Structure, Electronic and Ionic Phenomena on Durable Properties of Polymer Dielectrics in the Electric Field

T. M. VELİYEV, S. A. ABASOV, M. J. ZEYNALOVA, E. HALİLOVA
Institute of Physics, Azerbaycan Academy of Sciences,
H. Javid Avenue, 33, Baku, 370143 - AZERBAYCAN
H. MEMEDOV, I. ASKEROV, S. AYDOĞU
Dumlupınar University, Faculty of Arts and Sciences,
Department of Physics, Kütahya - TURKEY

Received 13.08.1998

Abstract

Influence of above-molecular structure (AMS) on electrothermoluminescence, the altering time and the mechanic time of polymer dielectrics in strong electric fields that depend on temperature have been investigated. It has been shown that change of AMS considerably influenced the processes of injection and stabilization of charges as well as the solidity properties of polymers.

It has been determined that the relaxation translations in large spherolite samples were observed at lower temperatures than the relaxation translations in small spherolite samples.

Key Words: Above moleculer structure, polymer dielectrics.

1. Introduction

It has been shown in previous work [1] that the decrease of waiting time of electrical longevity (τ_E) in mechanical field and mechanical longevity ($\tau_{\sigma E}$) of polymer dielectrics in a strong electric field considerably depends on their AMS. The observed decreases were explained by the change of conditions of various structural defects, the degree of tension among the transit chains, the process of injection and stabilization of charges in the polymers, as well as by the increase of probability of releasing electrons from traps and their participation in the destruction process.

The release of electrons from the traps is connected with the agitation of various types of molecular movements in the polymers. However, the mechanism of molecular movements (which may be considered a relaxation process) in crystalline and amorphous polymers is defined by the character of their above-molecular organization [2]. Practically, all properties of polymer dielectrics, including their durability, are defined not only by the molecular structure but also by the disposition of macromolecule segments, and their agitation by the peculiarities of AMS.

The aim of this work is to investigate the influence of AMS, the changes of temperature dependencies of electrical longevity wait time τ_E and mechanical longevity $\tau_{\sigma E}$ under the influence of strong electric field on the polymer dielectrics.

2. Material and Methods

Polypropylene (PP) and the polyethylene (PE) films have been chosen for this investigation. The reason for choosing those films was that these polymers are easily and widely varied in terms of size and form and, thus, elements of AMS over the temperature-time regime of crystallization. PP and PE initially were in the shape of granules. Molpen brand isostactic PP was chosen for the investigation. This particular PP has mean molecular mass M=2x10^5, softening temperature T_P=463 K and a fluidity index (also known as a melt index) MI=0.70 g/10 min. For PE, obtained via use of MgAlTi catalysts, T_p=443 K, M=44x10^3 and MI=4.0 g/10 min. The thickness of films obtained by hot pressing varied from 40-200 μm. The PP and PE melts were cooled with speeds 2 K/min and 2000 K/min, respectively. After 10-15 minutes, the PP and PE films with diameter 50 mm were manufactured by pressing between two polished sheets of aluminum foil with thickness of 15 μm at temperature 463 K and 443 K, respectively, and pressure 0.015 GPa. Two regimes of crystallization were chosen, both common in this type of structural research [3-4]: rapidly cooling of PP and PE melts at about 2000 K/min by way of putting it in contact with aluminum foil in ice-water; and slowly cooling to 273 K with average speed of 2 K/min.

The sizes of above-molecular formations (AMF) and relaxation transitions of obtained samples were determined. The optical investigation was carried out by the help of a metallographic microscope of the type “MIM-7” in polarized light. It is elucidated that rapidly cooled formations of PP and PE are optically transparent, i.e. composite spherolite formations are very small, 3 -5 μm, and for slowly cooled formations well formed radial spherolites with sizes about 100-150 μm may be seen.

Taking into account of the above, it is necessary to determine which formations, i.e. rapidly cooled (small spherolites, SS) or slowly cooled (large spherolites, LS) samples, accumulate the larger amount of charge during application of an electric field.

The charges were accumulated during a charging event by the application of an electirc field on the polymer dielectrics. The charges were then excited by temperature, causing them to be released and recombined, with radiation being to result of the recombination. The phenomenon is known as thermoilluminescence [5]. In this thermoillumination method, the polymers were applied the electric field of tension E $\geq 10^7$ V/m at 77 K during 15 min.

3. Results

Figure 1 shows the thermoillumination curve for LS and SS samples of PP. In the thermoluminescence curve, one can clearly observe two maximums of illumination, which occured at the end of recombination of the electrons released with relaxation phenomena in the polymer's ions. It should be noted that the intensity of thermoillumination in the LS sample was noticeably higher than the intensity of thermoillumination in the SS samples. The maximums in the curve show the intensity of illumination versis temperature depend on the molecular mobility, i.e. the relaxation process in PP [6]. This shows that for a definite value of applied electric field, LS PP was stabilized with more electrons than SS PP. The reason for this stabilization is that the charges in the LS samples were released at lower temperatures than the charges in the SS samples.

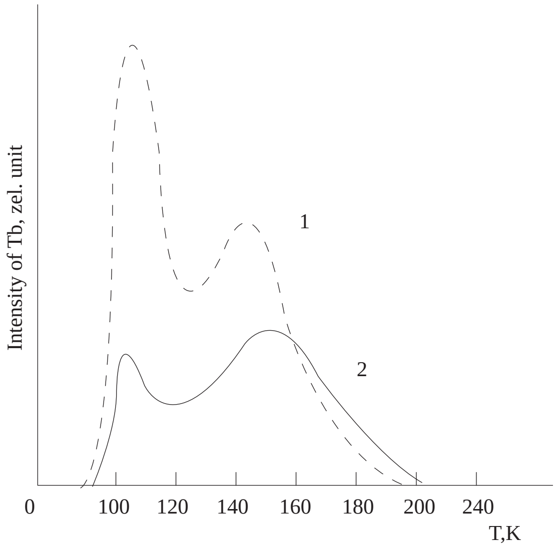

Figure 1. Thermoillustration curves for PP with various AMS,1-LS 2- SS samples.

LS samples accumulated more charge than SS samples. Because the dependencies of density of charges in the tension of polarization $E_n$was determined as a constant of time and temperature of polarization (t_n, T_n), which was given in the Figure 2, one can see that under the same conditions (constant E_n, t_n, T_n) more charge in the LS samples accumulated than in the SS samples.

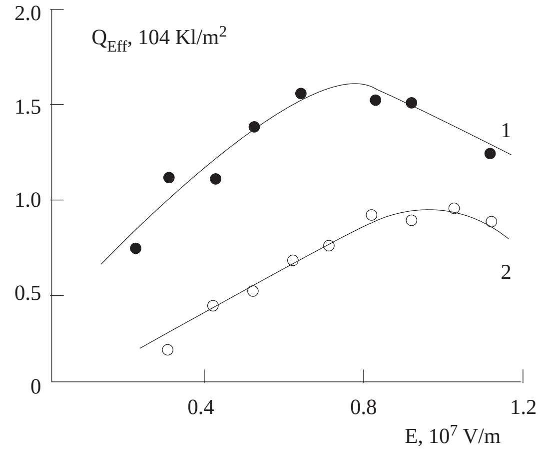

Figure 2. Accumulated charge density in 1- LS and 2- SS samples as a function of polarization intensity.

In this study, the longevity of polymer dielectrics has been compared with the longevity of polymer dispersions for the same values of applied electric field and temperature [7]. In this way, measurement of τ was carried out on 20-30 AMS samples for the same values of E and T. The temperature had values between 83 K and 300 K.

In Figure 3, one can see how temperature affects the longevity wait time, lg τ_E, of LS (1) and SS (2) PP in E= constant. Note the maximums and minimums τ_E. As the second, it can be obtained the regular regions in PP by the effect of longevity tension E and electric field: τ_E in the LS is noticeably lesser than in SS PP. It may further be noted that the minimums and maximums in the relaxation transitions of LS PP compared with the relaxation transitions of SS PP appear at lower temperatures, and the decrease of τ_E in the relaxation translations of LS PP are noticeably more than the decrease it in the relaxation translations of SS PP in the same temperature intervals.

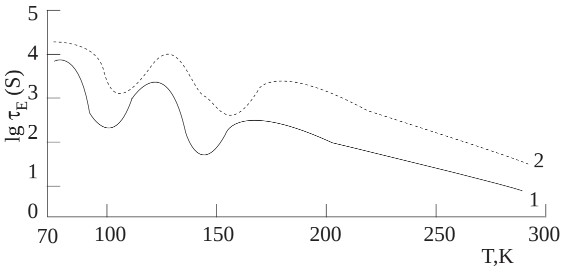

Figure 3. lg τ_E PP for various AMS in constant E as a function of temperature.
1. LS.sample, E=0,06. 10^8 V/m, 2- SS sample, E=0,8.10^8V/m.

Comparison of results in Figures 1 and 3 show that the temperature intervals of minimums of lg τ_E (Fig. 3) practically correspond with the temperature intervals of maximums in the thermoluminescence curve (Fig. 1) obtained for PP with various AMS. The coincidence of maximums of thermoillumination of PP with various AMS with minimums of its longevity wait time indicates a relation between the release of electrons from the traps and the electrical destruction of PP in high temperature interval.

Figure 4 shows the dependence of lg τ_E obtained for PE with various AMS as a function of temperature, and it can be observed that the minimums correspond to thermoilluminating maximums [8]. In both the case of PP and PE the temperature intervals of relaxation transitions of LS samples appear at low temperatures, as the in the SS samples. In Figure 5 it is shown that the logarithm of mechanical longevity lg $\tau_{\sigma E}$ of PE with various AMS in applied strong electric field depend on the temperature.

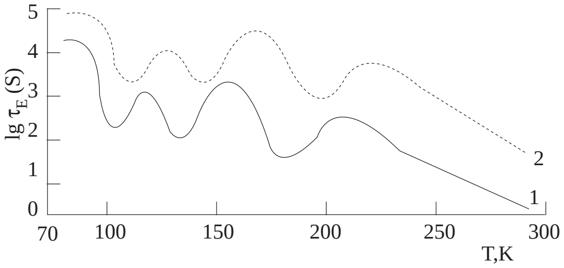

Figure 4. lg τ_E PE for various AMS in constant E as a function of temperature.
1- LS sample, E=0,6. 10^8 V/m, 2- SS sample, E=1,0.10^8V/m.

Note that the temperature intervals between the minimums of lg $\tau_{\sigma E}$ (Fig. 5) practically coincide with the temperature intervals between the minimums of lg τ_E(Fig. 4) and these temperature intervals between the minimums both in the case of lg τ_E=f(T) and in the case of lg $\tau_{\sigma E}$=f(T) coincide with the temperature intervals between the maximums of thermoillumination of the PE films [7-9].

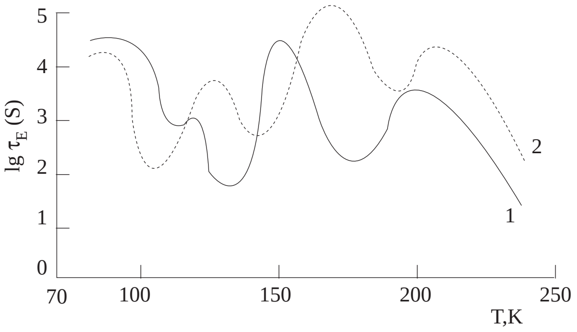

Figure 5. lg $\tau_{\sigma E}$ PE for various AMS in field E=3.10^7V/m as a function of temperature for samples: 1- LS sample, σ=0,050 GPa, 2- SS sample, σ=0,070 GPa.

4. Discussion

According to these experimental results it can be concluded that the main reason of changing (decrease) of the electrical and mechanical longevity of polymers in strong electric field and mechanical tension is the changing of polymer's molecular state due to acceleration of the electrons released from various traps in relaxation transitions [7-9].

A model for the reduction of mechanical durability in strong electric field and electrical durability in mechanical tension has been suggested [9]. Under the model, the spherolite-bearing polymers may be used with the transit and the tension relations and they can be increased under the influence of not great mechanical tension in collisions of the charged particles. With this, it is also shown that there are zones where the local tension of electric field is higher than average and, consequently, there are areas where the charged particles can be sped up. These areas are said to be tense-active. It may be supposed that in the LS samples there is greater probability of the existence of "tense-active" areas and subsequently, their longevity wait time is less than for the SS, PP and PE.

Heating of the various AMS, PP and PE, at the definite temperatures the molecular movements are transfered to the charges being released from traps and provided by the free charges defreezing in traps. A part of charges recombines and forms the maximums of illumination (Fig.1). But other part of them is accelerated by the field and takes part in electrical and mechanical destruction of polymer in strong electric field. We suppose that the charges are released as a result of molecular movements defreezing in spherolite-bearing samples in relatively low temperatures. The polymers, connected to each other with Van Der Waals forces, have very long length macromolecular structure. The decreasing of activation energy simplifies the destruction of polymer. Therefore, the temperature dependencies of τ_E and $\tau_{\sigma E}$ in the LS samples in comparison with the SS samples the removal of relaxation transitions to the side of low temperatures noticeable.

The above molecular structure (AMS) depends on the formation of various structural defects and on the degree of tension among transit chains. In addition to this, AMS increases with rising of destruction of the polymers by appling strong electrical field and strong mechanical field. The increasing of AMS affects on the injection and the stabilization processes of charges, on the relaxation and on the electronic-ionic processes. The intensity of these processes determines the durability properties of polymers at low temperature. For this reason, the reducting of $\tau_{E\sigma}$ and $\tau_{\sigma E}$ with the temperature in the relaxation transitions of the LS samples are more than in the relaxation transitions of the SS samples. The relaxation transitions appear at lower temperatures in the LS samples than in the SS samples.

References

[1] M. A. Kurbanov, S. A. Abasov, T. M. Veliyev, Izvestia Akad. Nauk. Azerb. SSR, ser. phys.-techn. I mat. nauk, **3** (1986) 97.

[2] I. I. Perepechko, Properties of polymers in low temperatures, Chemistry, (Moscow, 1977).

[3] B. Vunderlikh, The physics of macromolecules, Mir, (Moscow, 1976).

[4] A. D. Yakovlev, Technology the manufacturing of articles of plasmasses, Chemistry, (Leningrad, 1977).

[5] V. G. Nicolskiy, N. A. Mironov, Factory labrotary, **10** (1973) 1972.

[6] V. G. Nicolskiy, L. Y. Zlatkevich, L. A. Otsinsova, M. B. Kostantinopolskaya, High molec. comb. **16 (A)** (1974) 2755.

[7] S. N. Koykov, A. N. Tsikin, The electrical aging of solid dielectrics, Energy, (Leningrad, 1968).

[8] S. A. Abasov, M. A. Kurbanov, T. M. Veliyev, The physics of solid body, **24** (1982) 693.

[9] M. A. Kurbanov, S. A. Abasov, T. M. Veliyev, High molec. comb. **25 (A)**, (1983), 721.