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Unsaturated polyester resins modified with poly(ε-caprolactone)–perfluoropolyethers block copolymers

M. Messori[a,*], M. Toselli[a], F. Pilati[b], C. Tonelli[c]

[a]*Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, viale Risorgimento 2, 40136 Bologna, Italy*
[b]*Dipartimento di Chimica, Università di Modena, via Campi 183, 41100 Modena, Italy*
[c]*Ausimont S.p.A., via S. Pietro 50, 20021 Bollate MI, Italy*

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Abstract

Poly(ε-caprolactone)–perfluoropolyether–poly(ε-caprolactone) block copolymers (TXCL) synthesised from Fomblin Z-DOL TX (TX) have been mixed with conventional unsaturated polyester resins (UPR) to prepare fluorine modified UPR (FUPR). A preliminary investigation on the compatibility of uncured FUPR systems has shown that the presence of PCL blocks leads to an enhancement of compatibility with respect to pure perfluoropolyether macromers. The compatibility tends to decrease by increasing the TXCL concentration in the mixture depending on both molecular weight and TX/PCL ratio. Also the morphology of FUPR after curing was strongly affected by the rate of curing and by a critical balancing of TX/PCL ratio and molecular weight of TXCL copolymers. Both transparent and opaque FUPR were obtained for the same composition at different curing rates; high curing rates (i.e. high concentration of initiator/activator) favoured the formation of transparent FUPR through a kinetic control of phase separation. Scanning electron microscopy (SEM) analysis was in good agreement with the macroscopic results obtained by visual inspection. XPS analysis showed a very strong surface enrichment in fluorinated segments, which increases by increasing the TX/PCL ratio. Mechanical tests showed a slight plasticization effect (compared to UPR control) together with a very strong improvement in the absorbed energy at break E_B showing the best toughening effect for TXCL with intermediate TX/PCL ratio. Finally, a minimisation of the water diffusion coefficient value (five times lower than UPR control) was noted for UPR modified with TXCL having intermediate PCL segment length.

Keywords: Unsaturated polyester resins; Perfluoropolyethers; Surface modification

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1. Introduction

Unsaturated polyester resins (UPR) [1,2] are step-growth polymers widely used in the automotive field, construction and electrical applications, coatings etc. Usually, cured unmodified UPR have low strength and elongation at break, and are subjected to stress cracking and brittle fracture.

As applications of UPR become more and more specialised, an improvement of the required properties is needed; often it can be achieved by the addition of a second polymeric phase or by suitable comonomers, and it is important to understand the effects of resin formulation and curing on morphology and properties.

In this respect, fluorinated materials are in principle very attractive modifying agents for their unique properties, such as chemical inertness, solvent and high temperature resistance, barrier properties, low friction coefficient and low surface tension, that in principle may be transferred to other polymeric materials by blending or copolymerisation. Some applications of fluorine-modified UPR are reported in patent literature: thermosetting resins for gel-coating with excellent resistance to corrosion, water and atmospheric agents [3], formulations for resins and foams [4] and several others [5,6]. This type of modification has been usually achieved by the use of fluorine-containing comonomers of low molecular weight which usually lead to homogeneous UPR and therefore have to be added in significant amount to achieve an appreciable improvement of performances. Furthermore, the high cost of fluorinated monomers leads to very expensive polymeric materials.

Alternatively, surface properties can be modified by fluoro-modification of previously moulded items [7], however this is also a highly expensive technology.

The availability of telechelic perfluoropolyethers (PFPE) with reactive terminal groups [8] makes possible the preparation of multiblock copolymers containing fluorinated blocks

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* Corresponding author. Fax: +39-51-209-3218.
E-mail address: massimo.messori@mail.ing.unibo.it (M. Messori).

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by using PFPE as macromers during polymerisation [9–12]. It was shown that the PFPE segments contained in polyester–PFPE multiblock copolymers still maintained the ability to migrate onto the surface leading to a fluorine-rich surface even when the amount of PFPE in the bulk was very low [13–15].

In a previous work [16] we studied the fluorine-modification of UPR by using hydroxyl-terminated telechelic PFPE as comonomers during the synthesis of UPR. A significant increase in toughness with respect to UPR was observed under flexural tests for fluorine modified UPR (FUPR) containing PFPE with low molecular weight.

The main drawback of this last approach is that the chemical modification has to be done during polymerisation and that a fraction of PFPE remains unreacted at the end of the polymerisation; this may be economically not convenient and it can be exploited for a limited number of polymers, as it requires for the terminal groups of the telechelic macromers to be able to react with the monomers.

In a different approach, fluoro-modification can be achieved by blending fluorinated macromers with other polymers; the ability of fluorinated polymers to segregate preferably on the surface can allow for the reduction of the overall amount of fluorinated polymer necessary to produce a high fluorine concentration at the surface. However, due to thermodynamic reasons, fluorinated polymers are usually immiscible with non-fluorinated polymers and segregate in a separate phase with poor adhesion to the non-fluorinated matrix, leading to very poor mechanical properties.

A different and more versatile approach to obtain fluoro-modification of different polymer matrices is to prepare separately block or graft copolymers containing fluorinated segments and then to add them to other polymers. In this case the compatibility/miscibility with the host polymer and the potential capability of fluorinated segments to migrate onto the surface may be controlled by an appropriate choice of the type and length of the non-fluorinated blocks. In this respect, block copolymers with a limited and well defined number of blocks should provide better results than multiblock copolymers.

In a previous paper [17] we reported the synthesis and the characterisation of poly(ε-caprolactone)–perfluoropolyether–poly(ε-caprolactone) block copolymers (PCL–PFPE–PCL) taking into account that poly(ε-caprolactone) (PCL) is a polymer miscible with PVC, ABS, SAN, PC and several other polymers including copolyester such as those used in UPR [18].

Based on this evidence it appears very interesting to explore the use of these PCL–PFPE–PCL block copolymers to modify UPR with the formation of a pseudo-IPN system [19], where UPR forms a three-dimensional network with PCL–PFPE–PCL entrapped in. The introduction of these materials in the rigid UPR matrix can in principle improve surface and mechanical properties and reduce water absorption. These effects can be strongly affected by the resulting morphology which in turn is expected to depend on the molecular weight of both PCL and PFPE segments and on curing conditions.

Therefore, the aim of this work was to investigate the possible use of these fluorinated block copolymers as additives to modify some characteristics of conventional UPR, such as the mechanical and surface properties. In particular the effects of molecular weight of both PFPE and PCL segments and of curing conditions on miscibility, morphology, water absorption, mechanical properties and surface composition will be discussed.

2. Experimental

2.1. Materials

The fluorinated macromers were supplied by Ausimont (registered name Fomblin Z-DOL TX) and were used as received. They are liquids with the following formula:

$$\mathrm{H{-}(OC_2H_4)_n{-}OCH_2CF_2O{-}(C_2F_4O)_p}$$
$$\times\,\mathrm{(CF_2O)_q{-}CF_2CH_2O{-}(C_2H_4O)_n{-}H}$$

in which the constitutional units $-C_2F_4O-$ and $-CF_2O-$, randomly distributed along the macromolecular chains, constitute the internal body where $p/q \approx 0.9$. The poly(ethylene oxide) chain is the end-capping segment containing the functional hydroxyl groups, with an average n value close to 1.5. The molar mass of the three studied fluorinated macromers was 1100, 2200 and 3400 g mol^{-1} (in the following they are labelled TX1, TX2 and TX3, respectively).

Maleic anhydride (MA), phthalic anhydride (PA) and 1,2-propanediol (PD), styrene, methylethylketone peroxide (MEKP, ~30 wt% solution in dimethylphthalate) and cobalt n-octoate (Co), all purchased from Aldrich Chemicals, were used as received without any further purification. Hydroquinone (Aldrich Chemicals) was crystallised from water before use.

2.1.1. Poly(ε-caprolactone)–perfluoropolyether–poly(ε-caprolactone) block copolymers synthesis

Poly(ε-caprolactone)–perfluoropolyether–poly(ε-caprolactone) block copolymers with the following structure:

$$\mathrm{H[O{-}(CH_2)_5{-}CO]_y{-}(OC_2H_4)_n{-}OCH_2CF_2O{-}(C_2F_4O)_p}$$
$$\times\,\mathrm{(CF_2O)_q{-}CF_2CH_2O{-}(C_2H_4O)_n{-}[CO{-}(CH_2)_5{-}O]_yH}$$

(in the follow schematised as TXCL) were prepared by ring opening polymerisation of ε-caprolactone (CL) using Fomblin Z-DOL TX with different molecular weight as transfer agent and in the presence of titanium tetrabutoxide as catalyst [17].

As reported in Table 1, the copolymers are indicated with the code TX_xCL_y in which x (1, 2 or 3) and y (in the range from 5 to 55) identifies the type of fluorinated macromer and

Table 1
Molecular characteristics of TXCL block copolymers (the reported molecular weight is calculated from the initial reactants ratio, in good agreement with composition data obtained from ^{1}H NMR analysis)

Code	Molecular weight of blocks in PCL–TX–PCL	TX/PCL ratio (wt/wt)	F/C molar ratio
TX1CL10	1140–1100–1140	0.48	0.21
TX2CL5	570–2200–570	1.93	0.65
TX2CL10	1140–2200–1140	0.96	0.41
TX2CL15	1710–2200–1710	0.64	0.30
TX2CL20	2280–2200–2280	0.48	0.23
TX2CL25	2850–2200–2850	0.39	0.19
TX2CL30	3420–2200–3420	0.32	0.16
TX2CL40	4570–2200–4570	0.24	0.13
TX2CL55	6280–2200–6280	0.18	0.10
TX3CL15	1710–3400–1710	0.99	0.44
TX3CL25	2850–3400–2850	0.60	0.29
TX3CL55	6280–3400–6280	0.27	0.15

the average number of repeating units contained in each PCL segment, respectively.

2.1.2. UPR synthesis

The monomers MA, PA and PD (in the molar ratio MA/PA/PD = 2 : 1 : 3) were placed in a three-round necked flask equipped with a Dean-Stark trap to collect distilled water and were reacted at the temperature of 200–210°C and atmospheric pressure, under continuous mechanical stirring, and using a slight flow of nitrogen to remove water formed during polycondensation. The reaction was carried out for about 3–4 h until the achievement of an acid number lower than 50 (mg of KOH necessary to titrate 1 g of resin). At the end of the polycondensation reaction, styrene (50% by weight with respect to the final amount of resin) and hydroquinone (0.055% by weight, as free radical inhibitor) were added to the polyester.

2.2. Characterisation

2.2.1. Compatibility tests

In order to verify the compatibility characteristics of TXCL copolymers, several mixtures of additives with UPR having composition in the range 5–50% by weight were prepared by simple stirring at room temperature. The degree of compatibility of uncured systems was estimated by visual inspection (transparent, translucent or opaque) considering that transparency indicates the absence of segregation between different phases at least on the scale of visible light wavelength.

2.2.2. Curing

The initiator system, consisting of methylethylketone peroxide (MEKP, 1.0–4.0 parts by weight for 100 parts of resin, phr) as initiator and of cobalt *n*-octoate (Co, 0.5–2.0 phr) as activator, was added to the TXCL/UPR mixture (prepared by simple stirring at room temperature) just before curing. After vigorous stirring (1–2 min) the resin-initiator system was cast into cavities formed by a suitable silicon rubber mould blocked by two glass plates to produce specimens $127 \times 12 \times 4$ mm^3 thick. The resins were cured for 24 h at room temperature and postcured for 2 h at 100°C.

2.2.3. Morphology

In order to have information about the morphology, fracture surfaces of cured samples broken during flexural tests were gold-coated and examined by scanning electron microscopy (SEM) using a Philips XL-40 instrument.

2.2.4. XPS measurements

XPS spectra of UPR and FUPR were measured by a Perkin-Elmer Physical Electronics Photoelectron Spectrometer using a Mg Kα X-ray source (1253.6 eV) and a cylindrical mirror analyser. The X-ray gun was operated at 150 W, 15 kV and 10 mA. Base pressure was maintained at 2×10^{-8} mbar and a pass energy of 25 eV was employed for all high-resolution experiments. No significative radiation damage was observed during two times the data collection time and the charge correction in the binding energy scale was accomplished by setting the envelope of hydrocarbon C1s to 285.0 eV. Due to the use of a non-monochromatic source and a very large range of the signal in C1s region (when the PFPE segment is present in the sample: more than 10 eV), a subtraction has been done taking into account the position and the relative intensity of the photoelectron satellite peaks [22]. Data analysis was accomplished using XPSPeak 4.1 software. In the curve fitting a Shirley type non linear background subtraction was used and the C1s peaks were converted using a least-squares routine assuming a Gaussian/Lorentzian (90/10) sum fraction.

2.2.5. Mechanical tests

Flexural tests were carried out in a three points bending (3PB) with a span of 57.6 mm and a crosshead speed of 1.8 mm min^{-1} on freely supported cured specimens, using an Instron Series IX instrument.

In order to determine the stress intensity factor K_{IC}, 3PB flexural tests were also carried out on single edge notched (SEN) specimens having notch lengths *a* ranging from 2 to 5 mm with a span of 48 mm and a crosshead speed of 10 mm min^{-1}. The shape factor *Y* used for the SEN-3PB span/width (*W*) ratio of 4 is the following [20]:

$$Y = 11.6(a/W)^{1/2} - 18.4(a/W)^{3/2} + 87.2(a/W)^{5/2} - 150.4(a/W)^{7/2} + 154.8(a/W)^{9/2}.$$

All these flexural tests were carried out at 23°C on five specimens for each resin.

2.2.6. Water diffusion coefficient

Isothermal absorption of the specimen immersed in distilled water thermostated at 85.0°C was determined by following their weight increase until saturation condition. Water diffusion coefficient D was determined according to the following formula [21]:

$$D = \frac{\pi}{3600}\left(\frac{bm}{4W_\infty}\right)$$

in which m is the initial slope of the graph reporting the weight increase as a function of the square root of the immersion time, b, the specimen width and W_∞ is the weight increase percent in saturation conditions.

3. Results and discussion

3.1. Compatibility tests

A preliminary investigation on the compatibility of TXCL of different molecular weights and TX/PCL ratios with respect to UPR was performed for TXCL/UPR weight compositions ranging from 0/100 to 50/50. The results are reported in Table 2.

Tests carried out on a mixture of UPR with pure TX resulted always in opaque samples even for a concentration lower than 5 wt%, indicating a strong incompatibility between unmodified fluorinated macromer and UPR, as expected. On the contrary, from the data reported in Table 2, it can be seen that all the mixtures containing TXCL copolymers in low concentration (5 wt%) were completely transparent indicating miscibility or a very fine phase dispersion, and confirming the desired enhancement of compatibility due to the presence of PCL blocks. The compatibility tends to decrease by increasing the TXCL concentration in the mixture for TXCL copolymers containing short or long PCL segments. On the contrary, TX2CL20 and TX2CL30 based blends become translucent only at TXCL concentration higher than 40%.

Some apparently strange trends were found for samples from TX2CL10 to TX2CL55 for a TXCL/UPR ratio higher than 10/90 (from opaque to transparent to opaque again) and for the effect of the concentration for TX2CL10 (transparent for low and high concentration and opaque for intermediate concentration). These behaviours can be explained taking into account that the miscibility of TXCL copolymers in UPR segments is affected by both the molecular weight and the TX/PCL ratio; the immiscibility of TX2CL10 and TX2CL55 at concentration higher than 10% could be ascribed to the high TX/PCL ratio, for TX2CL10, and to the high molecular weight, for TX2CL55, respectively. In this way, the higher compatibility of TX2CL55 with respect to TX3CL55 can also be explained taking into account that this last sample has both a higher TX/PCL ratio and a higher molecular weight.

Table 2
Appearance of uncured TX/UPR and TXCL/UPR mixtures at room temperature (T: transparent; TL: translucent; O: opaque)

Mixture	Mixture composition (wt/wt)					
	0/100	5/95	10/90	20/80	40/60	50/50
TX1/UPR	T	O	O	O	O	O
TX2/UPR	T	O	O	O	O	O
TX3/UPR	T	O	O	O	O	O
TX2CL10/UPR	T	T	T	O	O	T
TX2CL20/UPR	T	T	T	T	T	TL
TX2CL30/UPR	T	T	T	T	T	TL
TX2CL55/UPR	T	T	TL	TL	O	O
TX3CL55/UPR	T	T	O	O	O	O

3.2. Curing

The morphology of IPN after curing is controlled by several factors, such as thermodynamic compatibility of the components, cross-linking density and mode and kinetics of curing. Thermodynamic compatibility is expected to decrease during UPR curing due to both cross-linking density increase and polymerisation of styrene. However, if curing rate is high enough, phase separation can be kinetically prevented because of the permanent entanglements produced by cross-linking. With highly incompatible polymers, the thermodynamics of phase separation can be so powerful and rapid that it occurs before it can be prevented by cross-linking, but in the case of complete or moderate compatibility the curing rate may be higher than the phase separation rate.

As general rule, the phase segregation rate can be controlled by the compatibility properties of TXCL copolymers with respect to UPR and, as already discussed, high compatibility can be obtained with an appropriate TX/PCL ratio and low molecular weight. On the other hand, high molecular weight results in a high number of entanglements which in turn are able to reduce the rate of phase segregation.

In order to verify the effect of curing conditions on the final morphology of FUPR, curing tests were carried out using different amounts of initiator/activator. Taking into account that UPR modification is economically attractive for a concentration of TXCL additives as low as possible, in this paper curing was carried out on mixtures containing TXCL with a concentration of 3 wt%, all transparent before curing. Data derived from visual inspection are reported in Table 3 from which it can be noted that cured FUPR were opaque or transparent depending on the amount of initiator system, and therefore on curing rate, as well as on molecular structure of TXCL.

At low curing rates (MEKP/Co 1.0/0.5 and 2.0/1.0 phr), the opacity increases with increase of the PCL segment length (i.e. with decreasing TX/PCL ratio and increasing the molecular weight of TXCL copolymers); on the contrary, for the highest curing rate (MEKP/Co 4.0/2.0 phr) only the FUPR based on TX2CL5 and TX2CL40

Table 3
Appearance of TXCL/UPR mixtures (TXCL 3 wt%) after curing with different amount of initiator system MEKP/Co (curing conditions: 24 h at room temperature, 2 h at 100°C; T: transparent; TL: translucent; O: opaque)

Cured mixture	%TX	MEKP/Co concentration (phr)		
		1.0/0.5	2.0/1.0	4.0/2.0
UPR control	0	T	T	T
TX2CL5/UPR	2.0	TL	T	T
TX2CL10/UPR	1.5	O	O	O
TX2CL20/UPR	1.0	O	O	O
TX2CL40/UPR	0.6	O	O	T

were transparent: this behaviour could be explained assuming that the segregation of the PCL segments is the driving force for the control of the morphology. At low PCL segment length (low molecular weight) the driving force for segregation is low and this is the reason why TX2CL5 is transparent, while for TX2CL40 (high molecular weight and high TX/PCL ratio) we can assume that the disentanglement rate is lower than the curing rate and therefore the sample is transparent even though there is a strong driving force for PCL segregation.

Data show that the segregation of PCL (probably as crystalline phase even though differential scanning calorimetry measurements didn't show any melting transition, probably due to the very low PCL concentration in FUPR) is strongly affected by a critical balancing of TX/PCL ratio, molecular weight of TXCL copolymers and rate of curing. In general, high curing rates (i.e. high MEKP/Co concentration) disfavour phase segregation favouring the formation of transparent FUPR. In these cases, phase separation can be kinetically controlled, since the entanglements related to the UPR network are permanent after cross-linking and phase segregation can not occur.

3.3. Morphology of cured FUPR

Some typical SEM micrographs of fracture surfaces of cured FUPR are shown in Figs. 1–6. Unless otherwise indicated the micrographs were similar for the same TXCL/UPR composition independently on the amount of initiator/activator used.

The appearance of fracture surfaces was in good agreement with the macroscopic results obtained by visual inspection. In fact the fracture surface of the UPR control (Fig. 1) was found homogeneous and uniform according to the transparency observed from a macroscopic point of view (see Table 3). Also TX2CL5/UPR systems were found to be transparent (at least for the two higher MEKP/Co concentrations reported in Table 3) and the fracture surface was homogeneous and uniform with only a slight increase of roughness compared to the UPR control (Fig. 2). On the contrary, in the case of TX2CL10/UPR system (Figs. 3 and 4) the fracture surface appeared rough and not homogeneous in agreement with to the opacity observed by visual inspection. Furthermore, cavities having a dimension of 0.2–0.5 μm, uniformly distributed on the surface and attributable to dispersed domains, were observed for higher MEKP/Co concentration (4.0/2.0 phr, Fig. 4). These last morphologies were also noted for the macroscopically

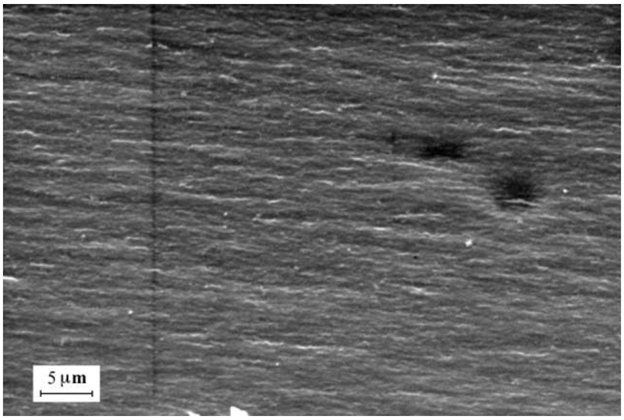

Fig. 2. SEM micrograph of fracture surface of TX2CL5/UPR blend (3/97 wt/wt) cured with MEKP/Co 2.0/1.0 phr (magnification 2000 ×).

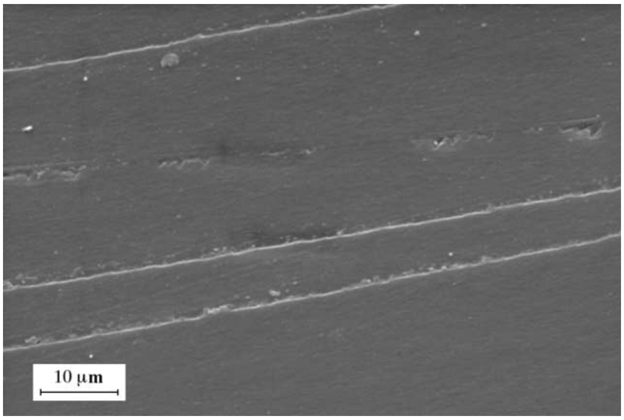

Fig. 1. SEM micrograph of fracture surface of UPR control cured with MEKP/Co 2.0/1.0 phr (magnification 1500 ×).

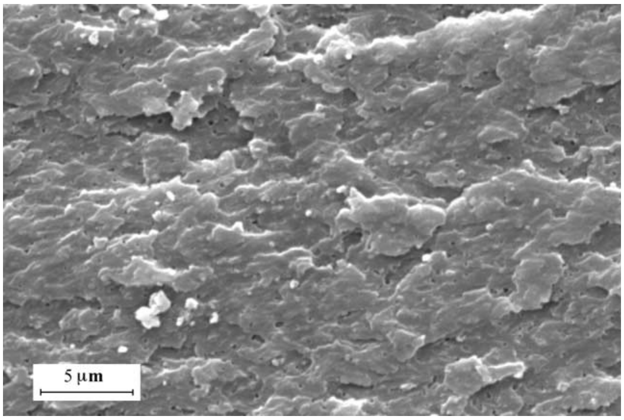

Fig. 3. SEM micrograph of fracture surface of TX2CL10/UPR blend (3/97 wt/wt) cured with MEKP/Co 2.0/1.0 phr (magnification 3500 ×).

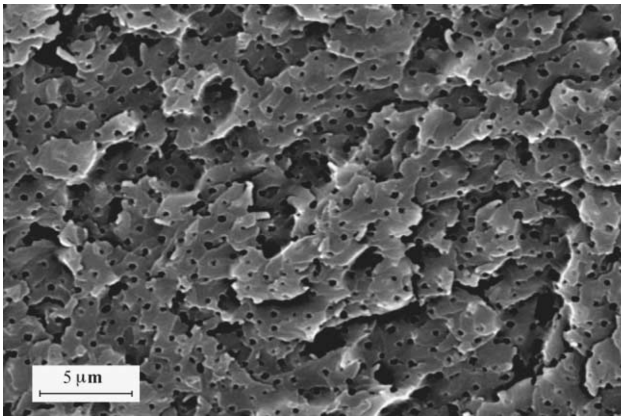

Fig. 4. SEM micrograph of fracture surface of TX2CL10/UPR blend (3/97 wt/wt) cured with MEKP/Co 4.0/2.0 phr (magnification 3500 ×).

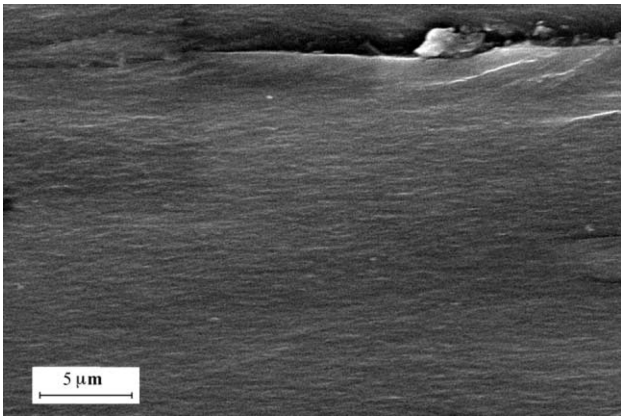

Fig. 6. SEM micrograph of fracture surface of TX2CL40/UPR blend (3/97 wt/wt) cured with MEKP/Co 4.0/2.0 phr (magnification 3500 ×).

opaque TX2CL20/UPR system (for both MEKP/Co concentrations) and TX2CL40/UPR system (MEKP/Co 2.0/1.0 phr) shown in Fig. 5. On the contrary, TX2CL40 based FUPR cured with the highest initiator system concentration (4.0/2.0 phr) showed a very uniform and homogeneous surface (Fig. 6) in full agreement with the transparency indicated in Table 3.

Finally, it is worth noting that SEM micrographs showed that the dimension of the cavities attributed to the segregated phase are much smaller than those of previously reported FUPR prepared using Fomblin Z-DOL TX directly as comonomer during the polyester synthesis [16], in which the particle sizes were in the range 5–10 μm in diameter, depending on the molecular weight of the fluorinated macromer and the reaction condition used. This could be ascribed to a more homogeneous chemical structure and a better compatibility of the TXCL additives compared to the use of unmodified PFPE as comonomers.

3.4. XPS analysis

The presence of a strong signal attributable to fluorine atoms was clearly evident in the XPS survey spectra of TXCL modified UPR notwithstanding the low PFPE concentration present in the mixture.

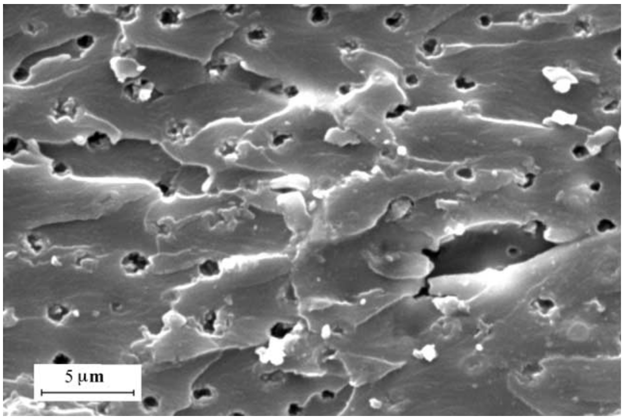

Fig. 5. SEM micrograph of fracture surface of TX2CL40/UPR blend (3/97 wt/wt) cured with MEKP/Co 2.0/1.0 phr (magnification 3500 ×).

Two methods of quantification were used to calculate the surface composition of the samples. The first method relates peak areas of the elements of interest to a surface percentage through the use of appropriate sensitivity factors [22]. The second method involved the curve fitting of high resolution C1s spectra, in particular the intensity of the C1s peaks in the range 292–298 eV (only related to carbon atoms bonded to fluorine) respect the overall C1s peak area (see Fig. 7).

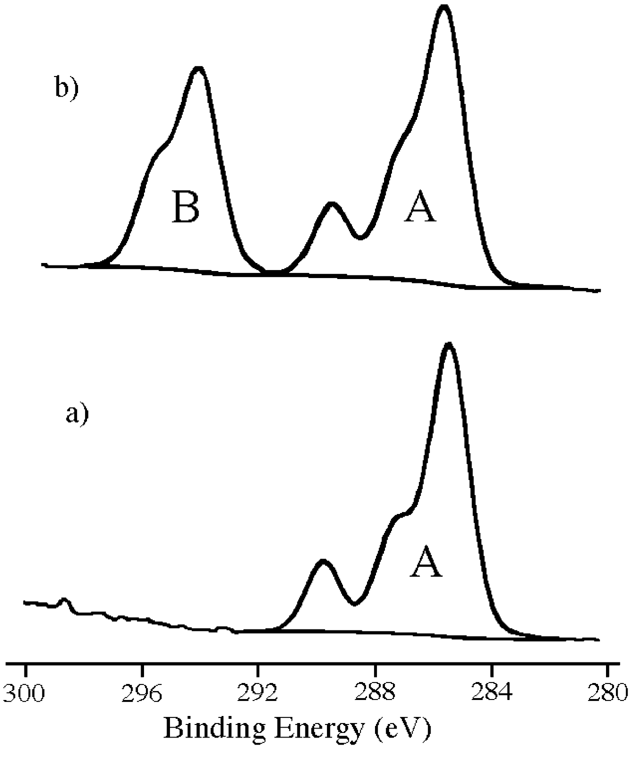

Fig. 7. XPS high resolution C1s spectra of (a) UPR control (MEKP/Co 2.0/1.0 phr) and (b) TX2CL25/UPR blend (3/97 wt/wt, MEKP/Co 2.0/1.0 phr).

Table 4
Bulk and surface compositions of some FUPR (TXCL 3 wt%, MEKP/Co 2.0/1.0)

Cured mixture	wt% of PFPE segments in UPR	F/C molar ratio[a]		%CF[b]	
		Bulk	From XPS	Bulk	From XPS
TX2CL5/UPR	2.0	0.010	1.74	0.5	66.5
TX2CL10/UPR	1.5	0.007	1.55	0.35	51.0
TX2CL25/UPR	0.8	0.004	1.18	0.2	39.0
TX1CL10/UPR	0.8	0.004	1.12	0.2	35.5
TX3CL15/UPR	1.4	0.007	1.50	0.35	49.5

[a] The F/C molar ratio for only the PFPE segment is 2.0.

[b] Atomic percentage of carbon atoms bonded to fluorine respect to overall carbon.

Table 4 lists the data resulting from XPS analysis of the air side surface and of the bulk of some FUPR for both the F/C atomic ratios (calculated according to the first method) and the atomic percentage of carbon bonded to fluorine respect to the overall carbon atoms (%CF, calculated as the $B/(A+B)$ ratio according to Fig. 7).

These results showed that all the modified resins had a surface F/C molar ratio which is more than two magnitude orders higher than that expected from the bulk composition, indicating a very strong surface enrichment of fluorinated segments. The same behaviour was confirmed from the reported %CF values.

For TXCL copolymers having the same PFPE molecular weight, the fluorine concentration on the surface increases by increasing the TX/PCL ratio (i.e. by decreasing the PCL segment length). Moreover, by comparison between TX1CL10/UPR and TX2CL25/UPR or between TX2CL10/UPR and TX3CL15/UPR (i.e. FUPR with similar values of PFPE bulk concentration) it can be noted that the better degree of fluorine surface enrichment was observed in the case of TXCL copolymers based on TX2, as already noted in previous works [13,14].

Furthermore, it is interesting to note that the experimental values of F/C molar ratio of FUPR were higher than those calculated for the correspondent TXCL copolymers (see Table 1). This is an indication that PFPE segments are preferentially located in the early surface while PCL segments tend to remain in the inner layers of the resin.

3.4. Mechanical tests

In order to investigate the mechanical properties-morphology relationship, flexural tests were carried out on cured specimens obtained with two different initiator system compositions. The results are reported in Table 5.

A slight plasticization effect was indicated by the decrease of the Young modulus of FUPR (compared to the UPR control) with increasing the PCL segment length of TXCL copolymers. The results were similar for both initiator system compositions investigated with the exception of TX2CL40/UPR cured with MEKP/Co 4.0/2.0 phr which presented a surprisingly high value of the Young modulus.

On the contrary, a very strong improvement was observed in the absorbed energy at break E_B (area under stress–strain curve) with maximum values observed for TX2CL10/UPR cured with MEKP/Co 2.0/1.0 phr (0.655 J compared to 0.232 J corresponding to UPR control) and for TX2CL20/UPR cured with MEKP/Co 4.0/2.0 phr (0.522 J corresponding to 0.275 J related to UPR control).

Table 5
Mechanical tests on FUPR (TXCL 3 wt%) cured with different amount of initiator system MEKP/Co (curing conditions: 24 h at room temperature, 2 h at 100°C)

Cured mixture	MEKP/Co (phr)	% PFPE	E_{Young} (GPa)	E_B (J)	K_{IC} (MN m$^{-3/2}$)
UPR control	2.0/1.0	0	3.57	0.232	1.37
TX2CL5/UPR		2.0	3.39	0.425	1.42
TX2CL10/UPR		1.5	3.40	0.655	1.43
TX2CL20/UPR		1.0	3.19	0.547	0.53
TX2CL40/UPR		0.6	3.16	0.460	0.44
UPR control	4.0/2.0	0	3.53	0.275	1.29
TX2CL5/UPR		2.0	3.21	0.522	1.32
TX2CL10/UPR		1.5	3.14	0.508	1.21
TX2CL20/UPR		1.0	2.94	0.590	1.40
TX2CL40/UPR		0.6	3.47	0.256	0.94

The critical stress intensity factor K_{IC} showed small changes with respect to unmodified UPR except for UPR modified with TX2CL40 which showed a significant decrease of K_{IC} for both opaque and transparent samples.

In general, mechanical properties of cured FUPR are strongly affected by several parameters (such as cross-linking density, phase segregation degree, morphology etc.) that influence the chain mobility of TXCL copolymers in the cross-linked structure. On the basis of our data and of these considerations, a straightforward correlation between final morphologies of FUPR and their mechanical properties was difficult. In general, it is interesting to note that the TX/PCL ratio represents a very critical factor for controlling the final mechanical properties of thermosets. For both initiator system compositions, a maximum in E_B and K_{IC} has been observed for intermediate TX/PCL ratio (remembering that all test have been performed with mixtures containing the same amount of TXCL copolymers, 3 wt%). From these results it is evident that toughening may be obtained with a strict control of molecular structure of TXCL copolymers and of curing rate.

3.5. Water diffusion coefficient

Water diffusion coefficients, *D*, determined from isothermal absorption of specimens immersed in distilled water at 85.0°C, are reported in Table 6. For all FUPR, *D* was lower than that of unmodified UPR except for FUPR containing TX2CL40 copolymer.

An increase of *D* by decreasing the PFPE content could be expected; indeed *D* decreases from TX2CL5 to TX2CL20 containing FUPR (i.e. by decreasing the amount of PFPE) and increases again to the values of UPR control for TX2CL40 based FUPR.

To explain this behaviour we have to assume that *D* is controlled by two concurring factors: PFPE content and PCL phase segregation, with the latter appearing the most important. Therefore, water absorption properties of FUPR can be controlled by several factors, such as TXCL molecular structure (molecular weight and TX/PCL ratio) and phase segregation. Furthermore, a surface reorganisation that decreases the surface concentration of PFPE when FUPR specimens are in contact with water can not be excluded taking into account the flexibility of TXCL chains, as already highlighted for pure TXCL copolymers [23].

Table 6
Water diffusion coefficient *D* of FUPR (TXCL 3 wt%) at 85.0°C

Cured mixture	MEKP/Co	% PFPE	$D \times 10^6$ ($cm^2\ s^{-1}$)
UPR control	2.0/1.0	0.0	0.10
TX2CL5/UPR		2.0	0.07
TX2CL10/UPR		1.5	0.03
TX2CL20/UPR		1.0	0.02
TX2CL40/UPR		0.6	0.10
UPR control	4.0/2.0	0.0	0.06
TX2CL5/UPR		2.0	0.05
TX2CL10/UPR		1.5	0.02
TX2CL20/UPR		1.0	0.02
TX2CL40/UPR		0.6	0.06

4. Conclusions

PCL–PFPE–PCL block copolymers were used as additives to modify UPR with the possible formation of pseudo-IPN systems. A preliminary investigation on the compatibility of uncured TXCL/UPR systems showed that, due to the presence of PCL blocks, all the mixtures containing TXCL copolymer in low concentration (5 wt%) were completely transparent indicating the desired enhancement of compatibility with respect to pure PFPE macromers. As expected, the compatibility tends to decrease by increasing the TXCL concentration in the mixture depending on both molecular weight and TX/PCL ratio.

After curing, the morphology of FUPR was strongly affected by the rate of curing and by a critical balancing of TX/PCL ratio and molecular weight of TXCL copolymers. Both transparent and opaque FUPR were obtained for the same composition at different curing rates; high curing rates (i.e. high concentration of initiator/activator) favoured the formation of transparent FUPR through a kinetic control of phase separation.

SEM analysis was in good agreement with visual inspection. In fact, fracture surfaces of FUPR were found homogeneous or not according to the transparency or opacity, respectively, observed by visual inspection.

XPS analysis showed a very strong surface enrichment of fluorinated segments, which increases by increasing the TX/PCL ratio. The better degree of fluorine surface enrichment was observed in the case of TXCL copolymers based on PFPE with molecular weight of 2200 (TX2).

Mechanical tests showed a slight plasticization effect (compared to UPR control) with increasing both the molecular weight and the PCL segments length of TXCL copolymers. A very strong improvement was noted in the absorbed energy at break E_B showing the best toughening effect for TXCL with intermediate TX/PCL ratio.

Finally, a reduction of the water diffusion coefficient value (five times lower than UPR control) was noted for almost all FUPR samples. The lowest values were observed for UPR modified with TXCL having intermediate PCL segment length.

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