ELENA FABBRI[1], PAOLA FABBRI[1], MASSIMO MESSORI[1], FRANCESCO PILATI[1],
CLAUDIO TONELLI[2], MAURIZIO TOSELLI[3]

Surface modification of unsaturated polyester resins with perfluoropolyethers

Summary — Fluorine-modified unsaturated polyester resins were prepared by using polycaprolactone-perfluoropolyether-polycaprolactone triblock copolymers having hydroxyl or methacrylate end-groups. Despite the immiscibility of the perfluoropolyether segment, all the modified resins were fully transparent after curing thanks to the compatibilization effect of the polycaprolactone segments. Contact angle measurements showed a very low water wettability for all investigated resin compositions. Also in the case of system with the lower bulk copolymer concentration (less than 0.3 phr) contact angle was higher than 94°. It has been demonstrated that the presence of methacrylate end-groups tends to hinder the surface segregation of the fluorinated additive.
Key words: unsaturated polyester resins, surface modification, perfluoropolyethers, water contact angle.

Unsaturated polyester (UP) resins [1, 2] represent a class of thermoset polymers widely used in several industrial applications such as automotive, construction and electrical fields, coatings, etc. One of the main drawbacks of cured unmodified UP resins is their sensitivity to water adsorption and a method to improve the hydrophobicity should be represented by a suitable surface modification without affecting the bulk properties of the resin.

Different approaches can be used with this aim, such as for example coatings deposition by plasma techniques [3—5] but there are drawbacks such as cost, poor adhesion to the substrate, loss of transparency, small item dimensions and complex geometrical forms that limit these processes.

Alternatively, surface modification can be achieved by the addition of another polymeric or oligomeric phase to UP resin before curing or by modification of UP resin with suitable comonomers during the resin synthesis.

In this respect, fluorinated materials are very attractive modifying agents because of 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 simply by blending or copolymerization. Several patents were already proposed for fluorine-modification of UP resins: thermosetting resins for gel-coating with excellent resistance to corrosion, water and atmospheric agents [6], formulations for resins and foams [7] and others [8, 9]. This type of modification was usually achieved by using fluorine-containing comonomers of low molecular weight which usually lead to homogeneous UP resins and therefore have to be added in significant amount to achieve an appreciable improvement of performances.

Telechelic perfluoropolyethers (PFPE) with reactive terminal groups [10] can be used for the preparation of triblock copolymers containing fluorinated segments [11, 12] and showing 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].

In a previous work [14] we studied the fluorine-modification of UP resins by using hydroxyl-terminated telechelic PFPE as comonomers during the synthesis of these resins. A significant increase in toughness with respect to unmodified UP resins was observed under flexural tests of fluorine modified UP resins containing low molecular weight PFPE (about 1000 Da).

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

[1] Università di Modena e Reggio Emilia, Dipartimento di Ingegneria dei Materiali e dell' Ambiente, via Vignolese 905/A, 41100 Modena, Italy.
[2] Solvay-Solexis, v.le Lombardia 20, 20021 Bollate (MI), Italy.
[3] Università di Bologna, Dipartimento di Chimica Applicata e Scienza dei Materiali, viale Risorgimento 2, 40136 Bologna, Italy.

In a different approach, fluoro-modification can be achieved by blending of fluorinated macromers with other polymers. The ability of fluorinated polymers to segregate preferably on the surface can allow to reduce 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 the 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.

Recently we studied the use of polycaprolactone-perfluoropolyether-polycaprolactone block copolymers (PCL-PFPE-PCL) for the surface modification of UP resins by formation of a pseudo-IPN system, where UP resin forms a three-dimensional network with PCL-PFPE-PCL entrapped in [15]. Analysis by X-ray photoelectron spectroscopy (XPS) showed a very strong surface enrichment in fluorinated segments, which increases with increase in PFPE:PCL ratio together with reduction of water diffusion coefficient value. Furthermore, mechanical tests showed a very strong improvement in the absorbed energy at break.

In the present work we synthezized PCL-PFPE-PCL copolymers with methacrylate end-groups in order to make them reactive towards UP resin during crosslinking reaction. The prepared copolymers were blended at different concentrations with a commercial UP resin and, after curing, a surface characterization was carried out in terms of water contact angle measurements for the evaluation of the final cured resin hydrophobicity. Aim of this paper was to study the effect of the presence of possible covalent linkages between fluorinated additives and UP resin network on the surface segregation of PFPE segments. For this purpose we compared the results obtained using methacrylate terminated copolymers with those obtained by using copolymers without methacrylate end-groups.

EXPERIMENTAL

Materials

Fluorinated oligomer used in this study was Fomblin Z-DOL TX® (supplied by Solvay-Solexis), which can be represented by the following formula:

$$H-(OC_2H_4)_n-OCH_2CF_2O-(C_2F_4O)-(CF_2O)_q-CF_2CH_2O-(C_2H_4O)_n-H$$

where the constituent units $-C_2F_4O-$ and $-CF_2O-$ are randomly distributed along the macromolecular chains with p/q ratio of 0.9 and the average value of n is 1.5. Molecular weight of this fluorinated macromer is $2150 \ g \cdot mol^{-1}$.

ε-Caprolactone (CL), purchased from Aldrich Chemicals, was distilled under reduced pressure in the presence of calcium hydride.

2-Isocyanatoethyl methacrylate (2-IEM), tin (II) 2-ethylhexanoate (SnOct₂) and dibenzoyl peroxide (BDP) (all purchased from Aldrich Chemicals) were used as received without further purification.

UP resin was a commercial ortho-resin supplied by S.I.R. (Italy) consisting of maleic anhydride, phthalic anhydride and 1,2-propandiol (molar ratio 1:1:2, respectively) dissolved in styrene monomer (35 wt. %).

PCL/PFPE/PCL block copolymers syntheses

Block copolymers of the following structure:

$$H[O-(CH_2)_5-CO]_y-(OC_2H_4)_n-OCH_2CF_2O-(C_2F_4O)_p$$
$$(CF_2O)_q-CF_2CH_2O-(C_2H_4O)_n-[CO-(CH_2)_5-O]_yH$$
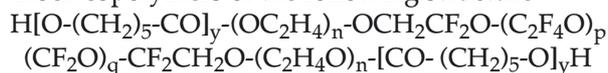
were prepared by ring-opening polymerization of CL using Fomblin Z-DOL TX as transfer agent and in the presence of SnOct₂ as catalyst according to a procedure previously reported [16, 17]. The final products, respectively coded as TXCL(y) (where y = 2, 5, 10 represents the average degree of polymerization of PCL segment), were dried overnight at room temperature under reduced pressure before use. The expected structures were confirmed by ¹H NMR analysis.

Modification of TXCL(y) copolymers with methacrylate end-groups

Methacrylate end-capping of fluorinated copolymers was carried out by bulk reaction of TXCL(y) with 2-IEM (molar ratio of 1:2). The reaction was carried out in a 50 mL glass flask, equipped with a calcium chloride trap, under magnetic stirring, at 100 °C, for 3 hours. The progress of the reaction was monitored by FT-IR spectroscopy. The final products, respectively coded as TXCL(y)Acr, were dried overnight at room temperature under reduced pressure before use.

Curing

TXCL(y)/UP resin and TXCL(y)Acr/UP resin clear mixtures were prepared at room temperature by simple stirring at a weight ratio of 0.3, 1.0 or 2.0/100. The initiator DBP (2 phr) was added to the system just before curing and, after complete dissolution, the system was cast onto microscope cover glass (20x20 mm). The resins were cured for 2 hours at 80 °C and postcured for 2 hours at 140 °C. All the prepared mixtures were transparent after curing.
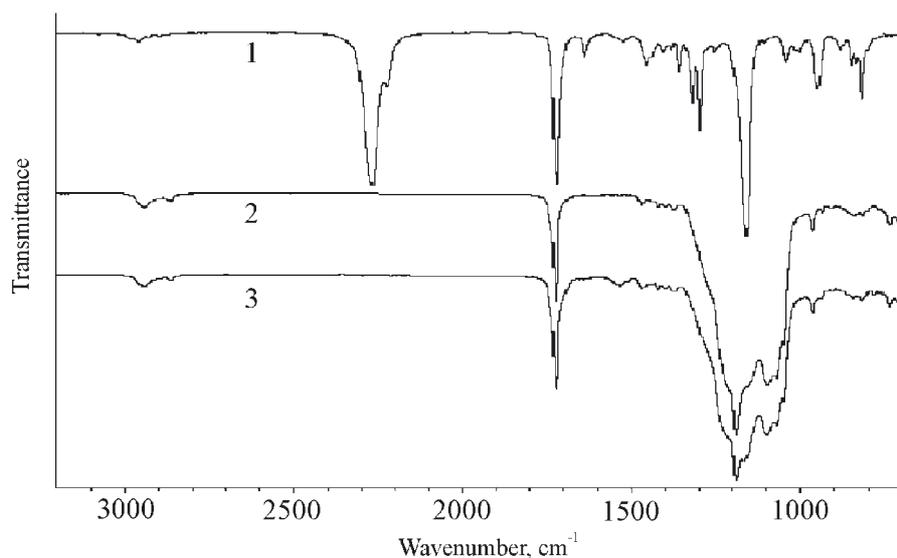
Fig. 1. FT-IR spectra of 2-IEM (1), TXCL(5) (2) and TXCL(5)Acr (3)
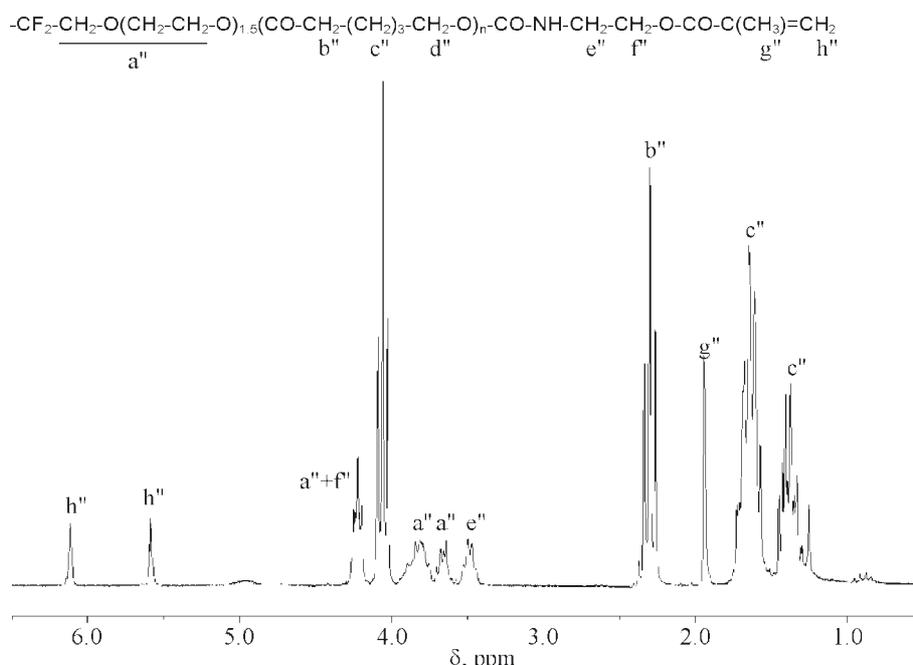
Fig. 2. ^{1}H NMR spectrum and signal assignments of TXCL(5)Acr (crude product)

Methods of characterization

FT-IR spectroscopy was performed using Avatar 330 FT-IR Thermo Nicolet spectrometer operating in ATR mode. A minimum of 32 scans with a resolution of 4 cm^{-1} were used.

^{1}H NMR analysis was performed using Bruker DPX200 spectrometer, using CDCl$_3$ as a solvent and tetramethylsilane as internal reference.

Static water contact angle (θ) measurements were carried out using DataPhysics OCA 20 apparatus. In order to avoid surface contamination, all specimens were rapidly washed with 1,1,2-trichloro-1,2,2-trifluoroethane (a specific solvent for perfluoropolyethers) and with

tetrahydrofuran before measurement. Contact angle determination was carried out for at least two different specimens of the same sample and average value of contact angle was determined on the basis of at least ten measurements.

RESULTS AND DISCUSSION

Modification of TXCL(y) copolymers with 2-IEM and characterization of products

The progress of the reaction between hydroxyl terminated TXCL(y) and 2-IEM was monitored using FT-IR spectroscopy by following the disappearing of absorp-

T a b l e 1. ^{1}H NMR assignments of TXCL(y) and 2-IEM [where y = n + 1 in present notation (here y = 5, n = 4)]

Group	δ, ppm
$-CF_2CH_2O(CH_2CH_2O)_{0.5}CH_2CH_2O-[CO-CH_2(CH_2)_3CH_2O]_n-CO-CH_2(CH_2)_3CH_2OH$ a a a a b c d e c d f	
a:	3.70—3.95 (m, 6 H)
b:	4.25 (m, 2 H)
c:	2.30 [t, 2(n + 1) H]
d:	1.40—1.65 [m, 6(n + 1) H]
e:	4.05 [t, 2(n + 1) H]
f:	3.65 (t, 2 H)
$CH_2=C(CH_3)-CO-OCH_2CH_2N=C=O$ a′ b′ c′ d′	
a′:	6.2 (s, 1 H)
	5.6 (s, 1 H)
b′:	2.0 (s, 3 H)
c′:	4.3 (t, 2 H)
d′:	3.55 (t, 2 H)

tion band related to isocyanate groups (at 2270 cm^{-1}). It was found that, under the experimental conditions used in this study, the reaction goes to completion within 3 hours.

An example of typical FT-IR spectra of reactants [TXCL(y) and 2-IEM] and the obtained crude product [TXCL(y)Acr] is reported in Fig. 1. Spectrum of the methacrylate end-capped product (spectrum 3) showed the absence of the peak at 2270 cm^{-1} indicating the complete reaction of the isocyanate groups of 2-IEM.

The expected structures were also confirmed by ^{1}H NMR analysis. The signal assignments of the reactants [TXCL(5) and 2-IEM] are reported in Table 1 and a typical ^{1}H NMR spectrum of the crude product TXCL(5)Acr is shown in Fig. 2.

The presence of the signal e″ in Fig. 2 at 3.45 ppm, attributed to CH₂ groups bonded to nitrogen atom of the urethane group, indicates the occurrence of the expected reaction between isocyanate and hydroxyl functionalities (note that the correspondent signal d′ of the reactant 2-IEM is at 3.55 ppm, as reported in Table 1). The peak integration is in good agreement with the expected molecular structures indicating that the double bond of methacrylate group was stable under the experimental conditions used.

Similar results were obtained also for TXCL(2)Acr and TXCL(10)Acr.

Surface characterization of systems TXCL(y)Acr/UP resin

Static contact angle values measured for water are reported in Table 2 for the three TXCL(y)Acr based products studied in the present work, also in comparison with TXCL(y) based resins. In Figure 3 the θ values are also reported as a function of the effective PFPE bulk concentration [*i.e.* eliminating the contribution of hydrogenated segments of TXCL(y) and TXCL(y)Acr copolymers].

T a b l e 2. Static water contact angle (θ) and standard deviation (s.d.) in deg for UPR/TXCL(y) and UPR/TXCL(y)Acr cured resins at different compositions

Copolymer [TXCL(y)Acr] content	0.3 phr		1.0 phr		2.0 phr	
Sample	θ	s.d.	θ	s.d.	θ	s.d.
UPR/TXCL(2)Acr	98.0	0.8	—	—	106.6	1.6
UPR/TXCL(5)Acr	94.2	1.2	103.8	0.9	106.1	2.6
UPR/TXCL(10)Acr	94.0	1.9	104.9	1.2	113.2	0.9
UPR/TXCL(2)	111.0	0.3	109.1	3.9	107.0	5.0
UPR/TXCL(5)	111.3	1.2	111.7	0.7	105.9	4.5
UPR/TXCL(10)	111.7	1.1	108.3	3.2	109.6	2.6

In all cases a strong surface modification was obtained as indicated by the high values of θ (*i.e.* the low wettability) taking into account that the typical θ values for unmodified UP resins range from 50 to 70°. It is interesting to note that for TXCL(y) additives an almost constant θ value (values between 106 and 113°) was shown by all samples with a little effect of fluorinated segment concentration. In other words, all concentrations investi-
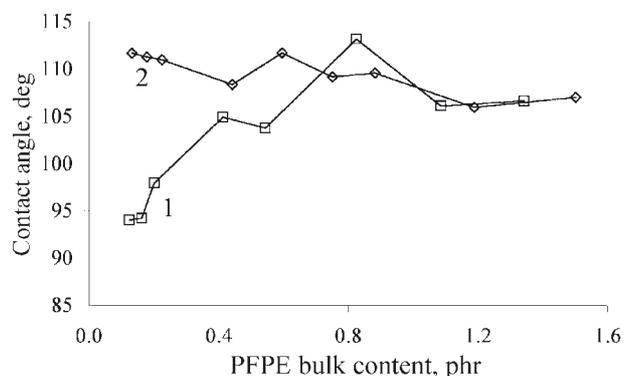

Fig. 3. Static contact angle as a function of the effective PFPE bulk concentration of UP resin/TXCL(y)Acr (1) and UP resin/TXCL(y) (2)

gated were high enough to ensure a strong and complete surface segregation of the fluorinated oligomer. On the contrary, TXCL(y)Acr additives present relatively high wettability at lower concentrations with θ about 94°. By increasing additive content θ value tends to increase up to reach a plateau for PFPE concentrations higher than 0.8 phr with θ values of about 106—110°.

Contact angle data seem to indicate that the presence of reactive methacrylate groups in TXCL(y)Acr oligomers tends to hinder the surface segregation because of the competitive crosslinking reaction between fluorinated oligomer and UP resin. In the case of TXCL(y) oligomers the fluorinated additive is not reactive towards UP resin and the surface segregation is favoured also at lower additive concentrations.

CONCLUSIONS

α,ω-Hydroxyl terminated polycaprolactone-perfluoropolyether-polycaprolactone block copolymers were easily end-capped with methacrylate functionalities. The expected structures were confirmed by FT-IR and ^{1}H NMR analysis. Fluorinated copolymers with and without methacrylate end-groups were blended with a commercial unsaturated polyester resin at different concentrations. All the mixtures were transparent after thermal curing indicating a compatibilizing effect thanks to the presence of polycaprolactone segments. Surface characterization showed a surface segregation of the fluorinated segments and thus a very high hydrophobic character of all the modified resins. Contact angles were higher than 94° even in the case of systems with a very low bulk copolymer concentration (less than 0.3 phr), even if in that case the presence of methacrylate end-groups tended to hinder the surface segregation of the fluorinated additive.

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