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Modification of polycarbonate with miscible polyurethane elastomers

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Polyurethane elastomers (PUEs) based on 4,4′-diphenylmethane diisocyanate and aliphatic polycarbonate diols and/or polytetramethylene glycols have been found to be miscible with polycarbonate (PC). Incorporation of 0–10% of PUEs in melt mixing decreases the glass transition temperature of PC (by 0–30°C), facilitates its processing, and improves its resistance to hydrothermal ageing. No phase separation in blends was detected by means of the absorption of the visible light and differential scanning calorimetry measurements. Dynamic mechanical and static bending measurements concurrently show a slight increase in the glassy state modulus, which can be viewed as an 'antiplasticizing' effect of PUEs in PC. This effect and the miscibility of PC with PUEs can be ascribed to their strong interaction, probably due to the formation of hydrogen bonds between urethane and carbonate groups. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polycarbonate blends; polyurethane elastomers; hydrothermal ageing)

INTRODUCTION

Applications of polycarbonate (PC) in blends with other polymers are frequently impeded by a high processing temperature, at which other components may undergo thermal degradation[1,2]. Furthermore, frozen-in thermally induced stresses may cause the formation of surface microcracks[3-5] which markedly reduce the service life of products. The deficiency can be alleviated by means of covering PC surface with a protective polymer, which is rather impractical. However, these problems can be partly solved by blending PC with a miscible elastomer, decreasing the glass transition temperature (T_g) and the processing temperature. The choice of modifiers is limited whenever the PC transparency is to be preserved. In our first paper[6] on this subject, we modified PC with various elastomers synthesized from toluene diisocyanate and aliphatic poly(carbonate diol)s or poly(propylene glycol)s; 1,4-butanediol was used as a chain extender to prepare linear polyurethane elastomers (PUEs). We based our concept on the results of previous studies of miscible blends of PC with elastomers[7,8] and thermoplastics[9-11]. Our PUEs were miscible[6] with PC up to 20 wt% and decreased the T_g by about 30°C (at 10 wt% of PUEs in blends), which was considered suitable for the practical modification of processing and mechanical properties of transparent PC.

Another serious obstacle encountered in PC applications is the propensity of PC for hydrolysis[12], particularly at elevated temperatures (say, above 70°C). It was observed[2,13] that a long-term treatment (60 weeks, 70°C, 70% RH) might cause a decrease in molar mass by two orders of magnitude. The hydrolysis of carbonate groups is accelerated by bases, the effects of acids is minor. On the other hand, poly(ester urethanes) are prone to hydrolysis which is accelerated by the acids produced (autocatalytic reaction)[14,15]. In our previous papers[16,17] we demonstrated that thermal and mechanical (namely ultimate) properties of poly(ester urethanes) deteriorated very much within 8 weeks of the exposition in water at 70°C. To the authors' knowledge, the question of hydrothermal degradation of PC/PUE blends has not yet been studied.

With regard to our previous results[6], we have synthesized—utilizing the technique of prepolymers—polyurethane elastomers consisting of 4,4′-diphenylmethane diisocyanate and aliphatic poly(carbonate diol)s or poly(tetramethylene diol)s extended by 1,4-butanediol. Single-phase blends of PC/PUE are interesting for at least two reasons: (i) they are transparent; (ii) due to lower T_gs and melt processing temperatures (than PC itself), they can be mixed with other polymers, e.g. poly(styrene-*co*-acrylonitrile), poly(methyl methacrylate) etc., at lower processing temperatures so that their thermal degradation can be reduced. To study the miscibility of PC with PUEs, we have prepared several series of blends with 2.5, 5, and 10 wt% of PUEs. The blends were prepared via melt mixing in an extruder at about 235°C which was followed by injection moulding of test specimens. The objective of this study was to evaluate the effects of selected elastomers miscible with PC on the decrease in T_g, the transparency and hydrothermal ageing of PC/PUE blends.

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EXPERIMENTAL

Polyurethane elastomers were synthesized via prepolymers. In the first stage, an oligomer was prepared (of a molar mass between 1000 and 3000) by the reaction of two parts of the diisocyanate and one part of a diol:

$$2\ \mathrm{OCN{-}R{-}NCO} + \mathrm{HO{-}R'{-}OH} \rightarrow$$
$$\mathrm{OCN{-}R{-}NH{-}COO{-}R'{-}OOC{-}NH{-}R{-}NCO}$$

In the second stage, an extender was used to complete the reaction and to obtain an elastomer of suitable molar mass[18–20].

Materials

Diisocyanate. A commercial grade of 4,4′-diphenylmethane diisocyanate (MDI) was used in the form of chips which facilitated the necessary manipulation.

Diols. Two types of aliphatic diols were used, namely (i) polycarbonate diols[21,22] and (ii) polytetramethylene glycols. The species of commercial polycarbonate diols (trademark Ravecarb, abbreviated as Rcb, EniChem, Italy), formally represented by a general formula

$$\mathrm{HO{-}[(CH_2)_6{-}O{-}CO{-}O]_{\mathit{n}}{-}(CH_2)_6{-}OH}$$

are summarized in *Table 1*. The products are denoted according to their molar mass which was determined by the analysis of hydroxyl groups[23].

Poly(alkylene ethers) are widely used for the synthesis of PUEs on industrial scale. In our work we used four species (*Table 1*) of poly(tetramethylene glycols) of the general formula

$$\mathrm{H(O{-}CH_2{-}CH_2{-}CH_2{-}CH_2)_{\mathit{n}}{-}OH}$$

with different molecular mass, i.e. 1000 and 2000, having either 'standard' or 'narrower' (N) molar mass distribution. Commercial products available under the trademark Terathane (abbreviated as Ter, DuPont, USA) were used in the PUE synthesis. In comparison with other poly(ether glycols), Terathanes have relatively low density and toxicity. Also their low melting temperature and low viscosity facilitate their applications. Each polyol was carefully dried (3 h; 70°C; vacuum of 2 mbar) in order to decrease the water content below 0.2% (measured by the Fischer method[24]).

Extender. To prepare linear polymers, a short-chain extender 1,4-butanediol (BD) was used as a 25% solution in dimethyl formamide (DMF).

Catalyst. Dibutyl-tin-dilaurate[6] (DBTDL) was used as a 20% solution in DMF.

Solvent. DMF dried by molecular sieves was used for both the prepolymer synthesis and extending reactions. DMF was selected for these purposes because MDI products are not sufficiently soluble in ethyl acetate which we used in our previous work due to its low toxicity and low boiling temperature (78°C at which no cross-linked products are formed). The use of DMF required very cautious temperature control during synthesis in order to avoid side reactions.

Polycarbonate. A commercial product (EniChem Polimeri, Italy) of molar mass 20 000 (PC20100) based on bisphenol A was selected. Polymers without additives were available in the form of granules.

Preparation of prepolymers

Prepolymers of a general formula

$$\mathrm{OCN{-}[R{-}NH{-}CO{-}O{-}(polyether\ or\ polyester){-}}$$
$$\mathrm{O{-}OC{-}NH{-}R]{-}NCO}$$

with NCO end groups were prepared by reacting MDI (used as-received) with polyols (67 wt% solution in DMF). The NCO/OH molar ratio was 2.1/1 for Terathanes and 2.5/1 for Ravecarbs. The excess of diisocyanate (stoichiometry requires ratio 2/1) was necessary to obtain a prepolymer[11] terminated with NCO and to compensate for secondary reactions[20] (e.g. caused by traces of water).

The reaction was performed in a flask provided with a $CaCO_3$ valve to eliminate the access of air humidity. Polyol was dissolved in DMF (ratio polyol/DMF was 1/0.7); then MDI was added and the flask was placed in a 60°C oil bath. The reaction was completed within 90 min, which was confirmed by the analysis of unreacted NCO groups[25]. Thus prepolymers were prepared containing (i) polycarbonate diols or (ii) poly(tetramethylene diols) or (iii) 50/50 mixtures of polycarbonate diols and poly(tetramethylene diols).

Preparation of polyurethane elastomers

PUEs were synthesized by mixing a prepolymer with the extender (molar ratio 1.1/1), both in the form of solutions in DMF. The reaction, catalysed with 1–2 wt% of the DBTDL, lasted about 24 h at 60°C. During the reaction, some DMF was added to prevent an excessive rise of the viscosity and to guarantee effective mechanical

Table 1 Characteristics of polyols

Polyol	Trademark	Hydroxyl number	Average molar mass	T_g (°C)	T_{m1} (°C)	$H_{\mathrm{fusion\,1}}$ ($\mathrm{J\,g^{-1}}$)	T_{m2} (°C)	$H_{\mathrm{fusion\,2}}$ ($\mathrm{J\,g^{-1}}$)
Rcb750	Ravecarb 102	144.2	780	−62	21	7	48	49
Rcb1000	Ravecarb 104	112.2	1000	−64	22	14	49	46
Rcb2000	Ravecarb 106	51.9	2160	−50	24	6	55	56
Rcb3000	Ravecarb 108	38.1	2950	−42	25	5	57	58
Ter1000	Terathane 1000	112–118[a]	1000	n.d.[b]	26	37	37	64
Ter1000N	Terathane 1000N	107–117[a]	1000	n.d.[b]	27	22	37	89
Ter2000	Terathane 2000	53–59[a]	2000	n.d.[b]	20	5	43	122
Ter2000N	Terathane 2000N	53–59[a]	2000	n.d.[b]	21	11	40	106

[a] As declared by the producer

[b] Not detectable

stirring of the reagents. After the completion of the reaction, the product viscosity was reduced (if necessary) by a suitable amount of DMF in order that polymer films might be cast at room temperature on a silicone foil in a vacuum stove (to evaporate the solvent at 70°C for 48 h). The thickness of prepared films was between 0.1 and 0.3 mm.

The rest of PUE solutions were evaporated for 2 weeks at 70°C to prepare bulk samples of PUEs for blending with PC. Bulky specimens were cut into pieces and treated under a pressure of about 100 mbar for at least 2 days until a constant weight of the product was achieved (no mass loss was detected below 200°C during thermogravimetric analysis, t.g.a.).

Preparation of polycarbonate/polyurethane blends

Melt blending of PC with PUE was implemented in a Banderino extruder (Bandera, Italy) at 235°C with a screw rate of 50 rpm; length to diameter ratio was $L/D = 40$. Before blending, PC and PUEs were dried at 120 and 35°C (under vacuum), respectively, for 3 h to prevent hydrolysis at processing temperatures. Test specimens were prepared by injection moulding (Negri e Bossi) at 290°C with a mould temperature of 70°C. The length and width of specimens were 126.5 mm and 12.7 mm, respectively; the thickness was 1.5 mm (for dynamic mechanical thermal analysis (d.m.t.a), flexural modulus, and hydrothermal ageing) and 3.2 mm (for single edge notch bending tests).

Methods

Differential scanning calorimetry. The differential scanning calorimetry (d.s.c.) test was carried out with a Mettler DSC 30: temperature range -100 to 200°C; heating rate: 10°C min^{-1}; specimen weight about 20 mg; nitrogen flux 100 ml min^{-1}. The T_g was determined as the temperature corresponding to the inflection point on the heating curve by means of a built-in program Graphware TA72. The melting temperature (if any), T_m, corresponded to the location of the melting peak on the temperature scale and the heat of fusion, H_{fusion}, was evaluated by integrating the peak. All the polyols showed two different melting peaks.

Thermogravimetric analysis. T.g.a. was carried out using the Mettler MT5 thermobalance combined with the stove, Mettler TG 50. The tests were conducted using about 10 mg specimens in the interval 20–600°C with a heating rate of 10°C min^{-1} and a nitrogen flow of 100 ml min^{-1}.

Absorption of visible light. The absorption in the visible region in the range 350–800 nm was measured at room temperature by means of a spectrometer Spectronic 1201 (Bausch & Lomb, New York, USA) on 3.2 mm thick specimens. The absorbance, expressed in cm^{-1}, was determined for the wavelengths 800, 700, 600, 500, and 400 nm (no absorption peak was observed) by using air as the reference medium.

Gel permeation chromatography. Gel permeation chromatography (g.p.c.) was executed with the aid of an apparatus consisting of an isocratic pump (Spectra Physics, P1500), refraction index detector (Shodex R171) and a chromatography column (Shodex KD 80M). Analyses were carried out at 1 ml min^{-1}; the calibration was performed with polystyrene standards having molar masses in the range from 5000 to 400 000. All samples were dissolved in DMF (the concentration of polymers was about 0.25 wt%) and then were characterized by weighed average molar mass, M_w, and polydispersity (the ratio of weight and number average molar masses).

Dynamic mechanical thermal analysis. D.m.t.a. was performed by using a PL-DMTA MkII instrument of Polymer Laboratories (Loughborough, UK). Bending storage modulus (E') and loss modulus (E'') were measured in the temperature interval -100°C to 180°C at a heating rate of 3°C min^{-1}, a frequency of 1 Hz and displacement of 0.064 mm. A single cantilever was found suitable for rigid PC/PUE specimens (12.7×12 mm $\times$ 1.5 mm), whereas PUE films were measured in double cantilever. The values of T_g were read off as the temperatures of the peak of the loss modulus. However, this temperature is 15–20°C higher than the T_g determined by means of volumetric methods[26–28].

Stress–strain measurements. Tensile tests were implemented for PUE films by using Instron Tester 4502 dynamometer. The dimensions of specimens used were 90 mm × 5 mm × 0.1 mm, the strain rate was 10% min^{-1}.

Three-point bend testing. Unnotched specimens of PC/PUE blends were used to determine flexural modulus, while notched specimens were tested to measure the brittle/ductile behaviour of the blends. The cross section of test specimens was 12.6 mm × 3.2 mm. The distance between supports was 100 mm for bending modulus and 50 mm for bending fracture. Cross head speed was equal in both tests, i.e. 5 mm min^{-1}. Specimens for single edge notch bending fracture (SENB) were obtained by introducing (by a fly cutter) and edge notch with a depth to width ratio $a/W = 0.5$ and with a tip radius of about 15 m. As aged PC/PUE blends were semiductile, the fracture energy was evaluated as the area below the force–displacement curve (up to 3.5 mm of the displacement).

Density of the polymer, D, was measured at 20°C as average value on at least three specimens according to ASTM[29].

Hydrothermal treatment. Test specimens were placed in a water bath (about 20 litres; 70°C) steadily circulated with the aid of a propeller. After the selected period of ageing (1 or 2 weeks), the specimens were taken out, dried at room conditions, and desiccated in a vacuum oven for 2 days at 60°C.

RESULTS AND DISCUSSION

Polyurethane elastomers

Cast films were employed to evaluate the T_g, mass loss up to 300 or 400°C, and some mechanical properties (*Table 2*). In all series, i.e. PUEs with (i) Ravecarb, (ii) Terathane, and (iii) mixtures Ravecarb/Terathane = 50/50, a decrease in T_g was observed with increasing molar mass of polyols. This trend is obviously associated with both decreasing polarity and rising

Table 2 T_g (d.s.c.), mass losses with the temperature of the highest degradation rate determined from a derivative of the t.g.a. thermogram (T_{peak}), and mechanical properties at 20°C of some polyurethane elastomers

Polyurethane elastomers	T_g (°C)	Mass loss at 300°C (%)	Mass loss at 400°C (%)	T_{peak} (°C)	Tensile modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
PU Rcb750	14	3.6	73.5	345	–	–	–
PU Rcb1000	2	2.7	73.0	350	8.2	6.0	439
PU Rcb2000	–24	3.1	80.1	357	–	–	–
PU Rcb3000	–30	2.9	89.3	359	–	–	–
PU Ter1000	–47	3.7	48.4	341	2.9	3.0	384
PU Ter1000N	–40	3.5	51.2	341	–	–	–
PU Ter2000	–65	2.1	61.7	378	–	–	–
PU Ter2000N	–61	3.0	44.7	397	–	–	–
PU Rcb1000Ter1000	–18	3.1	60.7	341	–	–	–
PU Rcb1000Ter1000N	–13	2.9	61.0	343	–	–	–
PU Rcb1000Ter2000	–38	7.3	61.5	336	14.3	14.2	431
PU Rcb1000Ter2000N	–28	4.0	65.8	350	8.5	24.9	502
PU Rcb2000Ter2000	–40	5.4	67.1	350	5.0	11.9	590
PU Rcb2000Ter2000N	–38	3.3	61.4	348	–	–	–

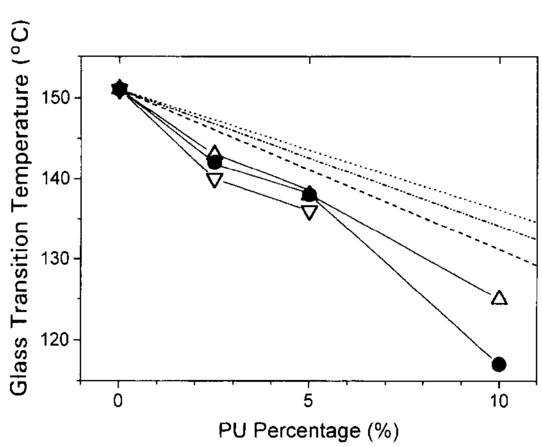

Figure 1 T_gs of PC/PUE blends determined by d.s.c. related to theoretical values calculated from the linear Gordon–Taylor equation: (△) experimental and (····) theoretical value of PC/PU-Rcb; (●) experimental and (-···-) theoretical value of PC/PU-RcbTer; (▽) experimental and (- - - -) theoretical value of PC/PU-Ter

flexibility of polyol chains. Besides, molar mass distribution of polyols is manifested by a somewhat higher T_g. A likely reason for the increase is that a reduction of the fraction of the short chains is accompanied by an appreciable decrease in the concentration of chain ends which generally introduce an additional free volume in polymers[26]. Stress–strain measurements (*Table 2*) document low modulus and high strain-at-break of PUEs which are typical of rubbery materials.

Though the t.g.a. tests encompassed the interval 20–600°C, the thermal stability of PUEs was evaluated according to the mass losses in the interval 20–300°C because the processing temperatures of PC blends are below 300°C. Most PUEs are characterized by mass losses in the interval 3–4% so that no significant difference between PU Rcb and PU Ter can be observed (*Table 2*). However, Ter with 'narrower' molar mass distribution impart appreciably better thermal stability to PUEs than counterparts with 'standard' molar mass distribution. Some combinations of Rcb and Ter are not useful because the highest mass losses 7.3 and 5.4 wt% were found for the mixtures Rcb1000Ter2000 and Rcb2000Ter2000, respectively. Comparing the mass losses at 300 and 400°C we can see that the decomposition at temperatures above 300°C is much faster. Taking into account thermal stability, T_g and blend processing, the following PUEs were selected for blending with PC: (i) PU Rcb1000; (ii) PU Ter1000; (iii) PU Rcb1000-Ter1000. These PUEs, identified as PU-Rcb, Pu-Ter and PU-RcbTer, have very similar weight average molar mass (147 000, 149 000, 140 000, respectively) and polydispersity (4.4, 4.3, 4.1, respectively).

Blends of polycarbonate with polyurethane elastomers

Blending of PC with rubbery PU significantly lowers its T_g and affects its mechanical properties. Thermal and dynamic mechanical analyses reveal only one glass transition in any of the prepared blends. This result does not unambiguously prove a single-phase character of the blends because a small amount of an immiscible component (say, less than 10%) can be hardly detected as the second glass transition. However, the decrease in T_g equal to 15 or 30°C achieved by 5 or 10% of a PUE evidences the miscibility of PC with PUEs. The T_g values, corresponding to the inflection point in the d.s.c. thermograms (not shown), or to the peaks of loss modulus in d.m.t.a. analysis are reported in *Figure 1* and *Table 3*, respectively. In particular, T_gs measured by d.s.c. showed a negative deviation from a linear Gordon–Taylor type[30] equation

$$T_{gB} = T_{gPC} W_{PC} + T_{gPUE} W_{PUE} \qquad (1)$$

which relates the T_gs of the blends, T_{gB}, to those of the neat polycarbonate and polyurethane, T_{gPC} (151°C) and T_{gPUE} (see *Table 2*) through their weight fraction, W. The lower the glass transition of PUE and the higher its percentage, the lower the T_g of the blend and the higher the deviation from the additivity rule. Similar results have been obtained from both loss (E'') and storage moduli (E') of PC blend, calculating the T_g as the maximum of E'' or the extrapolated onset of the drop of E', respectively. T_g measured by d.m.t.a. showed a

Table 3 T_gs determined by d.m.t.a. and storage bending modulus of PC blends prepared by extrusion and injection moulding

	T_g		Storage bending modulus		
Polymer blends	break E' (°C)	max E'' (°C)	at 20°C (GPa)	at 50°C (GPa)	at 70°C (GPa)
PC 100%	131.6	137.3	2.21	2.04	1.89
PU-Rcb 2.5%	117.7	125.9	2.44	2.26	2.09
PU-Rcb 5%	108.6	116.0	2.49	2.32	2.14
PU-Rcb 10%	96.9	105.8	2.59	2.39	2.16
PU-Rcb 100%[a]	−11.0	0.6	0.30	0.09	0.04
PU-Ter 2.5%	119.6	126.4	2.33	2.16	2.00
PU-Ter 5%	108.6	116.4	2.33	2.17	2.02
PU-Ter 100%[a]	−52.7	−42.3	0.11	0.05	0.02
PU-RcbTer 2.5%	123.8	132.7	2.23	2.10	1.95
PU-RcbTer 5%	109.5	117.5	2.63	2.46	2.26
PU-RcbTer 10%	87.3	101.5	2.40	2.22	2.00
PU-RcbTer 100%[a]	−36.5	−20.5	0.06	0.04	0.01

[a] Specimen of $2 \times 10 \times 0.2\,\text{mm}^3$

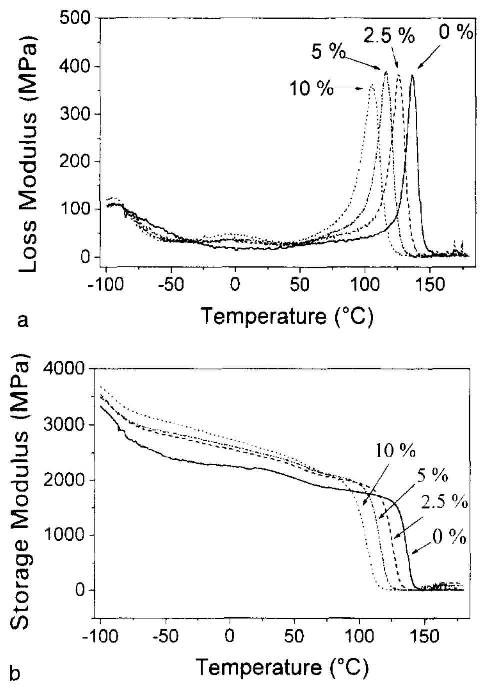

Figure 2 The effect of the PU-Rcb mass fraction on the temperature dependences of (a) loss modulus and of (b) storage modulus of the blends with PC

slightly higher negative deviation from additivity than that derived from d.s.c. analysis.

The effect of blending on the thermomechanical behaviour of PC with PU-Rcb is shown in *Figure 2*. The beta peak at −95°C of PC remained unchanged for all the materials, whereas in the range −50/ + 50°C a slightly higher loss modulus was found for the blends; consequently, due to a higher molecular mobility it is possible to expect some increase in the fracture energy. In the glass transition region, the loss modulus exhibits a peak which shifts to lower temperatures and becomes broader as the PUE percentage increases. The width of loss modulus peak measured at half height, i.e. $E''_{max}/2$, is 10.2°C for the neat polycarbonate and 27.6, 27.8 and 33.5°C for PU-Rcb, PU-Ter and PU-RcbTer, respectively. On the other hand PC-PUE blends exhibited intermediate values with a positive deviation from additivity, as reported in *Figure 3*. The higher the percentage of elastomer, the broader the peak and the higher the deviation. This effect increases in the sequence PU-Rcb, PU-RcbTer, PU-Ter, i.e. becomes more pronounced for PUEs with lower T_g. Obviously, the order in this sequence is given by chemical similarity between PC and PUEs. These results are in agreement with a previous paper[31], revealing that the loss peak is sensible to blending effect, and showing that PU materials derived from a mixture of different polyols or prepolymers were found to exhibit a broader peak than those derived from a single polyol or prepolymer.

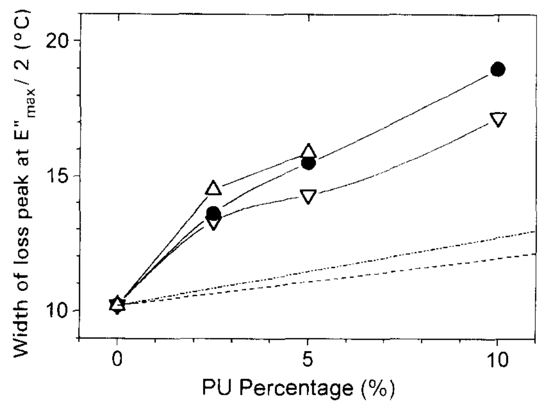

Figure 3 Width of loss modulus peak of PC/PUE blends as function of PUE concentration: (△) experimental and (····) theoretical value of PC/PU-Rcb; (●) experimental and (-·-) theoretical value of PC/PU-RcbTer; (▽) experimental and (- - -) theoretical value of PC/PU-Ter

Somewhat lower values of T_gs detected in d.m.t.a. at 1 Hz can be related to a lower heating rate in d.m.t.a. than in d.s.c., as previously reported for methacrylic polymers[27,32]. We believe that the achieved decrease in T_g can appreciably facilitate the processing of PC blends in the molten state and reduce the hazard of their thermal degradation.

A complete miscibility of PUEs (in the range 0–5%) with PC was proved by means of the absorption of visible light (*Table 4*). Though all PUEs augment the absorption, the blends preserve the transparency. The absorbance of the pure PUE, A_{PUE}, can be calculated as

Table 4 Absorbance of PC/PUE blends related to the thickness of 1 cm at different wavelengths

Polymer blends	400 nm	500 nm	600 nm	700 nm	800 nm
PC 100%	0.44	0.37	0.34	0.31	0.31
PU-Rcb 2.5%	0.95	0.59	0.48	0.40	0.36
PU-Rcb 5%	1.40	0.76	0.62	0.48	0.39
PU-Rcb 10%	5.80	3.22	2.10	1.53	1.20
PU-Ter 2.5%	0.65	0.41	0.36	0.30	0.28
PU-Ter 5%	0.98	0.44	0.40	0.30	0.28
PU-RcbTer 2.5%	0.80	0.56	0.46	0.38	0.36
PU-RcbTer 5%	1.02	0.54	0.46	0.39	0.36
PU-RcbTer 10%	2.08	1.25	1.00	0.85	0.85

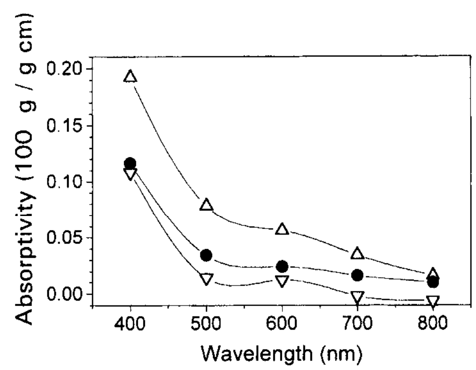

Figure 4 Absorptivity of the various PUEs, i.e. PU-Rcb (△), PU-RcbTer (●) and PU-Ter (▽), as functions of the wavelength (see text for further explanation)

difference between the absorbance of the blend, $A_{PC/PUE}$, and the absorbance of the PC, A_{PC}. The corresponding absorptivity, E_{PUE}, is derived from the Lambert–Beer law and is expressed in c^{-1} cm^{-1}.

$$A_{PUE} = A_{PC/PUE} - A_{PC} = E_{PUE} c l \qquad (2)$$

where c is the concentration in g PUE per 100 g blend and l is the path length through the sample in centimetres[33]. Equation (2) fits very well data up to 5% of PUEs and the resulting absorptivities at the various wavelengths are reported in *Figure 4*. As can be seen, the absorption rises with decreasing wavelength almost linearly, so that no maximum is observed. PU-Ter shows the lowest values of absorption, while the values for the mixtures PUTer/PURcb can be found inside the interval delimited by those of PU-Ter and PU-Rcb. Experimental absorbance of PUE at concentration of 10% is higher than that predicted by additivity, and this result can be attributed to the validity limit of the Lambert–Beer law. The experimental limits of the miscibility of PC with synthesized PUEs were not studied because a higher volume fraction of PUEs in PC would obviously cause an excessive drop in the T_g of the blends which may adversely affect their dimensional stability at the temperatures of ordinary applications.

D.m.t.a. patterns (*Figure 2b*) show that added PUEs increase the blend modulus at temperatures below T_g. If T_g (detected by d.m.t.a.) is high enough, say above 40°C, the increase in modulus with the PUE percentage can be observed even at room temperature, which is documented not only by dynamic (*Table 3*) but also by static tests (*Table 5*), despite the fact that the T_g of the system decreases. A similar result was observed also in our previous work[6], where the storage modulus of PC was increased due to the addition of PUEs based on polycarbonate diols, polypropylene glycols and toluene diisocyanate. Such effects, which are usually regarded as 'antiplasticization' phenomena[34], were firstly found by Jackson and Caldwell in polycarbonate based on BPA (bis-phenolA), where elasticity modulus and yield/break strength increased after the introduction of compatible aromatic substances containing polar atoms (halogen, nitrogen, oxygen, sulfur), such as for instance chlorinated biphenyl (Aroclor) or poly(styrene glycol)[35,36]. Similarly enough, BPA polycarbonate 'antiplasticized' with 30% of Aroclor showed a lower loss factor, and a higher shear modulus G' as well as tensile yield strength[37]. In the case of addition of low molar mass substances, the increase in modulus of the glassy polymers can also be interpreted as a reduction of the molecular mobility of the polymer in the glassy state[38,39]. Moreover, reduction of secondary relaxation and the consequent increase in modulus were found for miscible polymer/polymer blend[40]. In fact a small amount of polystyrene (up to 10%) added to poly(xylenyl ether)

Table 5 Bending modulus (GPa) of PC/PUE blends

Polymer blends	Initial[a]	1 Day	4 Days	10 Days	20 Days
PC 100%	2.54 ± 0.02	2.63 ± 0.08	2.62 ± 0.04	2.64 ± 0.03	2.66 ± 0.01
PU-Rcb 2.5%	2.77 ± 0.04	2.86 ± 0.04	2.74 ± 0.01	2.84 ± 0.01	2.82 ± 0.02
PU-Rcb 2.5%	3.1 ± 0.4	2.7 ± 0.3	2.8 ± 0.3	2.8 ± 0.2	2.9 ± 0.3
PU-Ter 2.5%	2.83 ± 0.02	2.70 ± 0.03	2.73 ± 0.01	2.78 ± 0.01	2.74 ± 0.04
PU-Ter 5%	3.15 ± 0.02	2.78 ± 0.04	2.74 ± 0.01	3.04 ± 0.04	3.08 ± 0.02
PU-RcbTer 2.5%	2.82 ± 0.03	2.54 ± 0.08	2.62 ± 0.04	2.73 ± 0.06	3.0 ± 0.1
PU-RcbTer 5%	3.14 ± 0.07	2.88 ± 0.08	2.83 ± 0.07	2.8 ± 0.1	2.88 ± 0.01

[a] The values at time zero refer to dry samples

increases its modulus and reduces its losses at low temperatures. Modulus at room temperature and shear yield strength showed a positive deviation[41] from the additivity rule

$$E_B = E_1F_1 + E_2F_2 \qquad (3)$$

where E_B, E_1 and E_2 are the modulus of the blend and of the two components, and F_1 and F_2 their weight fractions, respectively. As the blend showed an additive crazing resistance[42], Kambour interpreted the phenomenon as a consequence of negative heat and volume of mixing in the system[43].

In our case, all experimental values of storage modulus below T_g (*Table 3*) showed a positive deviation from the additivity rule (equation (3)). The data acquired show that there is no significant difference in the effectivity of synthesized PUEs as far as T_g and the room temperature modulus of the PC/PUE blends are concerned. The authors believe that the miscibility of PC with synthesized PUEs as well as the 'antiplasticizing' effect of PUEs can be assigned to strong interaction between the groups of constituents, most likely due to formation of hydrogen bonds between urethane and carbonate groups[44–47]. In order to verify this strong interaction and the consequent free volume reduction, density measurements of polymers and blends were performed at 20°C. PUE elastomers showed density of 1.180 ± 0.003 (PU-Rcb), 1.148 ± 0.004 (PU-RcbTer) and 1.115 ± 0.003 (PU-Ter), much lower than PC ($1.2000 \pm 0.0002\,\mathrm{g\,cm^{-3}}$). The density of PC blends (measured with an error of $\pm 0.0005\,\mathrm{g\,cm^{-3}}$) exhibited a positive deviation from the additivity (*Figure 5*). Obviously, the higher the percentage of PUE, the higher the deviation. Thus, a quite good correlation can be found between the excessive storage modulus and the excessive density of the blend (*Figure 6*). From these findings, it results that the lower the T_g of a blend (up to 10% of PUE), the higher the chain mobility, the larger the interaction between urethane and carbonate groups, and hence the higher the density and the modulus.

Hydrothermal ageing of PC/PUE blends

Table 6 shows that the time dependence of water sorption and its values after 20 days are not markedly affected by the type and fraction (2.5 or 5%) of PUE in PC. It can only be said that somewhat higher initial sorption rate is observed for the blends containing PU-Ter. The water sorption after 20 days reaches 3–5% for all the blends studied. The following d.s.c. analysis of redried specimens proved (*Table 7*) that T_gs were not noticeably influenced by hydrothermal treatment. However, our previous results[17,48] reveal that T_g shows only limited sensitivity to changes in molar mass produced during hydrolytic degradation.

On the other hand, the adopted hydrothermal treatment produces a significant drop in the M_w of PC as documented from the g.p.c. results (*Table 7*). In order to compare the hydrolysis kinetics of different polymers at each time, t, it is helpful to introduce the degradation rate R_d expressed in days^{-1} and defined as

$$R_d = -\mathrm{d}[M_w(t)]/\mathrm{d}t \times 100/[M_w(t)] \qquad (4)$$

where $M_w(t)$ is the best fit function of experimental molar mass, and $\mathrm{d}[M_w(t)]/\mathrm{d}t$ is the corresponding derivative[49]. R_d formally represents the daily molar mass reduction in percentage. *Figure 7* displays well the different behaviour of the materials: the initial hydrolysis rate of the blends containing 2.5 or 5 wt% of PUEs (ranging from about 2.5 to 5 days^{-1}), is much smaller than that of the neat PC (38 days^{-1}). However after 1 week, polycarbonate shows a significant reduction of hydrolysis rate, whereas the blends based on RcbTer-PUEs increase their degradation rate, reaching values higher than 20 days^{-1} after 2 weeks. On the other hand, blends based on PU-Rcb and PU-Ter, maintain almost the same degradation rate during the test period. Thus, our data show that (i) the hydrolysis of PC at 70°C is rather fast (which was expected) and that (ii) relatively small amounts of PUEs (say, 2.5 wt%) have a beneficial effect on hydrothermal stability of PC.

As mechanical properties of PC/PUE blends are most important for various applications, elastic and ultimate properties of blends were re-examined after the hydro-

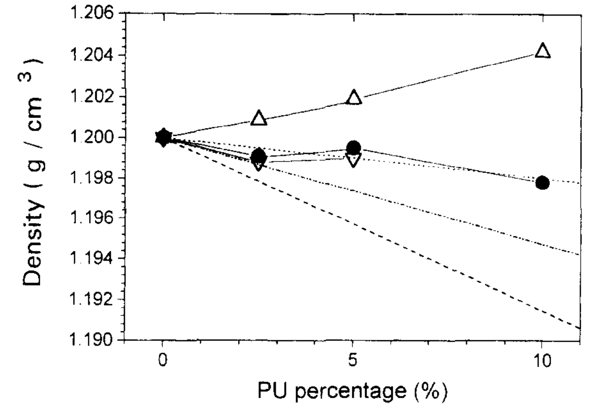

Figure 5 Density of PC/PUE blends related to theoretical values calculated from additivity: (△) experimental and (····) theoretical value of PC/PU-Rcb; (●) experimental and (-·-·) theoretical value of PC/PU-RcbTer; (▽) experimental and (- - - -) theoretical value of PC/PU-Ter

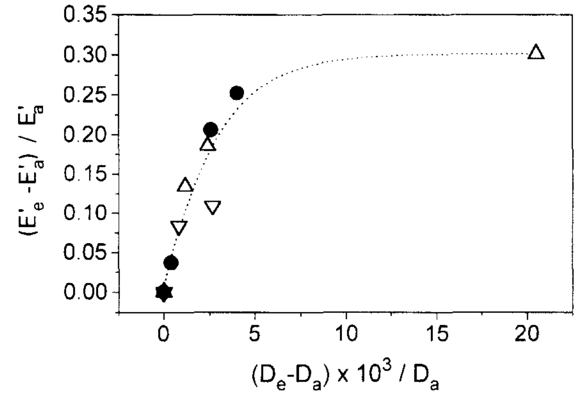

Figure 6 Excessive storage modulus *versus* excessive density for the various PC/PUE blends based on PU-Rcb (△), PU-RcbTer (●) and PU-Ter (▽). E'_e, D_e and E'_a, D_a represent experimental data and calculated values (according to the additivity), respectively

Table 6 Water sorption (in wt%) of PC/PUE blends at 70°C

Polymer blends	1 h	5 h	4 days	20 days
PC 100%	0.31	0.54	1.43	3.16
PU-Rcb 2.5%	0.37	0.60	1.69	3.28
PU-Rcb 5%	0.21	0.53	1.14	3.05
PU-Ter 2.5%	0.56	0.80	1.05	3.11
PU-Ter 5%	0.34	0.50	1.17	3.15
PU-RcbTer 2.5%	0.24	0.37	1.36	3.37
PU-RcbTer 5%	0.43	0.45	1.14	3.48

Table 7 Effect of hydrothermal ageing on T_g measured by d.s.c., molar mass and fracture energy of redried samples of PC/PUE blends

	0 Weeks			1 Week			2 Weeks		
Polymer blends	T_g (°C)	Molas mass	Fracture energy (kJ m^{-2})	T_g (°C)	Molar mass (%)[a]	Fracture energy (%)[a]	T_g (°C)	Molar mass (%)[a]	Fracture energy (%)[a]
PC 100%	153	27 000	6500	152	19	75	150	17	66
PU-Rcb 2.5%	143	40 000	5300	141	80	264[b]	145	73	211[b]
PU-Rcb 5%	138	40 000	n.c.[c]	130	73	n.c[c]	137	65	n.c.[c]
PU-Ter 2.5%	140	36 000	5000	139	75	272[b]	141	44	240[b]
PU-Ter 5%	136	41 000	n.c.[c]	136	88	n.c.[c]	134	85	n.c.[c]
PU-RcbTer 2.5%	142	39 000	5500	142	77	227[b]	140	11	189[b]
PU-RcbTer 5%	138	40 000	n.c.[c]	135	80	n.c.[c]	146	15	n.c.[c]

[a] Percentage of the original values
[b] Measured with displacement of 3.5 mm
[c] Not calculated because the fracture was brittle

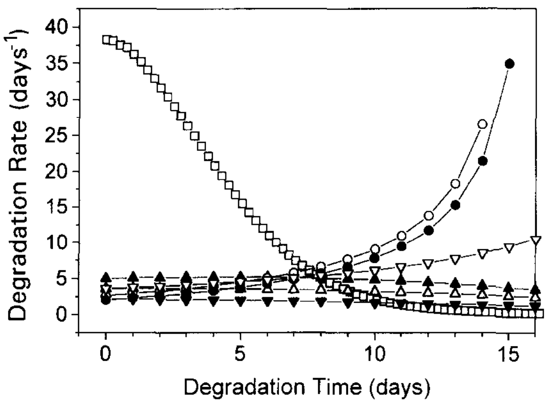

Figure 7 Degradation rate of PC (□) and PC/PUE blends with 2.5% (△) and 5% (▲) of PU-Rcb, 2.5% (○) and 5% (●) of PU-RcbTer, and 2.5% (▽) and 5% (▼) of PU-Ter during hydrolysis at 70°C (see the text for further explanation)

thermal treatment and drying process. As documented in *Table 5*, the decrease in molar mass does not have a measurable effect on the flexural (static) modulus of the blends. However, this result has been expected because the modulus as a 'bulk' property is not sensitive to changes in molar mass[16]. The slight increase of bending modulus exhibited by PC after treatment at 70°C can be ascribed to the reduction of free volume due to physical ageing[50].

Fracture tests such as SENB are known to reflect even small changes in the structure caused by any kind of degradation because the defects arising on a molecular level—under the action of stress—may become significant for the ultimate properties and/or service lifetime of a material[16]. The data summarized in *Table 7* make evident that the fracture energy of redried specimens of PC diminishes with the time of hydrolysis. As-received blends PC/PUE do not show higher values of the fracture energy than PC itself, probably because the blends remain single-phase materials without inclusions inducing local plastic deformation (multiple shear bands). Moreover, the documented increase of stiffness due to the strong interaction between PC and PUE, may account for slightly lower fracture energy of the blends. On the contrary, the hydrolytic ageing of blends with 2.5 wt% of PUE, produces a significant increase in fracture energy (from about 5300 kJ m^{-2} to more than 10 000 kJ m^{-2}), while blends with 5% of PUEs show brittle fracture. This difference is linked to the transition from semi-ductile to brittle fracture in the SENB test. A deeper insight into the observed effect would require more extensive data on ultimate properties and detailed analysis of the molecular structure, which was beyond the scope of this paper.

CONCLUSION

Polyurethane elastomers (PUEs) synthesized from 4,4′-diphenylmethane diisocyanate and (i) aliphatic polycarbonate diols or (ii) polytetramethylene glycols or (iii) the 50/50 mixtures of the latter components, were found to be miscible with polycarbonate (PC). The blends with 0–10 wt% of PUEs, prepared by melt mixing (followed by injection moulding of test specimens), constitute single-phase systems, which is evidenced by their transparency to the visible light and by a significant decrease (up to 30°C) in the T_g of PC. The effects of higher fractions of PUEs, or the eventual limits of miscibility, were not studied because the drop of T_g would be excessive from the viewpoint of intended applications. Dynamic mechanical and static flexural measurements reveal a slight increase in the modulus in the glassy state proportional to the PUE fraction. The miscibility of PC with PUEs as well as the 'antiplasticizing' effect of PUEs can be attributed to a strong interaction of constituents, probably due to formation of hydrogen bonds between urethane and carbonate groups. The data acquired show that all the PUEs have approximately equal effects on T_g and the room temperature modulus. Hydrothermal treatment (70°C, up to 2 weeks) brings about an essential decrease in molar mass of PC. On the other hand, the addition of 2.5 or 5 wt% of PUEs have a beneficial effect of hydrolytic stability: (i) the hydrolysis rate of blends is lower than that of PC itself; (ii) the mentioned hydrothermal ageing accounts for an increase in the fracture energy of blends with 2.5% of PUEs.

In conclusion, these polyurethane elastomers have been found useful not only for improving the processability of the molten PC, but also for modifying the properties of the polymer.

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