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DYNAMIC MECHANICAL THERMAL ANALYSIS OF POLYCARBONATE AND POLYESTER CARBONATE

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Dynamic mechanical behavior of polycarbonate has been compared with that of polyester carbonate. The nature of mechanical relaxations in these materials is discussed. The results indicate that the energy requirements for the motion of ester groups are not significantly different from those of the carbonate units.

Polycarbonate (bisphenol A carbonate) is a thermoplastic well-known for its impact strength. In the recent years, polyester carbonates (copolymer of bisphenol A carbonate and bisphenol A terephthalate) have been developed which offer improved properties such as superior heat distortion temperature, thermal aging characteristics, weatherability, solvent and abrasion resistance [1, 2]. Dynamic mechanical behavior of polycarbonate has been well described in the literature [3–5]. However, there are hardly any published data on the polyester carbonate as far as dynamic mechanical properties are concerned.

In the present manuscript we compare polycarbonate with polyester carbonate in terms of dynamic mechanical behavior.

Experimental

The polycarbonate used was a commercial sample. The polyester carbonate, CRL 42R (COPEC) was an experimental material made by Allied Corporation. The two materials were molded into sheets of about 0.125 cm thickness prior to characterization.

Dynamic mechanical analysis was carried out with a Polymer Laboratories DMTA unit attached to a Hewlett–Packard 9836 computer. A sample of approximately 4 cm length, 1 cm width and 0.125 cm thickness was used in the bending mode of deformation at a heating rate of 3 deg/min from – 150° to about + 200° under an argon atmosphere. All the experiments were carried out at a constant frequency of 1 Hz and a constant strain level ($< 1\%$).

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Infrared spectroscopy provided the chemical composition of the polyester carbonate sample. Bisphenol A: terephthalate ratio was obtained from a calibration curve of the 1770/1720 cm^{-1} absorbance ratio versus mole ratio of carbonate/ester [6].

Viscosity of the polyester carbonate was determined at 25° by dissolving it in a 60:40 solution of phenol and trichloroethane [6].

Results and discussion

The comparison of polycarbonate with the polyester carbonate in terms of temperature dependent dynamic storage modulus (E') and dynamic loss modulus (E'') is illustrated in Figures 1 and 2, respectively. A summary of the dynamic mechanical data is presented in Table 1.

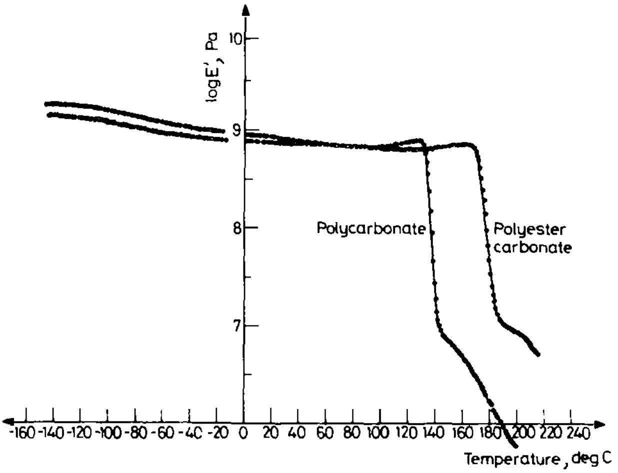
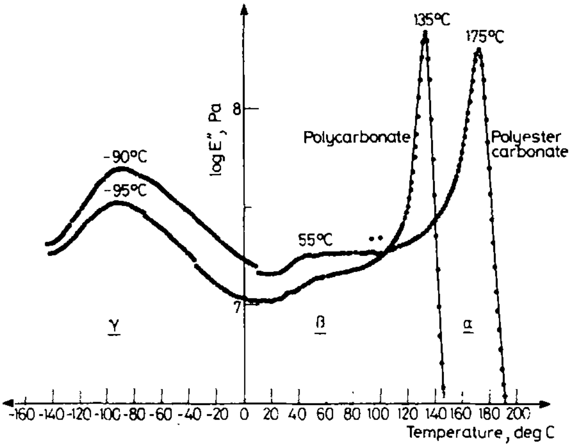


Fig. 1 Dynamic storage modulues (E') vs. termperature

Table 1 Dynamic mechanical analysis* of polycarbonate and polyester carbonate

Sample	log E'			log E''-relaxations			tan δ		
	− 100 °C	0 °C	+ 100 °C	γ–	β–	α–	− 100 °C	0 °C	+ 100 °C
Polycarbonate	9.10	8.95	8.92	− 92	85	140	0.036	0.027	0.035
	9.07	8.89	8.82	− 95	65	135	0.026	0.015	0.024
Polyester carbonate	9.12	8.87	8.74	− 92	70	180	0.023	0.018	0.024
	9.19	8.95	8.82	− 90	55	175	0.027	0.022	0.029

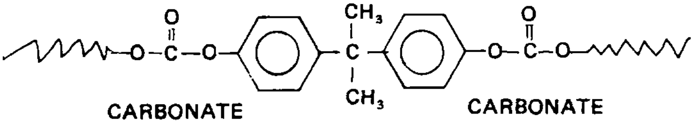
* Polymer Laboratories DMTA, 3 deg/min heating rate, argon atmosphere, 1 HZ frequency, constant strain, bending mode of deformation.



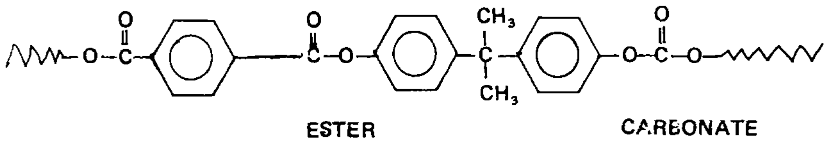
γ-peak temperature includes a correction of −10°C as per manufacturer

Fig. 2 Dynamic loss modulus (E'') vs. temperature

The structural units present in polycarbonate (a) and polyester carbonate (b) are shown below.



(a)



(b)

The polyester carbonate has a 2 : 1 ratio of bisphenol A/terephthalate which means that it can be regarded as a 1 : 1 copolymer of bisphenol A carbonate (i.e. polycarbonate) and bisphenol A terephthalate (polyester).

α-Relaxation

This is the most pronounced peak in both the polymers and is undoubtedly due to the large-scale segmental motion associated with the T_g. The α-peak occurs at 138° for the polycarbonate and at 178° for the polyester carbonate. The polyester carbonate has a higher T_g due to the presence of chain stiffening terephthaloyl moieties.

As shown in Figure 1, there is a slight increase in the elastic modulus E' prior to the T_g for both the polymers. For polycarbonate it has been suggested [7] that heat causes stiffening of the plastic and that the stiffening becomes quite rapid near the T_g.

One possible explanation is that at a lower heating rate (i.e. 3 deg/min) the polymers may undergo sub-T_g annealing [8] which has been known to densify the amorphous phase. Such a densification could increase the modulus prior to the T_g. However, further work would be needed before the possibility of an artifact can be ruled out.

β-Relaxation

It has been suggested [3] that the β-relaxation in polycarbonate involves motion of a short segment of the polymer chain. Also this relaxation has been reported to be very sensitive to thermal history [3]. We find the β-peak to be small, broad and poorly defined. This relaxation occurs at about 70±15° for both polymers.

γ-Relaxation

Recent studies [4] based on a systematic molecular substitution of polycarbonate conclude that motions of the phenylene units are involved in the γ-relaxation. It is further proposed that the motion of the phenyl rings cannot take place without concurrent motion of the interconnecting isopropylidene [$-C(CH_3)_2$] or carbonate ($>CO_3$) groups [4]. In other words, all sub-units of the monomer are responsible for the γ-relaxation.

In view of the asymmetric nature of the peak, it has also been suggested [3] that the γ-relaxation in polycarbonate is the result of three overlapping peaks γ_1, γ_2, and γ_3 each of which represents the motion of one or more sub-units of the monomer.

In the present study, the γ-peak occurs at about −90±5°. Since the polyester carbonate is not much different from polycarbonate in terms of structural units, it appears that the energy requirements for the motion of ester groups may not be significantly different from those of carbonate units. This is further supported by the similarity of the activation energy (ΔE) for the γ-relaxation which has been determined to be about 59 kJ/mol for both the polymers (Fig. 3).

The occurrence of a relatively large γ-relaxation at low temperature and its association with main-chain motion is cited as an explanation for the high impact strength of polycarbonate. The loss modulus (indicative of energy dissipation) at lower temperatures appears to be slightly higher for the polyester carbonate (Fig. 2) which is consistent with its slightly better impact strength [9]. For example, at −20° COPEC and polycarbonate have impact strengths of 6 and 3 ft.-lbs., respectively [9]. However, further work would be required to establish the correlation between the mechanical loss and impact strength data for these materials.

Conclusions

Except for the primary α-relaxation associated with the glass transition, there are no major differences in the dynamic mechanical properties of polycarbonate and polyester carbonate.

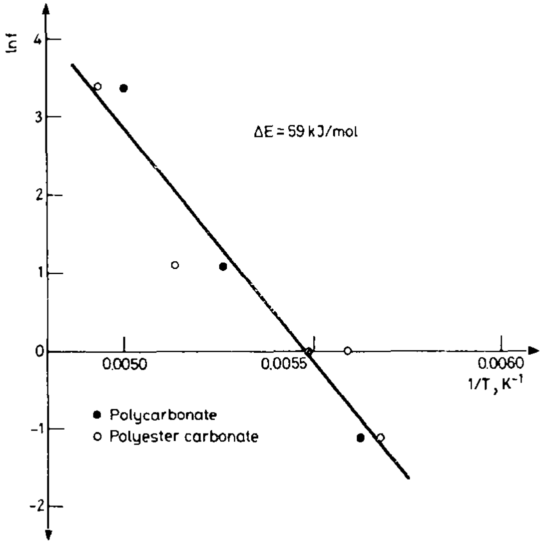


Fig. 3 Energy of activation (*ΔE*) for the γ-relaxation (frequancy *f*, dependence of the relaxation temperature, *T*)

The secondary β- and γ-relaxations, occur at 70±15° and −90±5°, respectively for polycarbonate as well as polyester carbonate. In polycarbonate β- and γ-peaks are known to represent motions of a short segment and of all the sub-units of the monomer, respectively. In view of the similarity of the secondary relaxations in polycarbonate and polyester carbonate, it appears that the energy requirements for the motion of ester groups may not be significantly different from those of the carbonate units.

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Zusammenfassung — Das dynamisch-mechanische Verhalten von Polykarbonaten wurde mit dem von Polyesterkarbonaten verglichen. Die Natur der mechanischen Relaxationen in diesen Materialien wird diskutiert. Die Ergebnisse zeigen, daß der Energiebedarf für die Bewegung der Estergruppen nicht signifikant verschieden von dem für die Karbonatgruppe ist.

Резюме — Проведено сравнение динамического механического поведения поликарбоната и полиэфирного карбоната, а также обсуждена природа механических релаксаций в этих материалах. Результаты исследований показали, что энергия, необходимая для перемещения сложноэфирных групп, мало отличается от таковой для карбонатных звеньев.