

## **The Effect of Physical Crosslinking on Dynamic Mechanical Properties of Polycarbonate Low Molecular Weight Additive Systems**

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### Summary

The studies of dynamic mechanical properties (torsional pendulum) of polycarbonate-low molecular weight additive (ester derivatives of Bisphenol A and di-butyl phthalate) systems show that the decrease of their glass transition temperature depends on the nature of the additive. The effect is greater for additives acting as plasticizers at room temperature as compared to antiplasticizers.

### Introduction

The addition of low molecular weight (l.m.w.) compound to polymer in a given conditions of temperature and concentration may cause two apparently different phenomena, namely plasticization and stiffening (antiplasticization). It was shown that those two phenomena are closely related. The same l.m.w. substance can soften or stiffen polymer depending on temperature and its content in the system (MAKARUK 1974; MAKARUK, RETKO 1975). In both cases the decrease of the glass transition temperature of polymer - l.m.w. additive composition is observed. The relaxation behaviour of such systems is quite complex. The  $\alpha$ -dispersion, corresponding to the glass transition, shifts to a lower temperature as the plasticizer content increases. The  $\beta$ -dispersion is usually completely suppressed by the presence of small amount of plasticizer. In some cases a new dispersion (labeled as  $\gamma$ ) not observed in both, neither pure polymer, nor pure additive, appears in these mixed systems (e.g. LEDNICKÝ, JANÁČEK 1971; ILLERS 1966; SHEN, CIRLIN 1970; KOLAŘÍK, JANÁČEK 1967). According to KINJO and NAKAGAWA (1973 a, b) the suppressing effect on the  $\beta$ -dispersion scarcely depends upon the l.m.w. species (plasticizer). They observed the decrease of magnitude of  $\beta$ -dispersion and the shift of its maximum towards lower temperatures with the increase of plasticizer concentration in PVC. The  $\beta$ -dispersion almost disappears at 12.5 wt.% of plasticizer concentration (KINJO 1973, 1974) in each

system. On the contrary, the relaxation mechanism of the  $\alpha$ -dispersion is affected by the addition of plasticizer and depends upon the nature of the additive (KINJO and NAKAGAWA 1973a). It means, that for some l.m.w. additives, in addition to the shift of  $\alpha$ -dispersion maximum towards the lower temperature, the change of the curve shape is also observed. It seems that the diverse effect of l.m.w. additives on the mechanical properties of polymers (plasticization - antiplasticization), might be fairly well understood from the viewpoint of the specific behaviour of the system in the  $\alpha$ -transition region.

The purpose of this work then is to study the influence of different l.m.w. additives on the relaxation behaviour of polycarbonate (PC) in the region of  $\alpha$ -transition.

### Experimental

Commercial Bisphenol A polycarbonate Makrolon 3200 (Bayer, Germany) having a viscosity average m.w.  $\bar{M}_v \sim 30,000$  and the following l.m.w. compounds were used in the investigations: 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2,2-trichloroethane diacetate (OCB III) and ester derivatives of Bisphenol A, i.e. 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane dibenzoate (BCD); 1,1-bis(4-hydroxy-3,5-dichlorophenyl)-2,2-propane di-2,4-dichlorobenzoate (CBCD). All the above listed l.m.w. compounds added to PC in a wide range of concentrations increase the tensile strength and tensile modulus and decrease the elongation at break of the systems, thus acting as antiplasticizers (MAKARUK et al. 1976, 1979). For the comparison di-n-butyl phthalate (FDB-n), a well known PC plasticizer (KOZLOV et al. 1962) has also been studied.

The film samples of PC containing the appropriate amount of l.m.w. additive were prepared from 5 wt.% solutions in methylene chloride in the manner described previously (MAKARUK, RETKO 1975). The measurements of the shear moduli ( $G'$ ,  $G''$ ) in the temperature range 20 to 160°C were carried out by the method of free damped torsional pendulum at frequencies 0.2 to 1 Hz using a strip shaped specimens ( $60 \times 10 \times 0.1 \text{ mm}^3$ ). The storage modulus  $G'$ , the loss shear modulus  $G''$  and the loss tangent were derived by the well known equations (SCHMIEDER, WOLF 1952, 1953).

### Results and discussion

Since both plasticizer and antiplasticizer added to polymer decrease its glass transition temperature ( $T_g$ ) it may be said, that their distinction can be made only with respect to the mechanical behaviour in the system. As it is well known, antiplasticizers increase the tensile strength and modulus and de-

crease the elongation at break of the polymer, while plasticizers reduce the brittleness of the material.

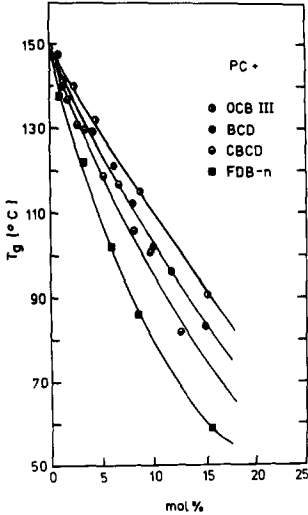


Fig.1.  $T_g$  of PC - l.m.w. additive compositions in relation to the molar concentration of the additive.

In Fig.1 the temperatures of  $\text{tg}\delta$  maximum of PC - l.m.w. compound systems, which correspond to  $T_g$ , are plotted versus the content of the additive. As it is seen, at the same molar concentration of l.m.w. substance the decrease of  $T_g$  of the system depends on the kind of the compound added. The data concerning the mechanical behaviour, namely an increase of the tensile modulus and tensile strength in respect to pure PC, as well as  $T_g$  of the same systems, are summarized in Table 1. The data indicate that incorporation of the same molar concentration of various l.m.w. compounds to PC decreases  $T_g$  of the system to different extent. The more effective additives (better antiplasticizers) lower  $T_g$  of the system to smaller degree, than those being very efficient

as plasticizers. As possible explanation of this fact

Table 1. Mechanical Properties of Polycarbonate - Additive Systems.

Additive	Additive Content mol %	wt %	Increase of the Tensile Strength %	Tg of the system °C	$\Delta T_g = T_g, c - T_g, PC$ °C
OCB III	12.5	23.2	34.5	92.2	48
BCD	12.5	24.4	33.2	10.4	56
CBCD	12.5	28.6	24.1	14.4	65
FDB-n	12.5	13.5	- a	- a	68

we consider that the stiffening of the polymers (anti-plasticization) should not be only connected with the mobility of the additive, but with the intermolecular

interactions in the system. As their magnitude depends on the polarity and the distances between the interacting molecules, the changes of the intermolecular interactions can be estimated from the measurements of the molar volume of the systems and the polarity of the additive molecules. Basing on such measurements it was shown that in the system consisting of polymer and antiplasticizer the stronger molecular interactions occur than in the composition where plasticization takes place (MAKARUK, POLANSKA and MIZERSKI 1979).

The different behaviour of l.m.w. additive in the mixture with PC can also be evaluated from the shape of loss modulus  $G''$  curve presented in Fig. 2. In PC plasticized with FDB-n the width and height of  $G''$  maximum are independent of the additive concentration. On the contrary, even small amount (4.8 wt%) of OCB III incorporated to PC causes broadening of loss maximum. For PC - BCD and PC - CBCD systems the additional suppression of  $G''$  curves can be observed. It seems that such a behaviour of mixtures is due to the restraining of the molecular motions of PC chains solvated by the molecules of additive containing the polar groups. This is in good agreement with our previous considerations on mechanism of antiplasticization, introducing the molecular concept of the phenomenon. According to this model, the so-called antiplasticizers are capable to interact simultaneously with two (or more) macromolecules, leading to a physical crosslinking of the system. Therefore, the molecular motions of PC chains should be restrained as compared to the system consisting of PC and plasticizer (MAKARUK 1974). The broadening of  $G''$  curves, observed in the case of antiplasticizers, can also be explained considering the variety of interactions between PC chains and additive molecules (for example PC - additive molecule - PC or PC - additive molecule) producing distribution of solvates. This affects the mechanism of viscoelastic relaxation and changes the width of the dispersion curves.

It should be also mentioned, that the broadening of  $G''$  curves for PC - antiplasticizer (OCB III, BCD, CBCD) systems depends on the additive concentration. That is, the  $\alpha$ -transition region widens at lower and becomes narrower at higher l.m.w. compound content in PC. The detailed description of the mechanical properties of all these systems were already published elsewhere (MAKARUK, POLANSKA and MIZERSKI 1979, MAKARUK et al. 1974). Taking into account this data, it can be shown that the lowest  $G''$  maximum corresponds to the composition exhibiting maximum tensile properties.

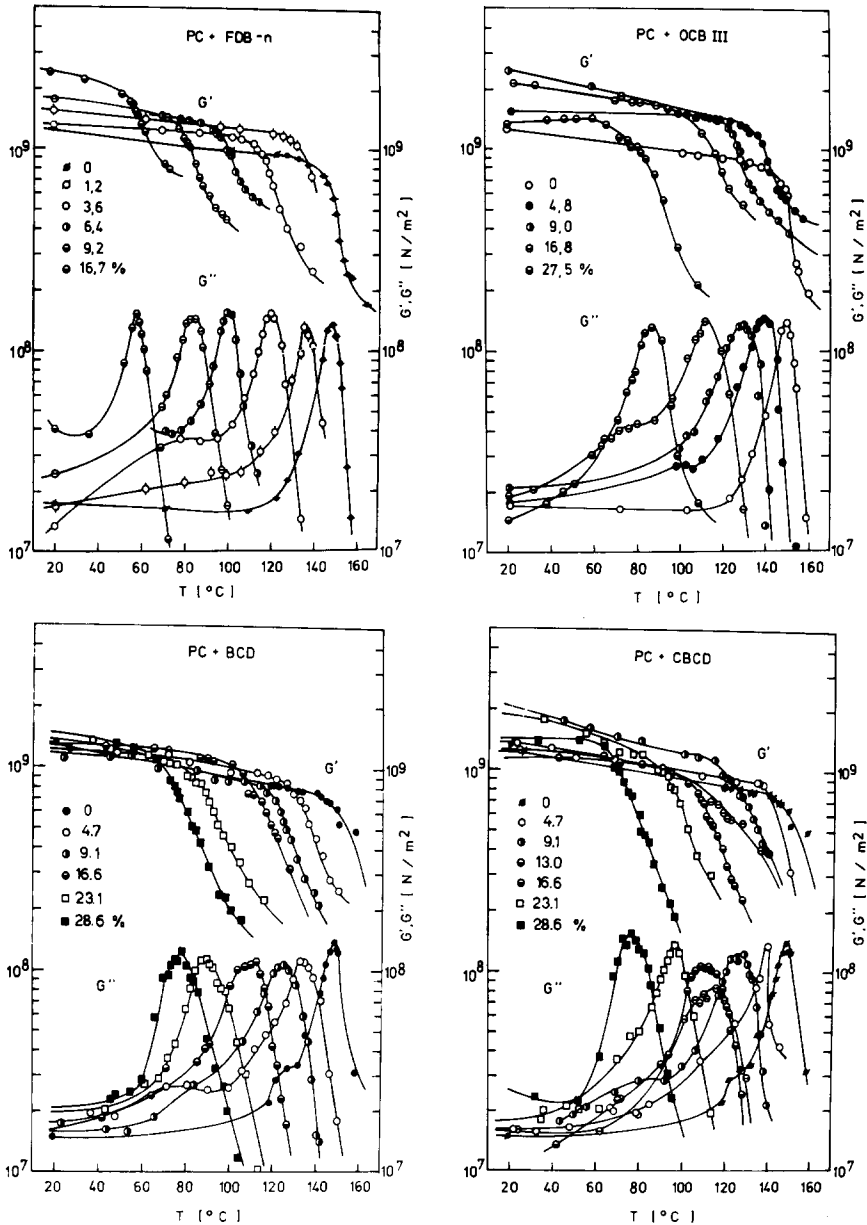


Fig.2. Temperature dependence of storage modulus  $G'$  and loss modulus  $G''$  for PC-FDB-n, PC-OCB III, PC-BCD and PC-CBCD systems. The numbers give the wt. concentrations of l.m.w. additives in the systems.

The dynamic mechanical behaviour of PC - l.m.w. additive systems in the glass transition region shows that the magnitude of the decrease of  $T_g$  and change of relaxation curves as well as mechanical properties depend upon the nature of l.m.w. compound. The pheno-

mena occurring in such systems can be fairly well understood assuming the physical crosslinking of polymer by incorporated additive.

### References

- ILLERS, K.H.: Ber.Bunsenges.Phys.Chem., 70, 353 (1966)  
 KINJO, N.: Japan Plastics 7, 6 (1973)  
 KINJO, N.: Japan Plastics 8, 6 (1974)  
 KINJO, N. and NAKAGAWA, T.: Polymer J. 4, 143 (1973a)  
 KINJO, N. and NAKAGAWA, T.: Polymer J. 5, 316 (1973b)  
 KOLAŘÍK, J. and JANÁČEK, J.: J.Polym.Sci., C16, 441 (1967)  
 KOZLOV, P.A., ASIMOVA, R.A. and PEREPELKIN, A.N.: Vysokomol.Sojed. 4, 124 (1962)  
 LEDNICKÝ, F. and JANÁČEK, J.: J.Macromol.Sci., Phys., B5, 335 (1971)  
 MAKARUK, L.: Mechanism of Antiplasticization of Polymers, Technical University of Warsaw Publication, Warsaw 1974  
 MAKARUK, L., CIPPERT, P., DOWBOR, M. and GRAD-KUMUNIECKA, Z.: Polimery 19, 190 (1974)  
 MAKARUK, L. and RETKO, I.: J.Polym.Sci., Part C, Symposium 53, 89 (1975)  
 MAKARUK, L., POLANSKA, H. and STAROS, E.: J.Appl.Polym.Sci., 20, 63 (1976)  
 MAKARUK, L., POLANSKA, H. and MIZERSKI, T.: J.Appl.Polym.Sci., 23, 1935 (1979)  
 SHEN, M. and CIRLIN, E.H.: J.Macromol.Sci., Phys., B4, 293 (1970)  
 SCHMIEDER, K. and WOLF, K.: Kolloid-Z., 127, 65 (1952)  
 SCHMIEDER, K. and WOLF, K.: Kolloid-Z., 134, 149 (1953)

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