CONCERNING THE STRENGTH AND FRACTURE OF THERMALLY AGED POLYCARBONATE

A. N. Machyulis, V. P. Korotkov, P. G. Konovalov, and M. I. Pugina

The change in the strength, fractography, and supermolecular structure of polycarbonate after thermal aging has been experimentally investigated. It is shown that the fall in the strength of the polycarbonate after aging (T ≤ 160°C) is chiefly related with the formation of dangerous defects as a result of the destruction of the supermolecular structure at the surface of the block. It is noted that under the same conditions there is some ordering of the supermolecular structure of the polycarbonate at depths of 150 μ or more, but this has practically no effect on the strength characteristics.

Polycarbonate (PC) is a promising structural material that is being increasingly employed in machine-building and instrument-making. However, like many other mass-produced plastics, the physicomechanical properties of PC are significantly affected by heat.

Our object was to determine the behavior of the strength of PC thermally aged at a temperature of 160°C and to study the fracture fractography and the characteristics of thermooxidative degradation in the presence of dynamic thermooxidation.

In these experiments we employed Diflon 1-2 PC with a molecular weight of 32,500. The specimens were obtained by injection molding at 100-105 MN/m², a molding temperature of 290-300°C, a mold temperature of 90-100°C, and a total molding cycle of 120 sec. The gauge dimensions of the specimens used for determining the breaking stress were 45 × 5 × 3 mm.

Derivatograms were recorded on a Paulik-Paulik-Erdelyi derivatograph. The structural investigation was carried out by means of an MBI-6 microscope.

It is known that in the case of PC thermally aged at temperatures not exceeding the glass transition point [1] the strength decreases only slightly, while in the event of extended storage (from two to four years) at room temperature the strength even increases, although the material is also embrittled [2].

In determining the tensile breaking stress (σB) of the thermally aged PC (aging temperature 160 ± 2°C, free access to air) we noted two phases in the fall of the breaking stress (Fig. 1). In the first phase the fall in strength is only slight, while in the second phase after 430 h aging σB is reduced by 50%. As the aging time increased, the PC became more brittle and the coefficient of variation of the strength increased from 6.5% for the starting PC to 18.5% after 430 hours of aging.

In order to determine the causes of such a considerable loss of strength we investigated the supermolecular structure (SMS) and fracture fractography of the PC (Fig. 2).
It was noticed that both at the surface of the block (see Fig. 2b) and at a depth of 150 μ (see Fig. 2c) or in even deeper layers, the SMS of the investigated PC consists of imperfect spherulites formed from fibrillar structures. The formation of imperfect supermolecular structures is attributable to the weak tendency of PC to crystallize, although it is known that when artificial structure-formers are introduced it is possible to obtain a structure with quite well-defined spherulites [3]. When the specimens investigated were thermally aged, the SMS on the surface of the block were completely destroyed with the formation of defects (see Fig. 2e), which are apparently important fracture centers that considerably reduce σ₁. In the presence of thermal aging the SMS at a depth of 150 μ (see Fig. 2f) or more continue to grow and become more ordered and very sharply defined. However, in brittle fracture, when there are defects at the surface of the specimen, their effect on the strength of the polymer block is not very important.

An analysis of the fracture fractography showed that both for the starting PC (see Fig. 2a) and for the aged PC (see Fig. 2d) both specular and rough fracture zones are observed. It should be noted that the first stage of fracture (specular zone), which is definitely known to be governed by a fluctuation mechanism, always begins at the surface of the aged specimens (see Fig. 2d) but may also start at the center of the untreated specimens (see Fig. 2a). This is evidently related with technological or structural factors.

An investigation of the thermooxidative failure of PC in the presence of dynamic heating showed it to be highly resistant. Intense thermooxidative degradation begins only at 380-400°C, but with further rise in temperature proceeds very rapidly, and at 500°C the entire specimen is completely destroyed (Fig. 3). In order to calculate the activation energy of the over-all thermooxidative degradation process (E) from the expression $E = -4.35 \frac{d \log \beta}{(d \log T)} \text{kcal/mole}$ [4], we obtained the dynamic thermogravimetric curves at various heating rates. It was established that both for the starting PC and for the aged PC E varies from 8 to 45 kcal/mole in the course of the degradation process. In this case no particular regularities in the behavior of E on the temperature interval 370-500°C were observed, except for the fact that the E for the starting PC varies less and has higher characteristics than that for the aged PC.