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Molecular mobility research in polyethylene composite films

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Abstract. α-relaxation in composite films of low-density polyethylene with soot particles was investigated through thermostimulated depolarisation and differential scanning calorimetry. It is shown that the joint application of these methods can be used to determine the number of relaxers involved in the relaxation processes of a polymer above its glass transition temperature. The parameters and the number of electrically active defects in composite polyethylene films filled with different percentages of technical carbon are calculated.

Keywords: polyethylene composite films, thermal activation spectroscopy, differential scanning calorimetry, relaxation, electrically active defects

Introduction

High-pressure polyethylene (LDPE) plates of 11503-070 (GOST 16337-77) with a density of 0.92 g/cm^3 were used as research objects. The polymer was mixed with the filler on laboratory microrolls at a temperature of 135 ± 5 °C with a mixing time of 3 min. The 0.2 mm thickness plates were prepared according to GOST 12019-66 at a temperature of 170 ± 5 °C with pressure hold time of 5 min.

Technical carbon (soot) was used as a filler. Radiographic investigation of soot particles has shown that they are composed of separate, small-sized, graphite-like crystalline cells. Carbon atom location in the layer is the same as in graphite, while the distance between the layers is greater than in graphite crystals. The locations of the ends of parallel layers on the surface show an increase in energy and, consequently, greater adsorption capacity (Shevchenko 2010).

As shown in (Alekhina et al. 2019; Boriev et al. 2019; Gorokhovatsky et al. 2020), polyethylene films demonstrate multiple relaxations, referred to as α-, β- and γ-in order of decreasing temperature of their observation. There is an α relaxation in the area of 60 °C, which is considered the most complex relaxation and involves at least two mechanisms of molecular mobility. One of them is the beginning of rotational movement inside the crystal, and the other is the sliding of grains' borders between layers, i. e., the shift of chains to half of the primitive cell along the molecular axis (Bharadwaj, Boyd 2001).

In the area −60 °C ÷ −30 °C, β-relaxation is observed in polyethylene, which is associated with glass transition of the polymer. γ-relaxation at a temperature of about −120 °C is usually attributed to a sufficiently localised molecular motion in the polymer chains (Beatty, Karasz 1979). It should be noted that the intensity of the α transition in polyethylene is usually much lower than the intensity of the transition in the field of glass transition. It was recorded in the temperature range of 10–120 °C, depending on sample preparation and measurement techniques. The temperature T_α, at which the α-transition occurs, correlates with the degree of crystallinity of the sample (Ashcraft, Boyd 1976). However, it was shown that this temperature primarily depends on average crystallite thickness (Alberola et al. 1990; Popli et al. 1984). The dependence of T_α on crystallite thickness is expressed particularly strongly in the range from 50 to 200 °C; with thicknesses exceeding the given one changes in the transition temperature are relatively small (Popli et al. 1984). This relationship is illustrated in Fig. 1.

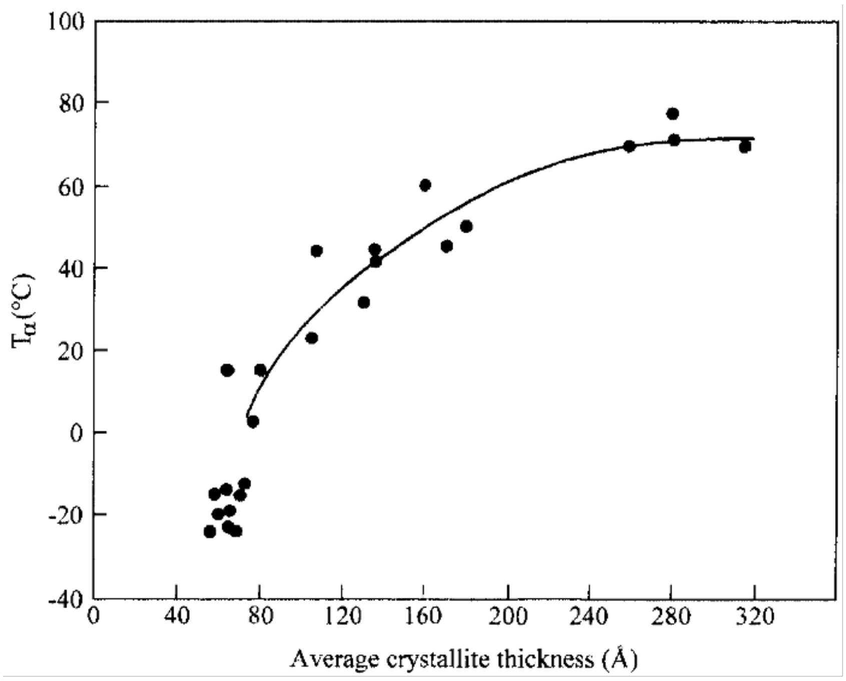

Fig. 1. The dependence of the temperature of α-relaxation in polyethylene from the average crystallite thickness (Popli et al. 1984)

In this paper, α-relaxation in low density polyethylene was investigated with thermostimulated depolarisation and differential scanning calorimetry.

Experimental results and discussion

For the study of electrical relaxation processes in polymeric materials, the methods of thermoactivational current or charge spectroscopy are widely used. This choice is explained by high data yield (high sensitivity and resolution) and ease of technical implementation and experimental data processing.

However, in many cases, e. g., near glass transition temperatures and mechanical relaxations of polymers, the use of traditional methods of experimental results processing for thermal activation spectroscopy leads to abnormally high values of activation energy of E_a electrically active defects (EAD) participating in the relaxation process and unrealistic relaxation time values less than 10^{-20} seconds (Shabanova, Temnov 2021). This is due to the fact that in this case the relaxation process involves the cooperative movement of molecular chain segments, and the precise determination of the activation energy of one relaxer requires taking into account the change in the free volume of the polymer during the relaxation transition.

There is an empirical analysis method, based on an equation of activated Eyring states, that is commonly used for such situations and that may give more physically realistic EAD parameters (Bucci et al. 1966). In this case, the following equation in used:

$$\tau(T)=\frac{h}{kT}\exp\left(\frac{\Delta H}{RT}\right)\exp\left(-\frac{\Delta S}{R}\right). \tag{1}$$

where k is Boltzmann's constant, h is Plank's constant, and ΔH, ΔS are the enthalpy of the activated states end the entropy and free energy, respectively. It follows that the construction of a graph corresponding to equation (1) in Arrhenius coordinates ln(1/τT) ~ 1/T makes it possible to calculate the enthalpy and the entropy, and only then the activation energy:

$$E_a=\Delta H-T\Delta S \tag{2}$$

and τ_0. Relaxation times$\tau(T)$ can be obtained from experimental spectra of TSC-TS (method of fractional purification) using the standard Bucci-Fieschi-Guidi method (Bucci et al. 1966).

Figs. 2–3 show the curves of the TSD in the temperature range of α-relaxation obtained for LDPE samples with 5% and 20% of technical carbon obtained with fractional purification (Shabanova, Temnov 2021).

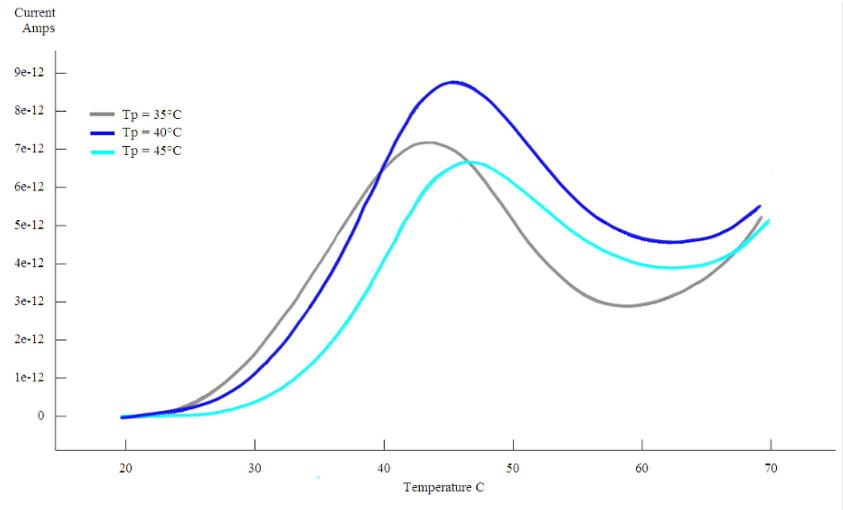

Fig. 2. TSC-TS curves for LDPE samples with 5% technical carbon

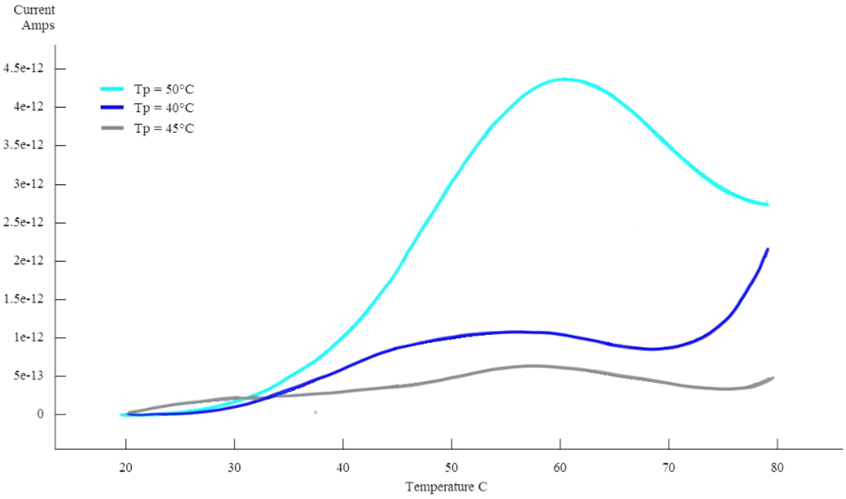

Fig. 3. TSC-TS curves for LDPE samples with 20% technical carbon

The graphs show that as the filler percentage increases, the maximum of the relaxation process shifts to the high temperature area by about 13–15 °C. According to (Popli et al. 1984), this may indicate some increase in the crystallite thickness while increasing the filler concentration.

The activation energy per EAD calculated on the basis of formula (2), taking into account the measurement error, was almost the same and equal to 0.94 ± 0.02 eV. However, the transition enthalpy ΔH for different filler concentrations differs significantly: it was 1.82 eV for 5% filler concentration and 0.87 eV for 20% concentration per relaxer.

Another quite popular method for testing α-transitions in polymers is differential scanning calorimetry. Many researchers investigate phenomena occurring in polymers above the glass transition temperature within the framework of kinetic representations, thermodynamics, fluctuation theory or free volume concept, which are not necessarily mutually exclusive (Berstein, Egorov 1990). With the DSC method, it is possible to determine the glass transition temperature, the width of the glass transition interval, as well as the activation energy of the transitions lying above the glass transition temperature calculated for a mass unit of the polymer.

The comparison of the data obtained for the α-relaxation of polyethylene by TSD and DSC methods makes it possible to determine the number of relaxers involved in this relaxation process.

Fig. 4 shows the DSC heating curves for LDPE samples with different technical carbon content.

In the range of 50–60 °C, a relaxation process is clearly observed, attributed to the α-relaxation of the LDPE. Experimental DSC data processing with dedicated Callisto software makes it possible to determine the change of enthalpy of this transition, indicated in Table 1.

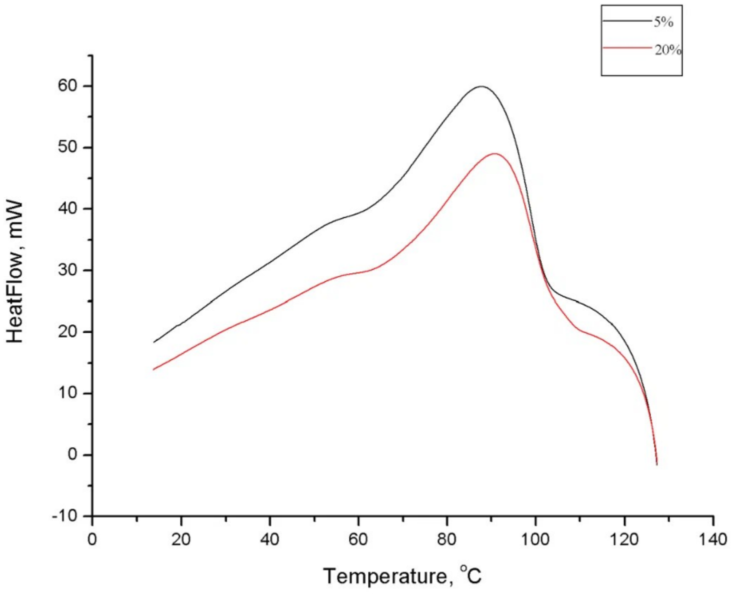

Fig. 4. DSC curves for LDPE samples with 5% and 20% of technical carbon

Table 1. Values of enthalpy changes for PEVD with different technical carbon content

Soot content (%)	Enthalpy change ΔH (J/g)	Number of relaxers (pc/g)
5%	−1.713	5.8 × 1018
20%	−1.601	1.1 × 1019

Taking into account the data obtained with TSD, the number of relaxers involved in relaxation was also determined. As the filler content increases, the number of relaxers increases significantly, which can be explained by the increase in the polymer's degree of crystallinity when the filler is applied and filler particles become the centres of crystallisation of the polymer matrix. Further research by independent methods is needed to accurately interpret the results.

Conclusion

The combined use of thermal activation spectroscopy and thermal analysis methods in polymer research makes it possible to obtain additional information on relaxation processes observed above the glass transition temperature. This paper shows that the increase in the filler content in polyethylene affects the parameters of the relaxation process: as the filler content increases, the crystallite thickness increases and the number of kinetic units involved in the relaxation process increases as well.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

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