

Unsaturated Polyester Resins Modified with Perfluoropolyethers

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ABSTRACT: Telechelic macromers based on hydroxyterminated perfluoropolyethers (HO-R_H-PFPE-R_H-OH) with different molecular weights were used for the preparation of fluorine-containing unsaturated polyester resins (FUPR). The products resulting from the reaction of the monomers usually employed for the preparation of unsaturated polyesters with HO-R_H-PFPE-R_H-OH were in any case milky liquids. The degree of reaction of the hydroxyl terminal groups of HO-R_H-PFPE-R_H-OH was monitored by ¹H-NMR analysis on the fractions collected after sedimentation experiments; amount and composition of the sediment and sedimentation rate were found dependent on both the molecular weight of fluorinated macromer and the method used for polyesterification. The molecular weight of HO-R_H-PFPE-R_H-OH and the reaction conditions had also a strong influence on the final morphology of crosslinked polymers. A very poor interphase adhesion was observed when unreacted HO-R_H-PFPE-R_H-OH was blended with the unsaturated polyester. On the contrary, when the fluorinated macromer was allowed to react during polyesterification, the adhesion of the fluorine-rich dispersed phase to the unsaturated polyester matrix was good for low molecular weight HO-R_H-PFPE-R_H-OH and when the fluorinated prepolymer had been modified by a previous reaction with chlorendic anhydride, but it was poor, as for unreacted macromers, for high molecular weight HO-R_H-PFPE-R_H-OHs. FUPRs prepared using a low molecular weight HO-R_H-PFPE-R_H-OH exhibited a significant improvement of the flexural strength even at very low level of addition (3% by wt). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1679–1691, 1998

Key words: unsaturated polyesters; perfluoropolyethers; fluorinated polymers; Fomblin

INTRODUCTION

Unsaturated polyester resins (UPR) are products obtained from polyesterification reactions gener-

ally between polyalcohols and polyacids or their derivatives (one at least containing reactive double bonds). At the end of the polycondensation, an unsaturated coreactant liquid monomer (usually styrene in accordance with cost-performance criteria) is added to enhance reactivity and processability and, finally, after the addition of a suitable initiator, a free radical curing is carried out to transform the liquid resin into a rigid thermoset.

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This kind of resin finds wide use in the automotive field, construction and electrical applications, coatings, etc.^{1,2} Usually, cured unmodified UPRs have low strength and elongation at break, and are subjected to stress cracking and brittle fracture. For this reason, for structural applications UPRs are reinforced, like most of the thermosetting resins, with fibers or fillers while reinforcements are not needed for coating furniture or electrical components. As applications of UPRs become more and more specialized, 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 of the final chemical structure on morphology and properties. For instance, a second rubbery phase dispersed in a rigid matrix is frequently used to improve toughness of brittle thermoset resins,³ whereas special comonomers can be used to improve some specific properties¹; among these latter, chlorine-containing monomers can assure UPRs a better flame resistance, neopentyl glycol improves the hydrolysis resistance, etc.

Fluorinated products are very interesting for their unique properties, such as chemical inertia, solvent, and high temperature resistance, barrier properties, low friction coefficient, and low surface tension, which, in principle, may be transferred to other polymeric materials by blending or copolymerization. Some applications of fluorine-modified unsaturated polyesters are present in patent literature: thermosetting resins for gel coating with excellent resistance to corrosion, water, and atmospheric agents,⁴ formulations for resins and foams,⁵ and several others.^{6,7} This type of modification has been usually achieved by the use of fluorine-containing comonomers of low molecular weight, which usually lead to homogeneous UPRs and, therefore, have to be added in a significant amount to achieve appreciable improvement of performances.

The recent availability of hydroxyl-terminated telechelic macromers (HO-R_H-PFPE-R_H-OH)⁸ based on perfluoropolyether (PFPE) made possible the preparation of fluorine-modified polyesters containing PFPE blocks⁹⁻¹¹; these fluorinated macromers, which are characterized by a very low glass transition temperature (it ranges from -115 to -90°C, according to the internal fluorinated chain length), can react completely or in part with the other comonomers and, depending on the ex-

tent of this reaction and the HO-R_H-PFPE-R_H-OH molecular weight, can segregate the fluorinated blocks preferentially on the surface,^{12,13} leading to a significant improvement of the surface properties even when a relatively small amount of PFPE is contained in the bulk.

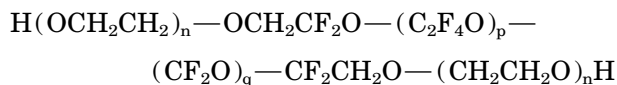
Based on these evidences it appears very interesting to explore the use of these fluorinated building blocks to modify UPRs. In fact, the introduction of very flexible PFPE chains dispersed in the rigid UPR matrix can, in principle, improve some properties, and in particular surface, mechanical, and water absorption properties. These effects can be strongly affected by the resulting morphology, which in turn, is expected to depend on the molecular weight of HO-R_H-PFPE-R_H-OH and on the degree of reaction of fluorinated macromers with the other monomers.

Therefore, aim of this work was to investigate the capability of the fluorinated macromers to react with the monomers commonly used to prepare UPRs, the morphology, and the mechanical properties of the resulting FUPRs. In particular, the effects of the polymerization method and of the molecular weight of fluorinated macromers on the extent of reaction, miscibility, morphology, and mechanical properties will be discussed.

EXPERIMENTAL

Products

Fluorinated macromers HO-R_H-PFPE-R_H-OH were supplied by Ausimont (registered name Fomblin Z-DOL TX); they are liquids with the following formula:



in which the copolymeric units —(C₂F₄O)— and —(CF₂O)—, randomly distributed along the fluorinated chain, constitute the PFPE internal body where p/q = 0.7. While the short poly(ethylene oxide) chain (schematically R_H) is the end-capping segment containing the functional hydroxyl groups; the average n value is close to 1.5. The number-average molecular weight (by ¹⁹F-NMR) of the three studied fluorinated macromers is 1100, 2200, and 3400 (in the following they are named: Z-DOL TX 1100, Z-DOL TX 2200, and Z-DOL TX 3400, respectively). Their density, mea-

sured using a DMA 48 PAAR densimeter at 20.0°C, was 1.7059, 1.7138, and 1.7763 ($\text{g} \cdot \text{mL}^{-1}$) for Z-DOL TX 1100, 2200, and 3400, respectively.

Maleic anhydride (MA), phthalic anhydride (PA) and 1,2-propanediol (PD) (all from Aldrich Chemicals, Milwaukee, WI) and Z-DOL TX were used as received for the preparation of resins with the following molar ratio: MA : PA : PD : Z-DOL TX = 2 : 1 : 3-x : x (x = moles of Z-DOL TX corresponding to 3% by weight with respect to the final resin).

Styrene, xylene, triphenyl phosphite, dibutyltin oxide, chlorendic anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride), methylethylketone peroxide (~30% by weight solution in dimethyl phthalate), and cobalt *n*-octoate (Aldrich Chemicals) were used as received without any further purification, while hydroquinone (Aldrich Chemicals) was crystallized from water before use. 1,1,2-Trichloro-1,2,2-trifluoroethane (TCTFE, supplied by Ausimont) was distilled before use and completely recovered from the reaction medium.

Polyester Synthesis

Different methods were employed for the polyesterification reactions. These methods are respectively named A, B, A' and A'', and their description is reported below.

Method A: the monomers were reacted at the temperature of 200–210°C and atmospheric pressure, under continuous mechanical stirring, with a slight flow of nitrogen and distillation of the water formed during polycondensation. The reaction was carried out (about 3–4 h) until the achievement of an acid number of 50 (mg of KOH necessary to titrate 1 g of resin).

Method B: in a first step PA, Z-DOL TX, and triphenyl phosphite (0.05% by weight with respect to the final polyester) as antioxidant, were reacted at the temperature of 140–150°C and atmospheric pressure for 90 min with the formation of a homogeneous reaction mixture. In a second step MA, PD, xylene (5% by weight with respect to the final polyester) as solvent, and dibutyltin oxide (0.1% by weight with respect to the final polyester) as catalyst were added and the reaction was carried out at the temperature of 180–190°C, under a slight flow of nitrogen and with distillation of the azeotropic mixture water–xylene; xylene returned to the reactor after it was separated from water in a Dean-Stark trap. The reaction

was stopped when the acid number was 50 (reaction time about 3–4 h), the residual xylene was finally distilled off under reduced pressure.

To enhance miscibility and reactivity of Z-DOL TX with respect to the other comonomers in the reaction system, Z-DOL TX was separately reacted with PA or chlorendic anhydride before polycondensation, as recently described for PFPE–epoxy resins.^{14,15} These modified reaction methods, named A' and A'' respectively, are described below.

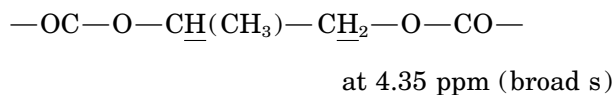
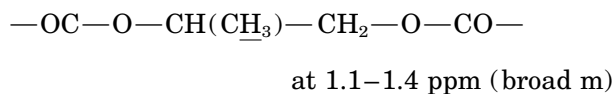
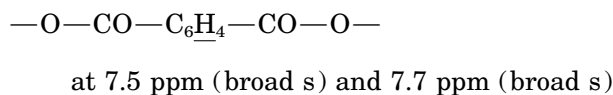
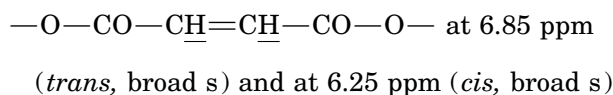
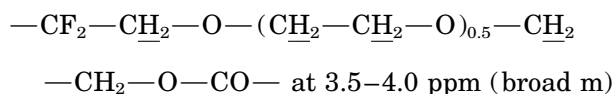
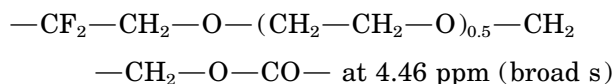
Method A': Z-DOL TX 2200 and PA (molar ratio 1 : 4) were prereacted in the presence of xylene (10% by weight) at the refluxing temperature and atmospheric pressure for 3 h. Xylene was finally distilled off under reduced pressure, while the excess of PA, which precipitates at room temperature from the liquid system, was eliminated by filtration. This fluorinated carboxyl terminated macromer was characterized by ¹H-NMR; a segmented molecular structure consisting of the original HO-R_H-PFPE-R_H-OH, with one molecule of PA reacted for each —OH terminal group, resulted. This intermediate was employed for the preparation of FUPR according to the previously described method A. The amount of PA contained in this product was subtracted from the amount of the corresponding anhydride in the base formulation to keep constant the settled molar ratio.

Method A'': Z-DOL TX 2200 and chlorendic anhydride (molar ratio 1 : 2.2) were prereacted in the presence of xylene (10% by weight) at the refluxing temperature and atmospheric pressure for 60 min, then xylene was distilled off under reduced pressure. This fluorinated carboxyl terminated macromer was characterized by ¹H-NMR; the resulting molecular structure consisted of the original Z-DOL TX with one molecule of chlorendic anhydride reacted for each —OH terminal group. This intermediate was employed for the preparation of FUPR according to the previously described method A. As in the previous case, the quantity of chlorendic anhydride contained in this product was subtracted from the overall amount of PA and MA in the base formulation to maintain the usual molar ratio.

A nonfluorinated UPR-control resin was prepared according to method A. In all cases, in the final resins styrene (50% by wt) and hydroquinone (0.055% by wt, as free radical inhibitor) were added to the polyester at the end of the polycondensation reaction. A list of all resins is reported in Table I.

¹H-NMR Analysis

¹H-NMR analysis was performed by using a CDCl₃/TCTFE mixture (50 : 50 vol/vol) as the solvent on a Varian Gemini System 300 MHz instrument. To assign the peaks in the spectra of the final resins some low molecular-weight model molecules were prepared by reaction between the diols (HO-R_H-PFPE-R_H-OH and PD) and the anhydrides (PA and MA). The corresponding peaks attribution is described below.



Sedimentation Test

The resins obtained according to the procedure described above are milky liquids because the fluorinated blocks are not miscible with polyester and styrene. As a consequence, sedimentation can occur before or during curing because the fluorinated blocks have higher density than styrene and polyesters. It is important to investigate sedimentation rate because the time needed for sedimentation can have significant effects on the final morphology if the sedimentation rate is faster than the curing rate. Sedimentation tests are also useful because the liquid settled out contains a concentration of fluorinated derivatives much higher than the bulk, and therefore, these tests combined with some analytical methods can be employed to estimate the extent of reaction of HO-R_H-PFPE-R_H-OH with the other monomers, information that, due to the low amount of PFPE in FUPRs, could not be obtained directly on the

Table I Some Characteristic Data for the Synthesis of the Unsaturated Polyester Resins Prepared

Resin Code	Molecular Weight of Z-DOL TX	Method of Synthesis
UPR-control	—	A
FUPR-M1	1100	Simple blend
FUPR-M2	2200	Simple blend
FUPR-M3	3400	Simple blend
FUPR-A1	1100	A
FUPR-A2	2200	A
FUPR-A3	3400	A
FUPR-B1	1100	B
FUPR-B2	2200	B
FUPR-B3	3400	B
FUPR-A'2	2200	A'
FUPR-A''2	2200	A''

crude products by any analytical method. In addition, we can obtain information about the miscibility of styrene and polyesters in the fluorine-rich phase.

For this purpose, 100 mL of each FUPR was thoroughly stirred and then poured into a separatory funnel; the volume of the heavy phase was measured at room temperature as a function of time, separated (using a separatory funnel with a stem consisting of a graduate burette with a stopcock and a precision of 0.05 mL) and analyzed by ¹H-NMR.

Curing

The initiator system, consisting of methylethylketone peroxide (2.5 parts by weight for 100 parts of resin) as the initiator and of cobalt *n*-octoate (0.2 parts by weight for 100 parts of resin) as the activator, was added to the resin under stirring just before curing. The mixture resin–initiator system was casted into cavities formed by a suitable silicon rubber mold blocked by two glass plates to produce specimens 127 × 12.7 × 4 mm thick. The resins were cured for 24 h at room temperature and postcured for 2 h at 100°C. The progress of the curing reaction was monitored by characteristic parameters such as gelation time and exothermic peak temperature and time; they were measured on 100 g of resin contained in a 200-mL beaker immersed in a bath thermostated at 30°C.

The gelation time was taken as the time be-

tween the addition of the initiator system and the appearance of a soft intractable gel; the exothermic peak temperature (measured with a thermocouple in the center of the beaker) was taken as the maximum temperature achieved in the bulk due to the heat generated during crosslinking; the exothermic peak time was taken as the time between the gelation time and the achievement of the exothermic peak temperature.

Morphology

Cured samples were broken by Izod impact tests at room temperature and the fracture surfaces were gold coated and examined by SEM to have information about the morphology.

Mechanical Tests

Flexural tests (Instron Series IX instrument) were carried out on cured specimens freely supported in a three-point bending with an MEF span of 57.6 mm and a crosshead speed of 1.8 mm/min. These flexural tests were carried out at 23°C on five specimens for each resin. An Izod pendulum having an energy of 1 J and a striking velocity of 3.46 m/s was used for impact measurements. These impact tests were carried out at 23°C on 10 unnotched specimens for each resin.

RESULTS AND DISCUSSION

Preparation of FUPRs

The polyester prepared by the polycondensation of PD with PA and MA is an homogeneous liquid that remains a clear liquid when blended with styrene (UPR control, with 50% by weight of styrene with respect to the overall resins). Unlike the UPR control, the reaction medium was always a milky liquid during the synthesis of FUPRs (with both A and B methods); this means that the unreacted fluorinated macromer and its reacted derivatives aggregated to form a second phase that remained during all the polyesterification reaction and also when styrene was added after polymerization. The presence of a second fluorine-rich phase does not negatively affect the time necessary to achieve the settled acid number, but, on the contrary, this time was usually slightly lower than for UPR.

The phase separation of the fluorinated mac-

romer could limit or completely hinder the reaction of hydroxyl terminal groups of HO-R_H-PFPE-R_H-OH with other comonomers, and the first point we checked was if and to what extent this reaction occurred. This is a very important point because the resulting block copolymers can have a strong effect on morphology and mechanical properties. However, due to the small amount of HO-R_H-PFPE-R_H-OH added, the concentration of terminal groups was so low in the crude products that spectroscopic methods, such as ¹H-NMR and FTIR, were not able to give an answer to this question. We were able to achieve more information about this point by the ¹H-NMR analysis of the fluorine-rich phase collected after sedimentation, as described below.

Chemical Characterization of FUPRs

As said before, the small amount of fluorinated macromer added and the not homogeneous nature of the FUPRs rise the problems of the evaluation of the extent of reaction of HO-R_H-PFPE-R_H-OH and of a possible sedimentation phenomenon, which can generate differences in composition within the thickness either in the container during storage and/or in the mold during the curing process. The driving force for sedimentation depends on the miscibility characteristics of the components and on the different densities of the phases; in the present case it finds its origin in the high density of the fluorinated blocks (see Experimental) and in the poor miscibility of the fluorinated compounds with styrene and polyester resin, as shown by the large differences in the solubility parameters.¹⁶ In addition, sedimentation can be strongly affected by the formation of polyester-PFPE block copolymers that can act as emulsifiers. Therefore, sedimentation rate measurements can be used to obtain indirect evidence about the extent of reaction of HO-R_H-PFPE-R_H-OH during polycondensation, and the ¹H-NMR analysis of the fluorine-rich phase settled out from the liquid resin can be used to obtain direct information about the composition of this phase and, due to the high PFPE concentration, about the extent of reaction of the hydroxyl groups of HO-R_H-PFPE-R_H-OH.

The volume fraction of the PFPE-rich phase settled out at room temperature was recorded against time for FUPRs and for blends of UPR control with 3% by weight of various Z-DOL TX (these blends were named FUPR-M_x, with x = 1,

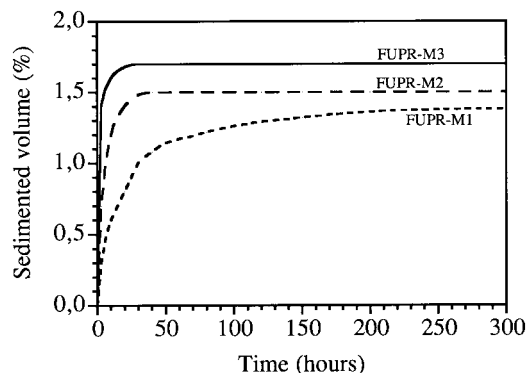


Figure 1 Sedimentation tests for FUPR-Ms.

2, 3 for Z-DOL TX 1100, 2200, and 3400, respectively).

Results of sedimentation-rate tests for FUPR-M containing HO-R_H-PFPE-R_H-OH with different molecular weight are reported in Figure 1 and Table II. The sedimentation-rate curves of Figure 1 reflect primarily differences of density and miscibility between phases, and as expected, show that both the maximum volume of sediment and the sedimentation rate increase by increasing the molecular weight of fluorinated macromers. The volume of sediment increases with time, and reach an asymptotic value of 1.4, 1.5, and 1.7 mL/100 mL, for FUPR-M1, FUPR-M2, and FUPR-M3, respectively. While most of the Z-DOL TX 3400 was sedimented in about 10 h, the rate of sedi-

mentation was significantly reduced for Z-DOL TXs with lower molecular weight. ¹H-NMR analysis of sediments was performed to achieve information about the miscibility of styrene and polyester resin with unreacted Z-DOL TX; ¹H-NMR spectra of pure Z-DOL TX and of the phase separated after sedimentation of FUPR-M1 are reported in Figure 2(a) and (b), respectively. As it appears, the spectrum of the phase recovered after sedimentation contains peaks attributable to the R_H segment of fluorinated macromer (3.5–4.0 ppm), but also signals at lower and higher fields (1.1–1.4 and 5.7–7.7 ppm); even though the spectrum appears quite complex, it was possible to assign these peaks to the monomeric units contained in the polyester and to styrene with the help of more simple model products properly synthesized (see Experimental). Consequently, from the relative intensity of these peaks, the amount of styrene and polyester in the sediment was estimated using signals at 7.4–7.9 ppm for phthalic moieties, at 6.8–7.0 ppm and 6.2–6.3 ppm for fumaric and maleic moieties, respectively, and at 6.7 or 5.7 ppm for styrene; the results are shown in Table III. From these data it is evident that polyester and styrene are slightly miscible in the fluorine-rich phase and that the percentage of both styrene and polyester decreases with increasing the molecular weight of HO-R_H-PFPE-R_H-OH.

From the density values of HO-R_H-PFPE-R_H-

Table II Sedimentation Tests: Asymptotic Volume of Sediment and Times for 1% of Sediment and for 50% of Asymptotic Volume

Resin Code	Asymptotic Volume of Sediment (%) ^a	Time to Obtain 1% ^a of Sediment (h)	Time for 50% ^b of the Asymptotic Volume (h)
FUPR-M1	1.4	30	16
FUPR-M2	1.5	8	6
FUPR-M3	1.7	0.8	0.6
FUPR-A1	0.5	— ^c	40
FUPR-A2	1.9	15	14
FUPR-A3	1.7	17	15
FUPR-B1	0.2	— ^c	27
FUPR-B2	1.3	60	36
FUPR-B3	1.5	16	12
FUPR-A'2	1.1	17	7
FUPR-A''2	1.9	60	— ^d

^a Percent respect to the volume of resin.

^b Percent respect to the volume of sedimented phase.

^c Asymptotic sedimented volume less than 1%.

^d For this sample the sedimentation process occurs in two steps.

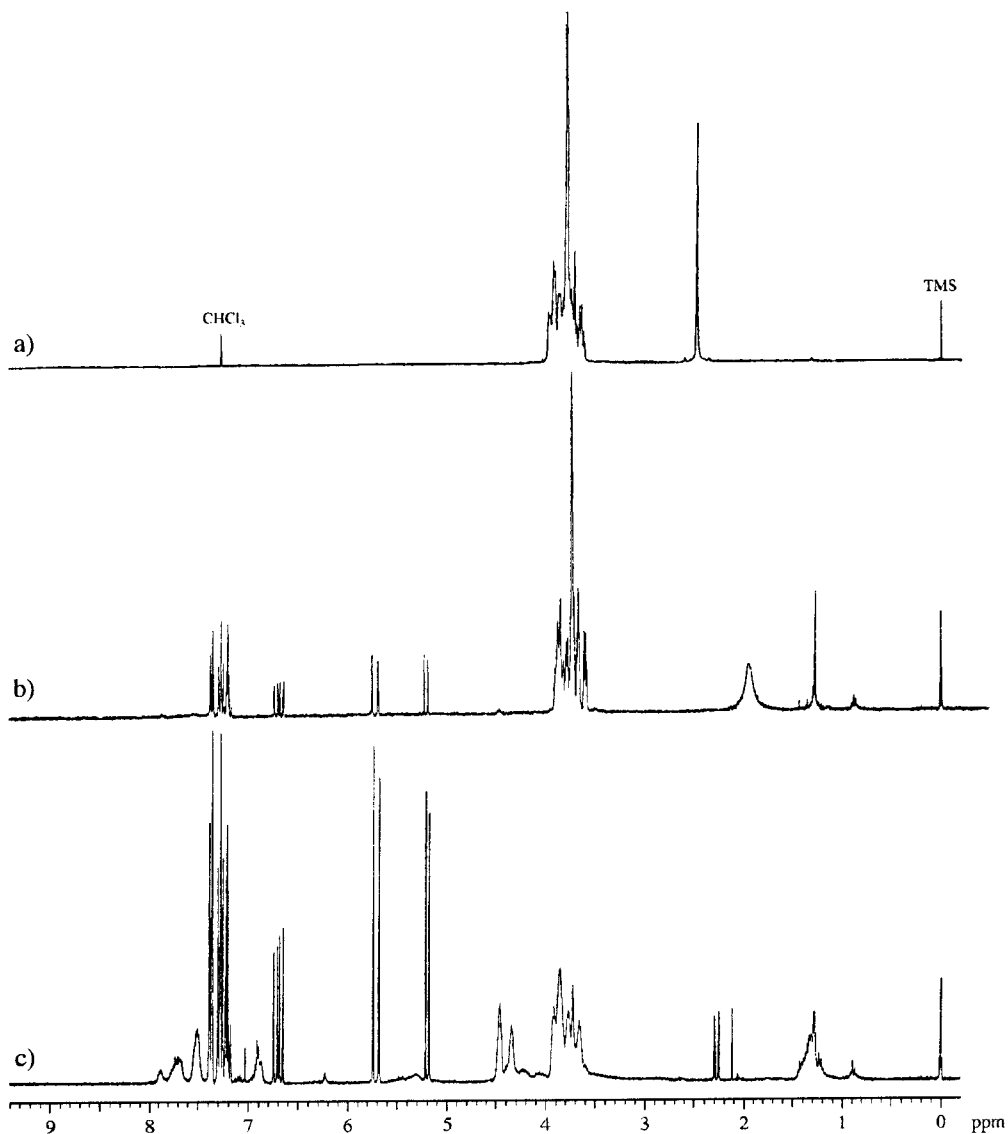


Figure 2 $^1\text{H-NMR}$ spectra of (a) Z-DOL 2200, (b) sedimented phase of FUPR-M2, and (c) sedimented phase of FUPR-B2.

O_Hs used (see Experimental), it was also possible to estimate the percentage of Z-DOL TX in the sediment; it resulted of 65, 76, and 90% of the initial amount for Z-DOL TX 1100, 2200, and 3400, respectively. These results can be explained by considering that the fluorinated macromers are not monodispersed species, and that the fraction of fluorinated molecules with low molecular weight and/or with long hydrogenated moieties R_H is "miscible" in the styrene-polyester matrix; of course, this fraction decreases when the average molecular weight of HO-R_H-PFPE-R_H-OH increases.

Sedimentation tests were also carried out for all FUPRs; some typical curves and data are reported in Figure 3 and in Table II. In some cases, sedimentation curves reflect a complex process of phase separation and sedimentation, as for instance, for samples FUPR-A'2 and FUPR-A1, for which there is clear evidence that sedimentation occurred in two or more steps. It is also evident that these curves are different from those of Figure 1, obtained by a simple blending of unreacted HO-R_H-PFPE-R_H-OH with UPR, and are dependent on the method of preparation of FUPR (compare curves FUPR-A2, FUPR-A'2 and FUPR-

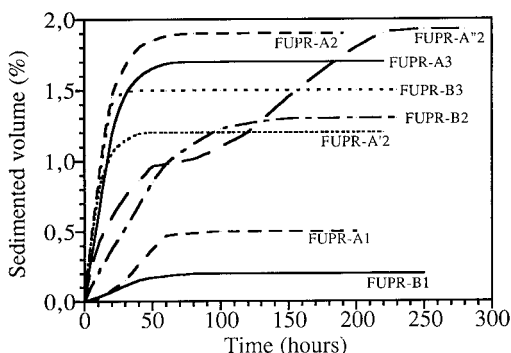
Table III H-NMR Analysis of Sedimented Phases

Resin Code	Asymptotic Volume of Sediment (%)	Composition of Sedimented Phase (% wt)			Sedimented PFPE (%) ^b	% of Reacted PFPE End Groups in Sedimented Phase
		PFPE	Styrene	UP Resin ^a		
FUPR-M1	1.4	91	6	3	65	0
FUPR-M2	1.5	96	3	1	76	0
FUPR-M3	1.7	97	2	1	90	0
FUPR-A1	0.5	60	12	28	14	40
FUPR-A2	1.9	84	6	10	80	36
FUPR-A3	1.7	92	3	5	83	32
FUPR-B1	0.2	57	13	30	5	60
FUPR-B2	1.3	76	8	16	50	57
FUPR-B3	1.5	76	8	16	57	56

^a Diol and anhydride moieties.^b With respect to the initial amount of PFPE.

A"2). It seems reasonable to explain these data by assuming that when a hydroxyl terminal groups of HO-R_H-PFPE-R_H-OH react with the other monomers the compatibility of Z-DOL TX with the UPR medium increases, and that this increase is higher when the polyester segments bonded to the PFPE block are longer. It derives that, for the same molecular weight of fluorinated macromer, the higher is the extent of reaction, the slower should be both the rate of sedimentation and the asymptotic volume of the sediment. Based on this consideration, it is noteworthy to compare curves of Figures 1 and 3 and data of Table II for samples containing Z-DOL TX of the same molecular weight simply blended with UPR-control (FUPR-Ms) or added as a comonomer during polyesterification (FUPR-Ax and FUPR-Bx). For Z-DOL TX 1100 it appears that the asymptotic volume of the sediment is significantly lower

for FUPR-A1 and FUPR-B1 than for the corresponding FUPR-M1. It is also evident that polymerization methods A and B gave products with a significantly different behavior towards sedimentation rate. According to the above considerations, we can conclude that the reaction of the fluorinated macromer in sample FUPR-B1 occurred to a higher extent. This conclusion is also supported by the ¹H-NMR analysis. A typical spectrum of sediment is shown in Figure 2(c); according to the assignment reported in the experimental part, from the relative intensity of the peak at 4.4–4.5 ppm (typical of a reacted hydroxyl terminal group of Z-DOL TX) with respect to the peaks at 3.5–4.0 ppm (typical of the protons of the unreacted hydrogenated R_H segment) it was possible to estimate the extent of reaction of the hydroxyl terminal groups of Z-DOL TX contained in the dispersed phase. Analogously, from the peaks attributable to styrene and to polyester (see Experimental) it was possible to estimate the composition of the sediment. The data are reported in Table III. For FUPR-B1 prepared with polymerization method B, the overall percentage of Z-DOL TX in the sediment is lower and the fraction of its hydroxyl terminal groups reacted is higher than for FUPR-A1, prepared with method A. Even though the volume fraction of the sediment is lower for FUPR-B1, it is interesting to note that the styrene and polyester content is almost identical with that of FUPR-A1. It is also noteworthy that a very limited amount of the initial Z-DOL TX 1100 is contained in the fluorine-rich phase (14 and 5% for FUPR-A1 and FUPR-

**Figure 3** Sedimentation tests for some typical FUPRs.

B1, respectively), while most of Z-DOL TX 1100 remains in the bulk, dissolved or suspended as a metastable finely dispersed phase in the styrene–polyester matrix.

If we compare data obtained for samples prepared from Z-DOL TX 2200 (FUPR-M2, FUPR-A2 and FUPR-B2) we can observe again that polymerization method B is more effective than method A (for FUPR-B2 the fraction of Z-DOL TX in the sediment is lower, the fraction of its terminal hydroxyl groups reacted is higher, and the amount of styrene and polyester is slightly higher). We can also observe that the volume of sediment for FUPR-A2 is higher than for FUPR-M2; this result can be accounted for by the higher amount of styrene and polyester contained in the sedimented phase of FUPR-A2 as it appears from $^1\text{H-NMR}$ analysis. Very similar results were observed and the same comments can be extended to FUPRs containing Z-DOL TX 3400 (see Table III).

From the above discussion we can conclude that the terminal hydroxyl groups of HO-R_H-PFPE-R_H-OH do not react completely during polycondensation, that the extent of reaction increases when the molecular weight of HO-R_H-PFPE-R_H-OH is lower, and when the polymerization method is B rather than A. Because the solubility of the resulting fluorinated products with styrene and polyester resin increases with the extent of this reaction, the inclusion of styrene and polyester in the dispersed phase increases with decreasing the molecular weight of HO-R_H-PFPE-R_H-OH. As a consequence, both the morphology

before curing and the tendency to sedimentation are strongly affected by the molecular weight of the Z-DOL TX and (to a less extent) by the method of polymerization; in principle, an appropriate choice of HO-R_H-PFPE-R_H-OH and polycondensation method can be used in the control and fine tuning of morphology.

Curing

Another important aspect that may be influenced by the presence of the fluorinated products is the curing rate of the FUPR. Gelation time, exotherm peak time, and exotherm peak temperature are the parameters usually employed to characterize the curing process; they are reported in Table IV for FUPRs and UPR control. It is interesting to note that the curing behavior is affected by both the type of Z-DOL TX used and the method of preparation of the polyester resin. In general, the polymerization method A leads to a slight decrease of gelation time with respect to UPR control and a more significant decrease with respect to method B. Although gelation time decreases regularly with increasing the molecular weight of Z-DOL TX for method A, the opposite effect was observed with method B. The increase for FUPR-B3 was so high that the crosslinking reaction did not take place with the usual amount of initiator, and it was necessary to increase the amount of the initiator to have curing in a reasonable time. Gelation time and exotherm peak time are approximately the same for the resins prepared with method A, A', and A". As expected, the tempera-

Table IV Curing Reaction: Gelation Time, Exotherm Peak Time, and Temperature

Resin Code	Gelation Time (min)	Exotherm Peak Time (min)	Exotherm Peak Temperature (°C)
UPR-control	68	18	168
FUPR-M2	61	14	176
FUPR-A1	72	19	173
FUPR-A2	51	16	178
FUPR-A3	48	13	181
FUPR-B1	68	25	158
FUPR-B2	89	35	155
FUPR-B3 ^a	70	17	173
FUPR-A'2	51	12	180
FUPR-A"2	60	15	175

^a A greater amount of initiator was needed to obtain gelation.

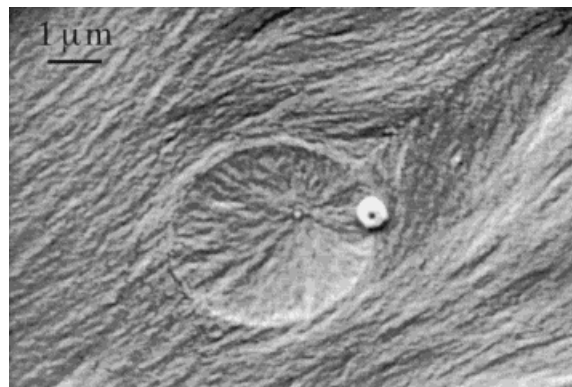


Figure 4 SEM micrograph of FUPR-A1.

ture corresponding to the maximum in the exotherm peak is higher for the resins with a higher gelation rate.

The differences observed for the curing behavior of the resins prepared with method B could be attributable to the presence of triphenyl phosphite and/or tin catalyst that may interfere with the initiator system, leading to a marked delay in the crosslinking process. Also, the volume and the dimension of the dispersed phase seems to play an important role, particularly in the case of method B; FUPR-B1, having a little volume of sedimented phase (0.2% at equilibrium), exhibits a delay in the curing reaction shorter than FUPR-B2, which has a maximum volume of sedimented phase of 1.3%, and for FUPR-B3, which has a maximum volume of sedimented phase of 1.5%. Preferential segregation of initiator, catalyst, and/or triphenyl phosphite in the fluorine-rich phase may explain the observed results.

In any case, gelation times at room temperature are always much shorter than times typical of the sedimentation process; this rules out significant effects of sedimentation phenomena on the final morphology.

Morphology of Cured FUPRs

Micrographs of all the resins containing PFPE segments exhibit a fracture morphology typical of brittle thermosets in which the presence of a dispersed phase in a continuous matrix is evident. Some typical SEM micrographs of the fracture surfaces of FUPR-A1, FUPR-A'2, FUPR-A3, FUPR-B2, and FUPR-M2 are shown in Figures 4–8.

In accordance with the above discussion, the morphology is strongly dependent on the molecu-

lar weight. The fracture surfaces of samples FUPR-A1 and FUPR-B1, containing Z-DOL TX 1100, look very similar; they show few particles, spherical in shape, attributable to a fluorine-rich phase. Interestingly, a lamella-like texture similar to that of the matrix is observed in the dispersed particles (see Fig. 4), probably as a consequence of the relatively high miscibility of styrene and polyester in the fluorine-rich domains (see Table III) where they polymerize by free radical curing. The particle sizes are about 3–5 μm in diameter, and it is noteworthy the very good adhesion to the matrix and that the lamellas in the particles appear ordered in corona; these domains are in part or totally crossed by fracture lines. Similar morphologies were previously observed for PFPE-modified epoxy-resins.^{14,15}

On the contrary, the fracture surfaces of FUPRs prepared with Z-DOL TX 2200 (FUPR-A2, FUPR-A'2, and FUPR-B2) exhibit particles with greater sizes (5–15 μm) having generally a very poor adhesion to the matrix (see Fig. 5). However, sample FUPR-A'2 represents an interesting exception (see Fig. 6); in this case, Z-DOL TX 2200 was reacted with chlorendic anhydride before polycondensation, and the observed significant modification of the morphology can be explained by a chemical compatibilization of Z-DOL TX before polymerization. The dispersed phase appears similar to that of FUPR-A1 and FUPR-B1, but with a greater size of the particles (about 10 μm).

Figure 7 shows the fracture surface of FUPR-A3, a resin containing Z-DOL TX 3400; again, the fluorine-rich phase is dispersed in the UPR matrix (with typical sizes of 3–10 μm), but, unlike the above cases, the dispersed phase presents large cavities and occlusions of granular aspect near

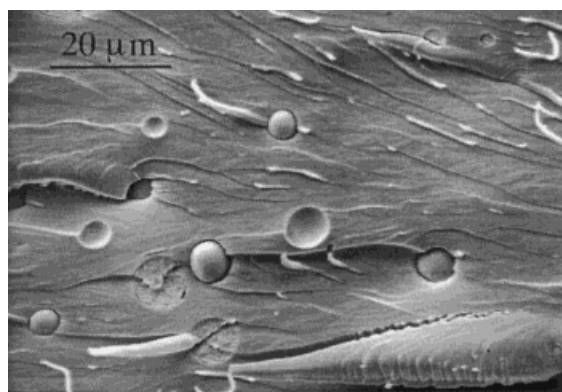


Figure 5 SEM micrograph of FUPR-B2.

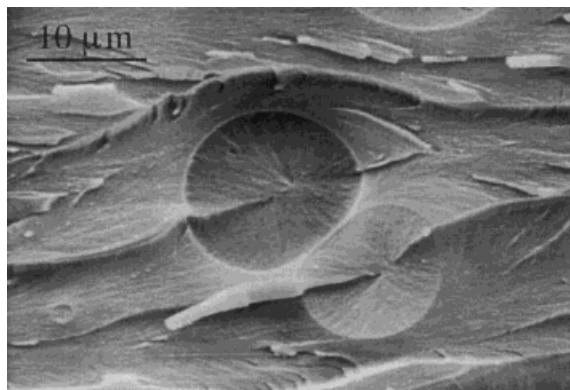


Figure 6 SEM micrograph of FUPR-A'2.

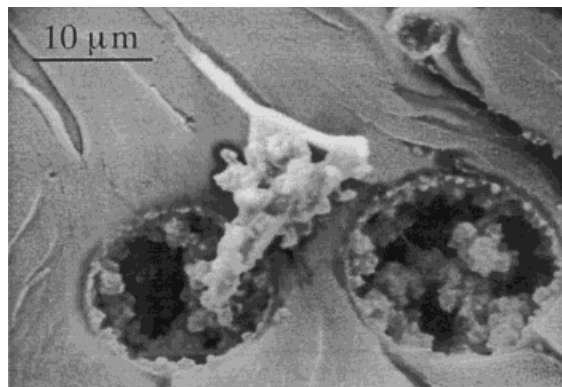


Figure 8 SEM micrograph of FUPR-M2.

the interface. The same type of morphology was observed also for FUPR-B3 and for FUPR-M2 (see Fig. 8), prepared by simple mixing of UPR control and Z-DOL TX 2200. A similar morphology was previously observed for UPR containing carboxyl-terminated poly(butadiene-*co*-acrylonitrile) liquid rubber.¹⁷ In that article the nodules were ascribed to crosslinked UPR deriving from the polymerization of the styrene and UPR initially dissolved in the dispersed phase. We can tentatively extend that interpretation to the morphology observed for FUPR-A3, FUPR-B3, and FUPR-M2 resins, even though the volume occupied by the nodules seems higher than expected from the data of composition reported in Table III for the sediment at equilibrium. However, in a liquid reactive system such as polyester resins, the molecular weight and the viscosity of the matrix change dramatically during curing, and the final morphology is, therefore, fixed by the competition of thermodynamics and kinetics of phase segregation and curing.

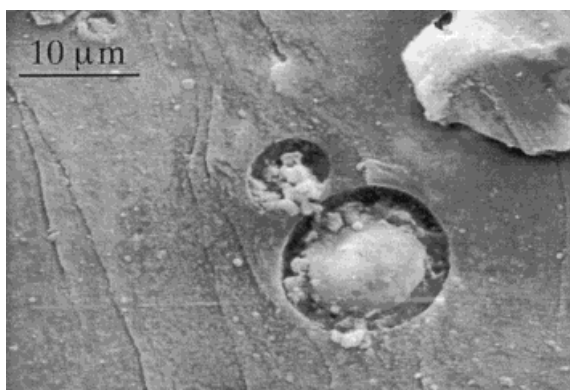


Figure 7 SEM micrograph of FUPR-A3.

According to our results the morphology of FUPRs seems primarily dependent by the mutual miscibility of fluorinated and hydrogenated products, which in turn, depends on the molecular weight and the extent of reaction of the fluorinated macromer. As a consequence, the adhesion between dispersed phase and matrix is improved by decreasing the molecular weight of ZDOL TX or by a suitable chemical modification through reaction of the fluorinated macromers (method A''), which increases the compatibility with respect to the other comonomers.

Mechanical Properties

The results obtained by flexural tests for FUPRs containing Z-DOL TX 1100 (FUPR-A1 and FUPR-B1) and those obtained by impact tests for all the FUPRs are reported in Table V.

It is well known that toughening of UPRs is a formidable task and that until now UPR-additive systems with significant toughening is still unknown.¹⁷ In this case, impact tests data show that modification of UPR with PFPE leads to a general decrease of impact energy, irrespectively of the initial molecular weight of the fluorinated macromer and of the polymerization method. The highest values of resilience for FUPR resins were obtained for FUPR-A1 and FUPR-B2, containing Z-DOL TX 1100 and 2200, respectively, with morphologies quite different (compare Figs. 4 and 5). The lack of correlation between impact properties and morphology seems a general rule; for instance, FUPR-A1 and FUPR-B1, which show very similar morphology, have quite different impact resistance, and also FUPR-A'2, which showed a very good adhesion, has the lowest value of impact resistance.

Table V Mechanical Properties of FUPRs: Flexural and Impact Behaviour

Resin Code	Flexural Tests				Impact Tests Resilience (kJ/m ²)
	Young Modulus (GPa)	σ_b (MPa)	ϵ_b (mm)	Adsorbed Energy (J)	
UPR-control	3.8	80	3.09	0.244	4.8
FUPR-M2	3.4				2.6
FUPR-A1	3.4	102	4.90	0.483	4.0
FUPR-A2	3.4				3.1
FUPR-A3	3.2				2.8
FUPR-B1	2.8	81	4.34	0.355	3.0
FUPR-B2	3.2				4.0
FUPR-B3	3.2				2.9
FUPR-A'2	3.5				3.8
FUPR-A''2	3.5				2.6

On the contrary, the effect of miscibility and morphology seems significant for low-rate loading tests such as flexural tests. It is interesting to note that both FUPR-A1 and -B1 show significantly greater values of maximum load and elongation with respect to UPR control resin. This means a marked increment of the energy adsorbed in the fracture, twice for FUPR-A1 with respect to UPR control. The increase in strength is accompanied by a slight decrease in modulus. Based on the data from sedimentation tests (see Table III) from which it results that more than 80% of the initial fluorinated macromer remains dissolved or very finely dispersed in the styrene–polyester matrix, we can tentatively explain the improvement of the flexural strength to the presence of very flexible PFPE blocks included in the rigid network formed by curing.

CONCLUSIONS

Fluorine-modified unsaturated polyester resins (FUPR) can be prepared by using telechelic perfluoropolyether-containing macromers during the preparation of the polyester. The final characteristics of the resulting FUPR depend on the method of synthesis of the polyester and on the molecular weight of the PFPE-based macromer. In particular, the lower is the molecular weight of fluorinated macromers, the higher is the degree of reaction with other monomers and the compatibility of the PFPE blocks with the polyester resin. This is reflected in the sedimentation behavior, in the composition of the phases, and in the final mor-

phology. For the fluorinated macromers with the lowest molecular weight (1100) a very good adhesion of the fluorine-rich phase with the matrix was found for both the polymerization methods tested. On the contrary, for PFPE of higher molecular weights we usually observed a very poor adhesion, except when the fluorinated macromer of molecular weight 2200 was previously reacted with chlorendic anhydride, in which case good adhesion was observed.

A significant increase in toughness with respect to UPR was observed under flexural tests for FUPRs containing PFPE with molecular weight 1100, whereas the impact resistance was always lower for FUPRs than for UPR control.

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