

Mechanical Properties of Polycarbonate Antiplasticized with a Charge-Transfer Complex

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Synopsis

Polymers doped with low-molecular-weight charge-transfer (CT) complexes exhibit interesting electrical and photoelectrical properties. On the basis of the results of thermally stimulated depolarization (TSD) for polycarbonate (PC) doped with tetracyanoethylene-*t*-stilbene complex and its components, some information about the mechanism of mutual interaction was obtained. The measurements of stress relaxation, mechanical moduli, and ultimate strength in a wide temperature range fully confirmed the predicted behavior of PCs doped with CT complex and its components. Doping the PC with CT complex and its components lowers the glass-transition temperature and increases the modulus in the range -60 to $+60^{\circ}\text{C}$. The effects of doping on the mechanical properties of PC are explained in terms of α - and β -relaxations.

Polymers doped with low-molecular-weight charge-transfer complexes (CT complexes) have been widely investigated in recent years because of their electrical and photoelectrical properties. We reported the results of thermally stimulated depolarization (TSD) measurements on bis-phenol-A-polycarbonate doped with the *t*-stilbene tetracyanoethylene (TCNE) CT complex.¹ The TSD of doped PC showed marked differences when compared with pure PC. The low-temperature TSD maximum due to carbonyl and phenyl group relaxation was shifted towards higher temperatures, whereas the glass-transition and α -relaxation temperatures shifted to lower temperatures. The effect was explained in terms of CT and electrostatic interactions between the molecules of the doping substances and the polymer chains. The complex of TCNE with phenylene groups of PC chains was concluded from an analysis of absorption spectra in the visible range. The nature of interactions between *t*-stilbene of *t*-stilbene/TCNE complex and polymer is difficult to prove directly, but an analysis of the changes of the TSD spectra leads to the conclusion that there are some electrostatic interactions, e.g., dipole-induced dipole with polar carbonyl groups of PC chains.¹

These interactions can lead to some "physical crosslinking" of the polymer, thus improving its mechanical properties in the low-temperature region (the effect of antiplasticization of the polymer). At higher temperatures these relatively weak bonds are broken, and the additive acting as a plasticizer lowers the T_g and α -relaxation temperature. Aoki and Brittain² used the TSD method and investigated the influence of annealing on the mechanical properties of PC. They observed that the decrease of the low-temperature maximum on TSD spectrum is connected with an increase in the sample strength. It has also been found³ that doping with TCNE causes an increase of the modulus of PC at room temperature.

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In order to confirm the conclusion drawn from TSD measurements that the influence of the investigated additives on the mechanical properties of PC is different at different temperatures, we carried out measurements of some mechanical properties of these systems in the temperature range -70 to 120°C .

EXPERIMENTAL

Bisphenol A polycarbonate provided by BDH Chemicals was used without further purification. Henceforth, by pure PC we mean PC without additives. The *t*-stilbene and TCNE were purified by crystallization and/or sublimation under vacuum. The doped film samples contained 10% of the complex or 4.2% of TCNE or 5.8% of *t*-stilbene, by weight respectively, making the molar ratio of each additive to polymer the same in each case. It was determined from spectrophotometric measurements that in the case of the films containing both *t*-stilbene and TCNE, only a fraction of the donor and acceptor molecules form CT complex *t*-stilbene/TCNE.^{1,4-6} It has been reported that some "free" TCNE molecules form a CT complex with a polymer.⁷⁻⁹ However, for the sake of simplicity, the term "PC doped with CT complex" is used throughout this paper.

The samples were 25–35 μm films obtained by casting the solution of the polymer and the additive from solvent (a 1:1 mixture of methylenechloride and ethylenechloride) on a glass substrate. The films were then dried at 65°C for 2 days in vacuum to remove the residue of the solvent. Films obtained in this way were transparent, and polarizing optical microscopy did not show any traces of crystallization or precipitation of the additives. The samples in the form of strips 6 \times 35 mm were used to determine the mechanical properties in an Instron Testing Machine equipped with a thermostated chamber permitting measurements in the temperature range from -70 to 300°C .

The modulus was measured every 10°C from -70 to 130°C for ten deformation cycles. The relative elongation, proceeding at the rate of 3%/min, was consistently smaller than 3% (the range of linear deformation). This method was chosen because of the observed changes of the modulus found for the successive cycles (see text below).

Stress relaxation experiments were carried out on strips 5 \times 10 mm at ambient temperature (23°C).

RESULTS AND DISCUSSION

It can be seen that at temperatures lower than $+60^{\circ}\text{C}$, all investigated doping substances increase the modulus of PC, i.e., they act as antiplasticizers. At higher temperatures the modulus of doped PC foils falls below that for pure PC. PC is, in all cases, plasticized in this temperature region (Fig. 1).

The addition of 10% *t*-stilbene/TCNE CT complex causes the highest increase of the modulus in the low-temperature region, with the strongest plasticizing effect occurring at temperatures higher than 60°C .

In contrast, a relatively weaker antiplasticization, due to the addition of 4.2% TCNE, can be observed until higher temperatures are reached. Plasticization occurs in this case at temperatures higher than 100°C . The dependence of the modulus on the *t*-stilbene TCNE content (at room temperature) is shown in

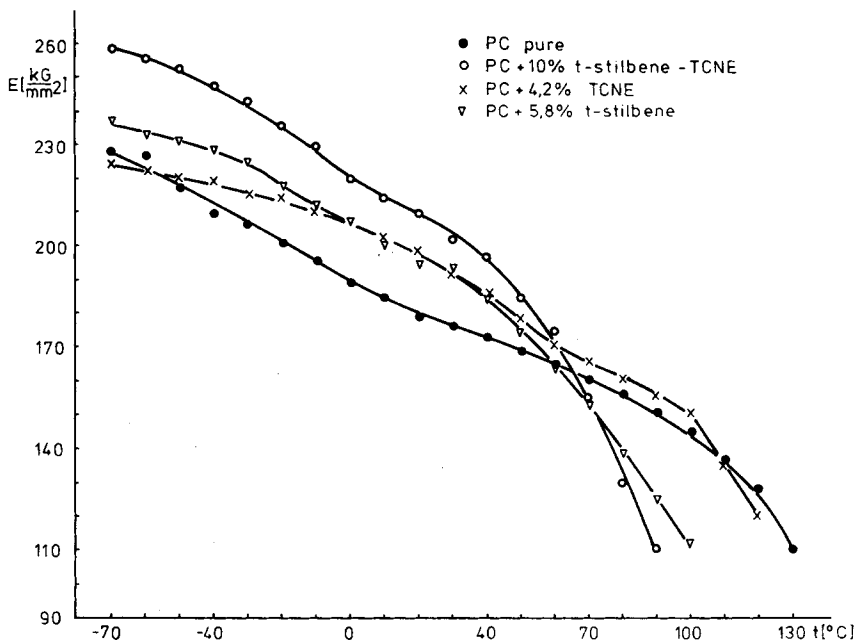


Fig. 1. Temperature dependence of the mechanical modulus of doped and pure PCs.

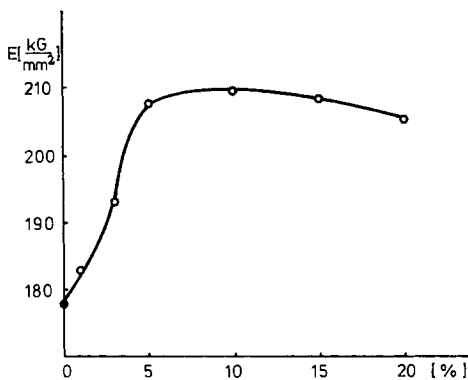


Fig. 2. The dependence of the modulus of the PC on *t*-stilbene/TCNE content.

Figure 2. It is noteworthy that the relatively high (15%–20%) increase of the modulus of PC takes place for the samples containing 5%–20% of the complex by weight.

When the sample was stretched, and relaxation was repeated many times, it was observed that the moduli from the successive cycles increased slightly up to a certain constant value.

Figure 3 presents the value of the modulus as a function of the cycle number for doped PC films at 30°C. At higher temperatures these changes did not occur. (Comparison curves for 60°C are also shown in Fig. 3).

Figure 4 presents the temperature dependence of the ultimate tensile strength of doped and pure PC. The changes in the ultimate tensile strength due to doping are of the same character as those of the modulus. The CT complex causes a larger *increase* in the tensile strength in the low-temperature region

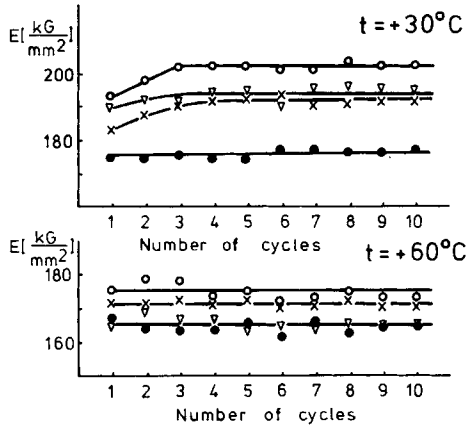


Fig. 3. Mechanical modulus of pure and doped PCs as a function of the cycle number. Indication of experimental points as in Figure 1.

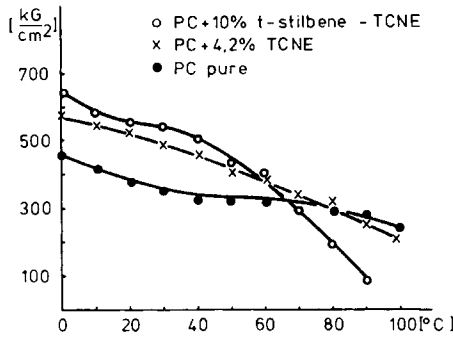


Fig. 4. Temperature dependence of the ultimate tensile strength of doped and pure PCs.

and a larger decrease in the high-temperature region with the additive TCNE.

Figure 5 presents the results of the stress-relaxation experiments. The stress

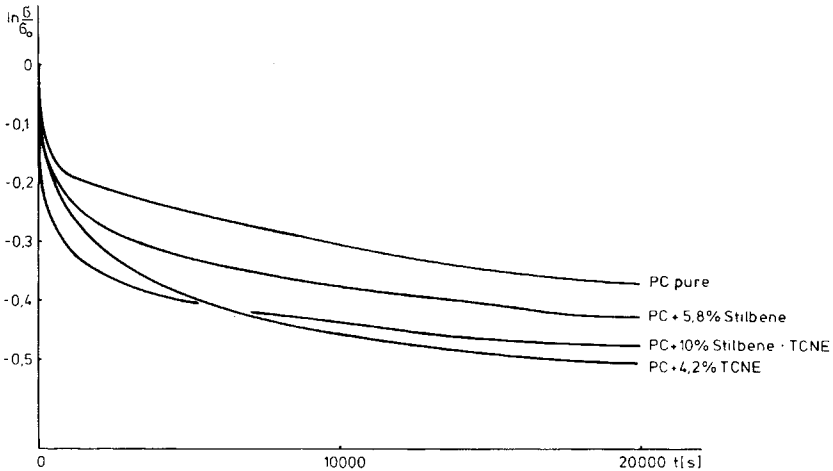


Fig. 5. The stress relaxation of doped and pure PCs at 23°C.

decay for doped PC is faster than for pure PC. Thus, the relaxation in the case of doped films is greatly determined by short relaxation times.

Assuming discrete distribution of relaxation times, the relaxation curve can be described by the eq. (1):

$$\frac{\sigma(t)}{\sigma_0} = \sum A_i \exp - \frac{t}{\tau_i^\gamma} \quad (1)$$

Hence the relaxation times can be determined from $\ln(\tau/\tau_0)$ vs t plot by extrapolation of the straight line corresponding to the long relaxation time. The relaxation times τ_i^γ are the reciprocals of the tangents of the slope of subsequent straight lines. The abscissa of the straight lines at $t = 0$ yields the log of the factor (A_i) of the given relaxation time.

The dielectric relaxation times should correspond to mechanical retardation times τ^σ when comparing the mechanical stress relaxation with dielectric relaxation.¹¹ The distribution of retardation times can be calculated if the distribution of mechanical relaxation times is known.¹² Relaxation times differ considerably in most cases. To obtain approximate values¹¹ we can use the following equation for the single relaxation time:

$$\tau^\sigma/\tau^\gamma = E_U/E_R \quad (2)$$

where E_U is the unrelaxed modulus and E_R is the relaxed modulus. We used the value for the modulus as the E_R found. In the case of the longest relaxation time, only the lower limit can be found. The retardation times found using this method and their factors (A) are listed in Table I. The sum of A is less than 100% because the method used does not make it possible to find the entire spectrum of τ^σ .

The parameters of the relaxation processes, obtained from the TSD experiments described in reference 1 are listed in Table II. Using the results of the partial heating experiments, the relaxation times τ_0 have been calculated using the maximum condition.¹³ The relaxation times at room temperature were calculated using the activation energy values.

The observed changes of the modulus and ultimate tensile strength of PC, brought about by doping with additives, confirm our former conclusions.¹ Both the *t*-stilbene/TCNE CT complex and its components have a plasticizing effect on PC in the high-temperature region and an antiplasticizing effect in the low-temperature region. The differences in the TSD spectra correspond to the changes in the mechanical properties of these systems. The sample of PC doped with 10% of the CT complex has the low-temperature TSD maximum shifted to the highest temperature. In mechanical properties it corresponds to the highest increase of the modulus and ultimate tensile strength in the low-tem-

TABLE I

PC		PC + 10% Stilbene/ TCNE		PC + 5.8% Stilbene		PC + 4.2% TCNE	
A (5)	τ_{23}^σ (sec)	A (%)	τ_{23}^σ (sec)	A (%)	τ_{23}^σ (sec)	A (%)	τ_{23}^σ (sec)
				5	8×10^1	5	7×10^1
5	6×10^2	20	7×10^2	8	9×10^2	10	9×10^2
7	2×10^4						
77	$>4 \times 10^5$	69	$>3 \times 10^5$	73	$>4 \times 10^5$	66	$>4 \times 10^5$

perature region. The high-temperature α -relaxation found for this sample shifted to the lowest temperatures, and the mechanical properties of these systems showed the strongest plasticizing effect of this additive in high-temperature regions.

The components of the complex have a slightly different effect on the properties of PC. The differences are most likely due to the different character of their interactions with the polymer matrix. The dipole-induced dipole interactions between the polarizable molecule of *t*-stilbene and the polar C=O groups in the polymer chain are weak but relatively long-range. Thus, the antiplasticizing effect of this compound at lower temperatures is stronger than that of TCNE. The CT interactions between the TCNE (strong electron acceptor) and phenyl rings in the polymer chain are stronger but short-range. Consequently, at high temperatures the thermal motions destroy the arrangement due to the interaction of *t*-stilbene with the polymer. The additive above +60°C already has a plasticizing effect. By "arrangement" we mean here only the proper orientation of C=O groups, and not of the larger segments of polymer chains. In the case of TCNE, the stronger CT interactions are more "temperature resistant" and therefore increase the modulus of PC up to +100°C.

In the lowest temperature region the addition of TCNE does not cause the increase in the modulus of PC (Fig. 1). At a temperature lower than ca. -100°C, all relaxation movements in pure PC (except methyl group rotations) are hindered. The effect on the mechanical properties of the system is similar to the effect of antiplasticizer, which stops the relaxation of some groups in polymer chains in the temperature range of its activity.

The modification of the properties of PC by the *t*-stilbene/TCNE complex is not a simple superposition of the effects of pure *t*-stilbene and TCNE. In the lowest temperature region (Fig. 1), significant modulus increase is caused by the complex addition, whereas the same effect produced by pure components is negligible. At room temperature, the complex causes a stronger modulus increase for the same content than does *t*-stilbene or TCNE (Figs. 1 and 2). The significance of CT interaction between *t*-stilbene and TCNE is also supported by the fact that pure TCNE in PC (in more than 6% w/w) crystallizes; whereas in the form of the complex with *t*-stilbene up to 30% (corresponding to 12% TCNE w/w), it does not crystallize.

The interesting effect presented in Figure 3 can be explained by some rearrangement of the polymer chains induced by stretching. A similar phenomenon was observed by Baer et al.¹⁴ while stretching collagen tendons. When stretched, the chain ordering is increased and the molecules alter their mutual position, thereby increasing the interactions. This results in the increase in modulus. The phenomenon can be observed at temperatures close to the β -relaxation temperature. This suggests that when the movements of smaller chain segments occur, the mutual position of the polymer chain and the molecules of the doping substance can be further altered by stretching. Movements of the larger chain segments are possible at higher temperatures, and the molecular arrangement is subjected to relaxation in the course of stress releasing. Hence, in this case the external forces have no additional effect. Consequently, no change of the modulus in the successive cycles is observed (Fig. 3).

Comparing the results of TSD and the mechanical relaxation experiment (Tables I and II), one can see the qualitative agreement of the results obtained.

No quantitative agreement should be expected, since in both cases the calculations are approximate. The relaxation of undoped PC is determined at room temperature mainly by long relaxation times. At this temperature the relaxation times related to the β -relaxation are very short ($10^{-1} + 10^{-2}$ sec, Table II); hence, relaxation takes place during the initial stretching. In the case of doped PC films, the β -relaxation times are relatively long (10^2 sec, Table II), and they can be observed in step-function experiments (Table I). Hence, the influence of short relaxation times on the relaxation in doped PC is much larger than in pure PC.

CONCLUSIONS

The results show that doping PC with suitable low-molecular-weight substances changes its mechanical properties. The increase in modulus and true tensile strength of the polymer was observed in the temperature range from -60 to $+60^\circ\text{C}$. The decrease in glass-transition temperature can also be advantageous from the point of view of processing.

It was also shown that the TSD technique can be a useful method of investigating molecular motions in polymers. Such measurements make it possible not only to predict the changes of mechanical properties of the polymers induced by doping with low-molecular-weight compounds, but also to draw conclusions about the molecular mechanism of the changes.

References

1. M. Kryszewski and J. Ulanski, *J. Appl. Polym. Sci., Polym. Symp.*, to appear.
2. Y. Aoki and J. O. Brittain, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 199 (1977).
3. L. Makaruk and H. Polanska, *Polimery*, **7**, 313 (1976).
4. M. Kryszewski and P. Wojciechowski, *Electrical Properties of Organic Solids*, Wroclaw, 1974, p. 350.
5. R. E. Merrifield and D. W. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).
6. C. E. Looney and J. R. Downing, *J. Am. Chem. Soc.*, **80**, 2850 (1958).
7. T. Sulzberg and R. J. Cotter, *Macromolecules*, **1**, 554 (1968).
8. T. Sulzberg and R. J. Cotter, *Macromolecules*, **2**, 146 (1969).
9. T. Sulzberg and R. J. Cotter, *Macromolecules*, **2**, 150 (1969).
10. J. M. Ward, *Mechanical Properties of Solid Polymers*, Wiley, London, 1971.
11. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967.
12. B. Gross, *Kolloid Z.*, **131**, 161 (1953).
13. C. Bucci and R. Fieschi, *Phys. Rev. Lett.*, **12**, 16 (1964).
14. S. Torp, R. G. C. Arridge, C. D. Armemiades, and E. Baer, *Proceedings of 1974 Colston Conferences*, Department of Physics, University of Bristol, U.K.

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