

New Fluoro-Modified Thermoplastic Polyurethanes

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Received 10 December 2001; accepted 23 May 2002

ABSTRACT: New fluoro-modified thermoplastic polyurethanes containing perfluoropolyether (PFPE) blocks were synthesized by the reaction of a fluorinated macrodiol with a hydrogenated prepolymer based on poly(tetramethylene glycol) and 4,4'-methylene-bis-phenylisocyanate, followed by subsequent chain extension with 1,4-*n*-butanediol. This multistep bulk process opened the way for a new family of polymeric materials whose tensile properties appear to be excellent and unchanged in comparison with the corresponding unmodified hydrogenated polymers. Dynamic mechanical analysis and differential scanning calorimetry revealed peculiar characteristics. These polymers showed an unusual multiphase structure in which not only the hard

and the hydrogenated soft segments were self-organized, but also a second soft phase, constituted by the PFPE segments, was present. Moreover, an easier hard-phase segregation and self-organization were observed, as was evidenced by the higher melting temperatures of the semicrystalline phase. This unique characteristic combined with a selective enrichment of PFPE segments to the surface, as indicated by the unusually low coefficient of friction data and superior chemical resistance. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2279–2294, 2003

Key words: polyurethanes; macromonomers; elastomers; fluoropolymers; mechanical properties

INTRODUCTION

Polyurethane (PU) chemistry has proven to be a very versatile way to obtain high-performance materials useful for many different applications, including coatings, adhesives, and elastomers. These polymers, synthesized by a simple polyaddition reaction, show tailor-made properties coming from the broad variety of chemicals used.¹

Thermoprocessable polyurethane elastomers (TPUs) generally fall into two basic categories: polyester based and polyether based. The first polymers are more sensitive to hydrolysis but offer better mechanical properties and greater resistance to solvents and oxidative degradation. As a consequence, superior stability at the processing temperature is generally observed. Polyether-based TPUs, however, are hydrolysis resistant and have better low-temperature characteristics.^{2–5}

This class of polymeric materials owes its unique properties to a multiphase structure in which the hard domains, dispersed in a continuous soft phase, act as physical crosslinks, improving the mechanical properties of the polymeric network.⁶

The nature of the reagents largely affects the final properties of the polymer, not only because some of the specific characteristics of the reagents can be transferred to the material, but also because the composi-

tion and the compatibility of the comonomers rule the morphology and the extent of the phase segregation.^{7–10} In fact, the incompatibility between low-polar soft segments and polar hard blocks is a very effective driving force promoting the microphase separation.

Many scientific contributions have referred to the influence of the soft-segment structure, molecular weight (MW), MW distribution, and functionality on the final properties.^{11–14}

Moreover, literature data have shown that surface characteristics are strictly correlated with the composition and morphology of the polymer, being the enrichment phenomena of certain components at the surface governed by the bulk structure, the extent of phase separation near the surface, and the surface free energy difference between the main components. These surface characteristics are very important for many applications; for this reasons, some special polymers, obtained by the partial incorporation of different macrodiols (i.e., polyether diols with different MWs and structures or polyether/polyester mixtures), have been synthesized.^{15–19} In all cases, useful combinations of properties have been obtained, but even if macrodiols with significantly different structures and chemical-physical characteristics have been incorporated into PUs (i.e., mixture of apolar and polar diols), a single soft phase has always been observed.^{20–22}

The effect of fluorinated monomers on the final properties has also been explored. However, only a few examples of fluorine-containing PUs have been described.^{23–27} The lack of extensive research in this field is mainly due to the poor availability of useful

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fluorinated monomers or macromers. In fact, the largest part of the scientific contributions refers to the use of short fluorinated chain extenders. These diols, because of their low MW, do not show any tendency to self-segregate from the hydrogenated moiety. Consequently, these materials present neither improved elastomeric properties nor a fluorine enrichment to the surface.

Completely different results are achieved if a poly-(fluoroalkylene)diol 1 [perfluoropolyether (PFPE) diol], having a relatively high MW, is used. In this case, a general fluorine enrichment at the surface is observed; this tendency seems to be independent of the composition and nature of the polymer, being observed in PUs,²⁸ polyester, and polyacrylates.^{29–33}

Earlier studies,^{34,35} focused on both crosslinked and linear PUs obtained by a full replacement of the hydrogenated soft macromer by a PFPE segment, have confirmed the previously mentioned results. They have shown that PFPE-containing PUs offer a larger service temperature range than conventional PUs, combined with superior chemical resistance and surface characteristics.

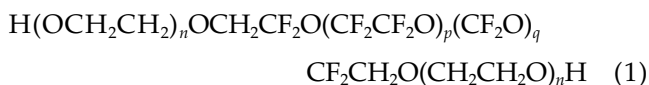
Therefore, PFPE-based PUs offer significant advantages in applications where unusual bulk and surface properties are required. In fact, this approach allows one to design new structures that depending on the extent of fluorine modification, can maintain most of the outstanding properties of the fluorinated macrodiols.

For all these reasons, we were interested in focusing this work on the synthesis of new fluorine-containing TPUs obtained by a partial substitution of the conventional macrodiols with PFPE-based building blocks.

EXPERIMENTAL

Materials

The poly(fluoroalkylene)diol (1) (ZDOLTX, Ausimont, Bussi, Italy) used in this work was a commercially available building block³⁶ containing a mixture of oligomeric species, whose structure consisted of a random distribution of $-\text{CF}_2\text{CF}_2\text{O}-$ (C_2 unit) and $-\text{CF}_2\text{O}-$ (C_1 unit), end-capped by ethoxylated units $-\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, (number-average MW = 2300, polydispersity = 1.6, $\text{C}_2/\text{C}_1 = 1.0$, $n = 1, 2$):



This macromer was dried before use under vacuum at 90°C for 2 h.

Poly(tetramethylene glycol) (PTMEG; PTMEG 2000 MW and PTMEG 1000 MW, Aldrich, Milan, Italy) and polybutadienediol (PBD; PBD 2400 MW, Aldrich) were dried before use under vacuum at 90°C for 2 h.

1,4-*n*-butanediol (BDO; Aldrich) was dried before use in vacuum at 70°C for 2 h. 4,4'-methylene-bis-phenylisocyanate (MDI; ICI) was purified from the dimer and urea impurities by filtration at 40°C.

Hydroquinone *bis*(2-hydroxyethyl)ether (Hy Aldrich) was used as received.

Finally, the solvents used for the chemical aging test, dimethylformamide (DMF), methyl ethyl ketone (MEK), tetrahydrofuran (THF), and ethyl acetate (all from Aldrich) were used as received. Fuel C was prepared according to ASTM specifications by the mixture of 50% v/v *iso*-octane and toluene (Aldrich, without further purification).

Synthesis of polymeric materials

All of the polymers were prepared with a two-step (fully hydrogenated polymers) or a three-step (PFPE-containing PUs) polymerization techniques. In both cases, bulk conditions were applied.

Fully hydrogenated PUs

The appropriate amount of diisocyanate (MDI) was added to the macrodiol under nitrogen with vigorous stirring. The temperature was then gradually raised to 90°C, and held for 3 h to complete the prepolymer synthesis.

The prepolymeric mass was degassed, and the amount of chain extender (BDO or Hy) that was necessary to provide 95% stoichiometry was added and blended in well for 2–4 min.

The mixing temperature was varied between 40 and 100°C, depending on the polymer composition and mass viscosity.

The mass was cast in a mold and placed in a press to complete the polymerization (2 min at 220°C plus 7 h at 130°C).

The completion of the reaction was monitored by IR analysis through the disappearance of the isocyanate absorption band at 2260 cm^{-1} .

PFPE-containing PUs

A different technique was used to synthesize the PFPE-containing polymers. In this case, the adopted three-step procedure allowed us to reduce the homopolymerization tendency due to the strong incompatibility between the hydrogenated and fluorinated reagents.

In the first step, the synthesis of the hydrogenated $-\text{NCO}$ end-capped prepolymer was carried out by the bulk reaction of the conventional macrodiol with MDI ($\text{NCO}/\text{OH} = 2$) at 90°C for 3 h under nitrogen. Then, the defined amount of fluorinated macrodiol was added, and the reaction mass was kept at 90°C for 3 h to complete the conversion to the corresponding

TABLE I
Polymer Compositions

Sample	Equivalent ratio M/MDI/BDO	Hard phase (vol %)	ZDOLTX (equiv wt)	Fluorine content (wt %)
PTB-500-33	1:2:1	33.0	—	—
PTB-500-39	1:2.5:1.5	39.0	—	—
PTB-500-44	1:3:2	43.8	—	—
PTB-500-46	1:3.2:2.2	45.7	—	—
PTB-1000-20	1:2:1	19.8	—	—
PTB-1000-24	1:2.5:1.5	24.2	—	—
PTB-1000-28	1:3:2	28.1	—	—
FPTB-500-32	1:2:1	31.6	1150	15.4
FPTB-500-37	1:2.5:1.5	37.4	1150	14.1
FPTB-500-42	1:3:2	42.3	1150	13.0
FPTB-500-44	1:3.2:2.2	44.1	1150	12.6
FPTB-1000-22	1:2:1	21.5	1150	15.8
FPTB-1000-23	1:2.2:1.2	23.4	1150	15.5
FPTB-1000-26	1:2.5:1.5	26.2	1150	14.9
FPTB-1000-30	1:3:2	30.3	1150	14.1
PBD-1200-23	1:3:2	23.2	—	—
PBD-1200-29	1:4:3	29.3	—	—
PBD-1200-35	1:5:4	34.5	—	—
FPBD-1200-24	1:3:2	24.1	1150	4.3
FPBD-1200-30	1:4:3	30.3	1150	3.9
FPBD-1200-36	1:5:4	35.6	1150	3.6
FPBD-1200-40	1:6:5	40.1	1150	3.3

fluoro-modified prepolymer. MDI was eventually added if required by the stoichiometry. The addition of 95% of the stoichiometric amount of BDO completed the chain extension. The reaction mass was vigorously stirred under vacuum for 2–4 min at a temperature ranging from 70 to 100°C.

The mass was cast in a mold and placed in a press to complete the polymerization according to the same temperature profile used for hydrogenated polymers.

The completion of the reaction was monitored by IR analysis through the disappearance of the isocyanate absorption band at 2260 cm⁻¹.

Polymer characterization

All polymers were obtained as slabs (2 or 12 mm thick) by the casting process; the samples were conditioned 2 weeks at room temperature before testing.

All materials were characterized with respect to their hard-phase content, soft-segment equivalent weight, and fluorine content.

The designations PTB and PBD are used to describe polytetramethylene-based and polybutadiene-based PUs, respectively, chain extended with BDO, whereas the designation PTH and FPTH relate to a special series, based on Hy as a chain extender, synthesized for the chemical resistance test.

The designation F means that the hydrogenated soft segments were partially substituted by PFPE segments.

The number immediately following the system name refers to the hydrogenated soft-segment equivalent weight, whereas the last number following the dash refers to the hard-phase content (vol %, calculated on the base of composition and reagents density). Thus polymer PTB-1000-28 is a PTMEG 2000-based PU, chain extended with BDO and having 28% v/v of the hard phase. FPTB-1000-30 is the corresponding polymer modified by ZDOLTX (equivalent weight = 1150).

IR analysis

The IR measurements were made with a FTIR Nicolet 20 SX spectrometer (Madison, WI), with a miniature diamond navel cell P/N 2500 for polymeric material analysis.

Differential scanning calorimetry (DSC)

DSC was carried out with a PerkinElmer DSC 2 instrument (Wellesley, MA), *n*-hexane, *p*-nitrotoluene, and indium calibrated. Melting temperature (*T_m*) was measured on heating runs from 25 to 250°C (at 10°C/min), whereas glass-transition temperature (*T_g*) values were determined by heating (20°C/min) from -160 to 20°C.

TABLE II
DSC Events

Sample	<i>T_g</i> (°C)		Highest <i>T_m</i> (°C)	<i>T_c</i> (°C)	Highest second <i>T_m</i> (°C)
	F	H			
PTB-500-33	—	-44	109	44	125
PTB-500-39	—	-44	183	65	140
PTB-500-44	—	-42	221	79	146
PTB-500-46	—	-42	220	79	146
PTB-1000-20	—	-70	108	51	132
PTB-1000-24	—	-70	188	77	145
PTB-1000-28	—	-70	183	79	155
FPTB-500-32	-120	-44	193	61	131
FPTB-500-37	-121	-42	183	83	151
FPTB-500-42	-119	-42	190	91	176
FPTB-500-44	-123	-40	211	95	208
FPTB-1000-22	-120	-68	184	73	145
FPTB-1000-23	—	NA	NA	NA	NA
FPTB-1000-26	-120	-68	218	87	166
FPTB-1000-30	-119	-69	220	96	159
PBD-1200-23	—	-77	221	180	230
PBD-1200-29	—	-77	220	108	220
PBD-1200-35	—	-77	222	180	230
FPBD-1200-24	—	-76	221	180	228
FPBD-1200-30	—	-75	220	188	233
FPBD-1200-36	—	-76	220	180	230
FPBD-1200-40	—	-76	214	180	232

NA = not applicable.
F = fluorinated soft segment
H = hydrogenated soft segment

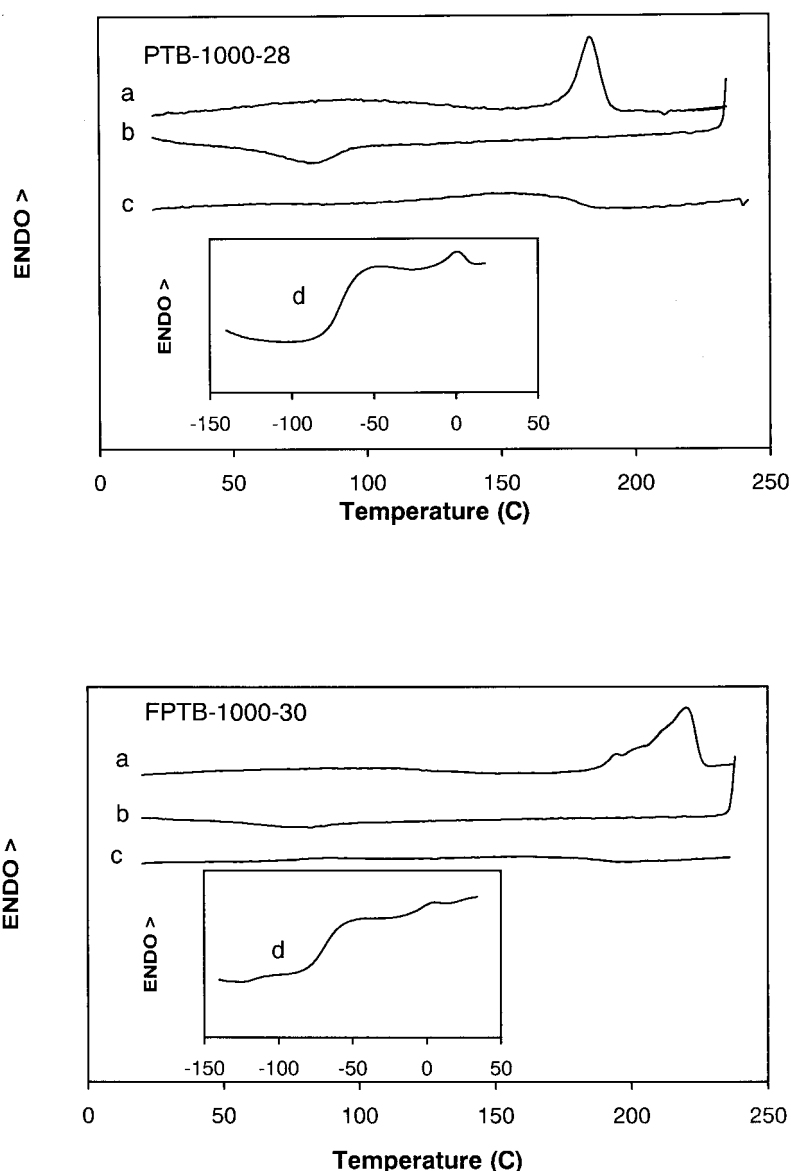


Figure 1 DSC traces for the PTB-1000-28 and FPTB-1000-30 materials: (a) first melting, (b) crystallization, (c) second melting, and (d) soft-phase T_g .

Crystallization Temperature (T_c) was determined by quenching from 250 to 20°C (at 10°C/min).

Dynamic mechanical analysis (DMA)

DMA was obtained with a Torsionautomat Brabender instrument (Duisburg, Germany) according to ASTM D 2236B.

Tensile properties

Uniaxial stress-strain and ultimate property measurements were made with an Instron dynamometer (model 1185) (Canton, MA) at a speed of 500 mm/min according to ASTM D 412. Tests temperatures other

than room temperature were carried out in an Instron thermostated oven.

Coefficient of friction

Coefficient of friction was evaluated on rubber disk injection mold, with a four steel spheres sledge, at 23°C, with a sliding speed 100 mm/min, and at three different applied loads (7.01, 4.07, and 2.11 N).

Chemical resistance

Chemical resistance was evaluated by the measurement of the swelling of specimens after chemical aging at 23°C for 72 h. To carry out these trails, a series of

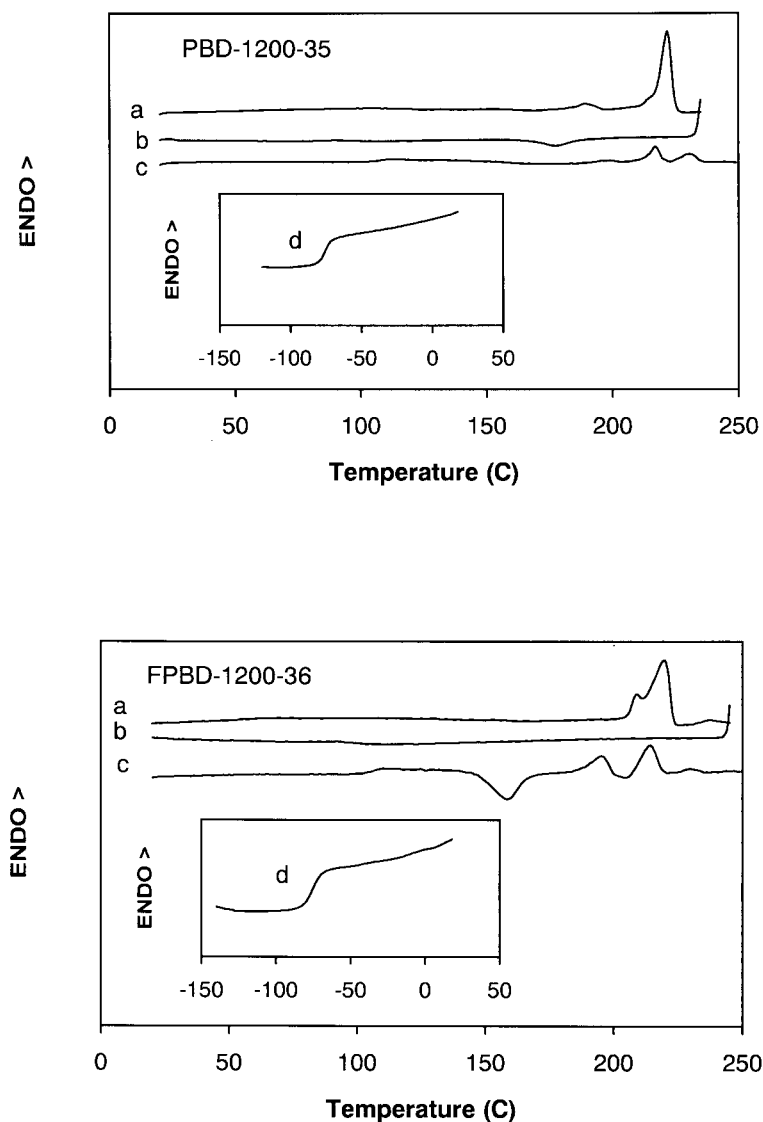


Figure 2 DSC traces for the PBD-1200-35 FPBD-1200-36 materials: (a) first melting, (b) crystallization, (c) second melting, and (d) soft-phase T_g .

solvents with different polarities were specifically selected.

RESULTS AND DISCUSSION

According to the described procedure (see the Experimental section), two series (PTB-based and PBD-based) of hydrogenated and PFPE-containing TPUs were synthesized. The composition of these polymers is shown in Table I.

The adopted procedure for the synthesis of the prepolymer allowed us to minimize the prepolymer growth, giving a more regular polymeric structure after the chain extension. Nevertheless, it is possible that a nonperfectly homogeneous growth of the polymeric chain occurred, especially if fluoro-modified materials were considered. This was due both to the

incompatibility between hydrogenated prepolymer and fluorinated diol and to the parallel side reaction of fluorinated diol with the free MDI arising from the first step of the process (the synthesis of the hydrogenated prepolymer).

Thermal behavior

First-order and second-order transitions

The transitions related to the amorphous and crystalline phases are reported in Table II. Typical DSC traces for hydrogenated and fluorinated PUs are shown in Figures 1 and 2. The observed trends and the presence of more than one melting peak were not unusual for PUs; for instance, Van Bogard and coworkers described a correlation between DSC transitions and microstructures.^{37,38}

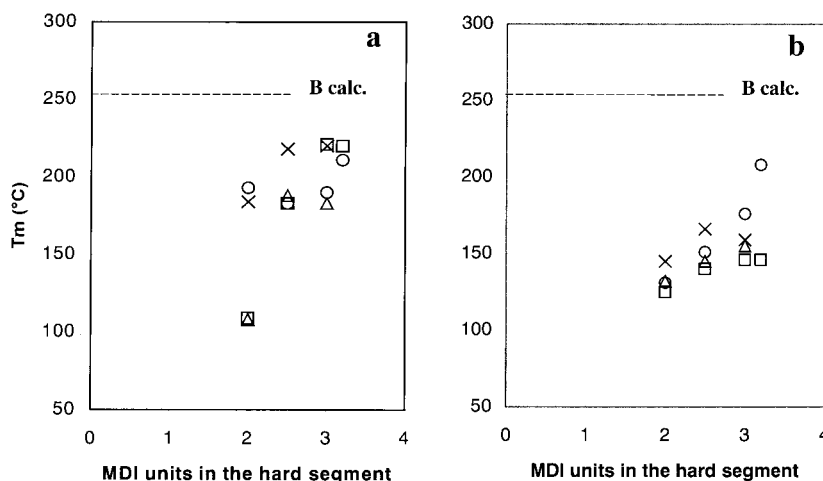


Figure 3 (a) First and (b) second scan T_m 's as a function of MDI units in the hard segment: (\square) PTB-500 series, (\triangle) PTB-1000 series, (\circ) FPTB-500 series, and (\times) FPTB-1000 series; the horizontal dashed line shows the limiting T_m for an MDI-BDO chain of infinite MW calculated by group contributions.

T_g of the soft phase was observed at $-119/-123^\circ\text{C}$ for PFPE, $-75/-77^\circ\text{C}$ for PBD, $-68/-70^\circ\text{C}$, and $-42/-44^\circ\text{C}$ for PTB 1000 and PTB 500, respectively. These transitions seemed to be independent of the hard-phase concentration for all of the investigated materials; this finding suggests that the soft phase was always well segregated. Moreover, when the hydrogenated soft macromonomers were partially substituted by PFPE diols, an unusual multiphase structure was evidenced by DSC analysis. Namely, the fluoromodified PUs showed two well-defined T_g 's, whose transitions closely corresponded to the expected values for the pure components. These evidences clearly indicate that the hydrogenated and PFPE soft chains were mutually incompatible even if they were bonded in a common segmented polymeric chain. This is, by far, the first example of a segmented PU in which two soft domains coexist. In fact, previous studies (in which segmented PUs incorporating polydimethylsiloxane or polyisobutylene macroglycols were synthesized) showed that also when low-polar soft chains were randomly incorporated during polymerization with more polar PTMEG, they did not form blocks of pure components. As a consequence, DSC traces showed only one second-order transition corresponding to the T_g of a unique mixed soft phase.²²

In this study, the lowest T_g , easily detected when the PFPE content exceeded 15–20% (w/w), corresponded to the fluorinated segment, whereas the highest second-order transition was related to the soft hydrogenated moiety. This unusual segregation was promoted by the strong difference in the solubility parameters between the hydrogenated and fluorinated chains, $\delta = 17.0$ and 10.5 (J/cm^3)^{1/2}, respectively.^{39,40}

The FPBD series did not show the lowest T_g because of the too-low PFPE content. However, the T_g value of the hydrogenated segment, which was very close to

the one expected for a pure PBD domain, suggests that in this case also, a neat segregation of the two soft phases occurred. Otherwise, this transition would have been lowered by the incorporation of the PFPE segments.

The calorimetric behavior of the hard phase (first melting peaks) for PTMEG-based PUs showed, as expected, a strong dependence on the volume fraction of the hard segments.

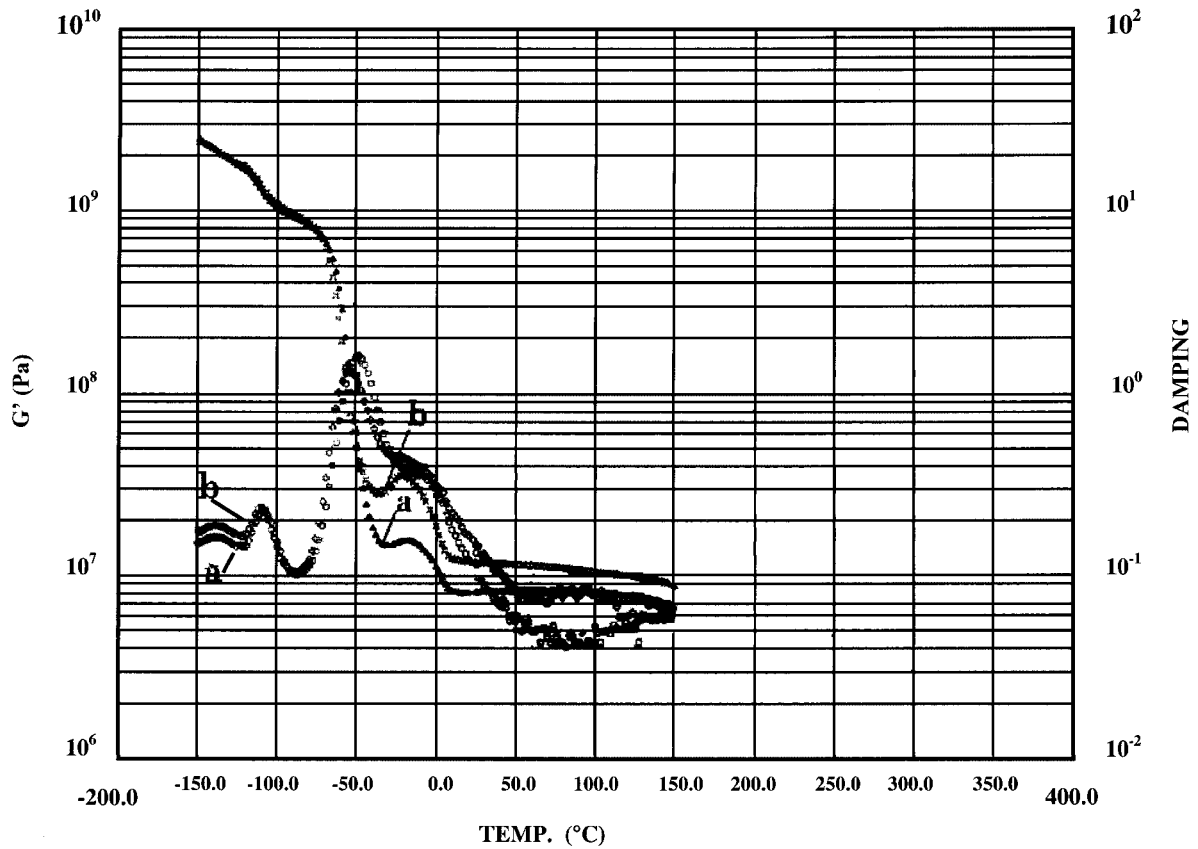
First melting data (only the highest T_m was considered) are plotted in Figure 3(a) against the number of MDI units in the hard phase, as given by stoichiometry. The horizontal line drawn in the upper part of the same figure is the limiting value of T_m for infinite MW, calculated by group contribution, for MDI-BDO (252°C).³⁹

Within these series, the presence of the fluorinated modifier seemed to impart significant differences. Namely, when the hard-phase volume fraction was kept constant, higher first T_m 's were observed when PFPE chains were incorporated into the polymeric structure.

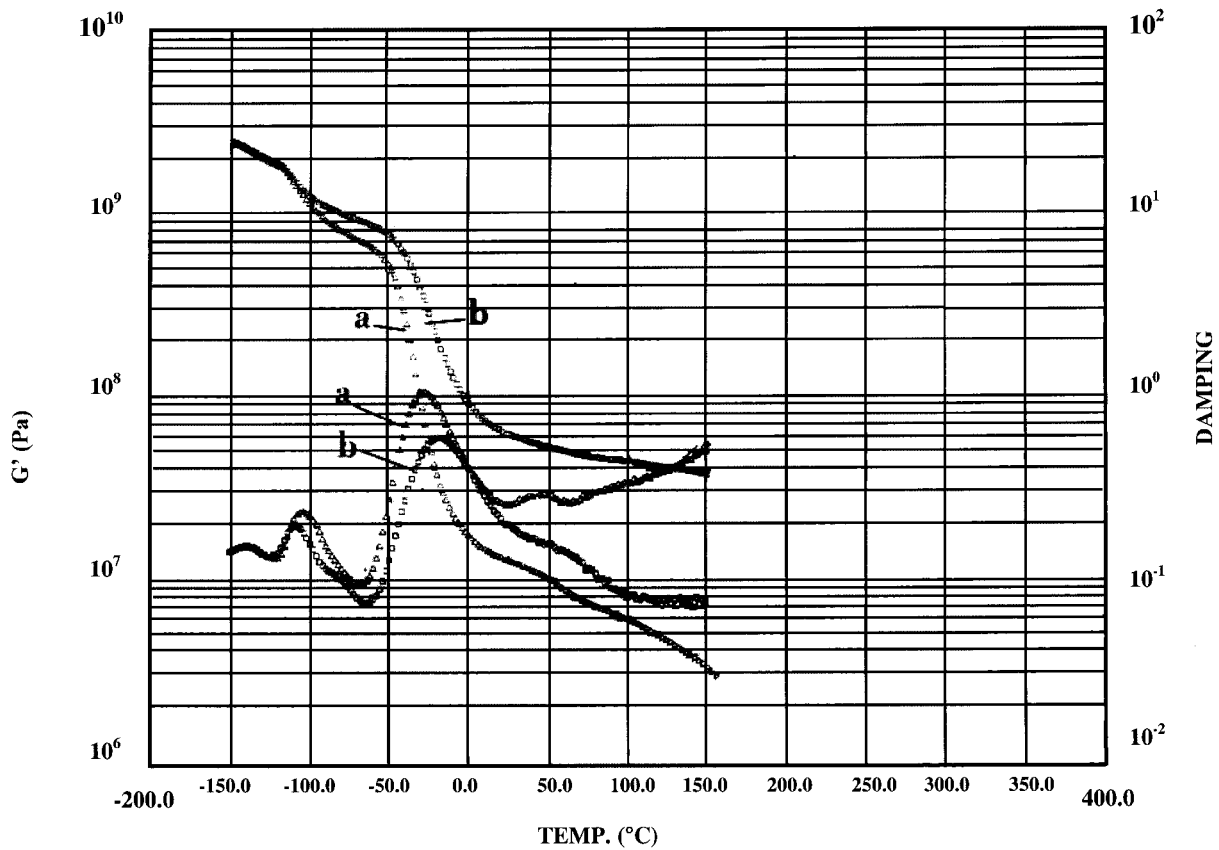
This evidence suggests that an easier phase segregation of the polar hard segments was promoted by

TABLE III
 ΔC_{p_e} and ΔC_{p_t}

Sample	$\Delta C_{p_e} \times 10^2$ (cal/g °C)	$\Delta C_{p_t} \times 10^2$ (cal/g °C)
FPTB-500-32	1.2	1.6
FPTB-500-37	1.0	1.5
FPTB-500-42	0.9	1.3
FPTB-500-44	1.2	1.3
FPTB-1000-22	1.5	1.7
FPTB-1000-26	1.5	1.6
FPTB-1000-30	1.2	1.5



(a)



(b)

Figure 4 (a) Dynamic mechanical spectra for (a) FPTB-1000-22 and (b) FPTB-1000-30. (b) Dynamic mechanical spectra for (a) FPTB-500-32 and (b) FPTB-500-37. (c) Dynamic mechanical spectra for (a) PTB-500-33, (b) PTB-500-39, and (c) PTB-500-46.

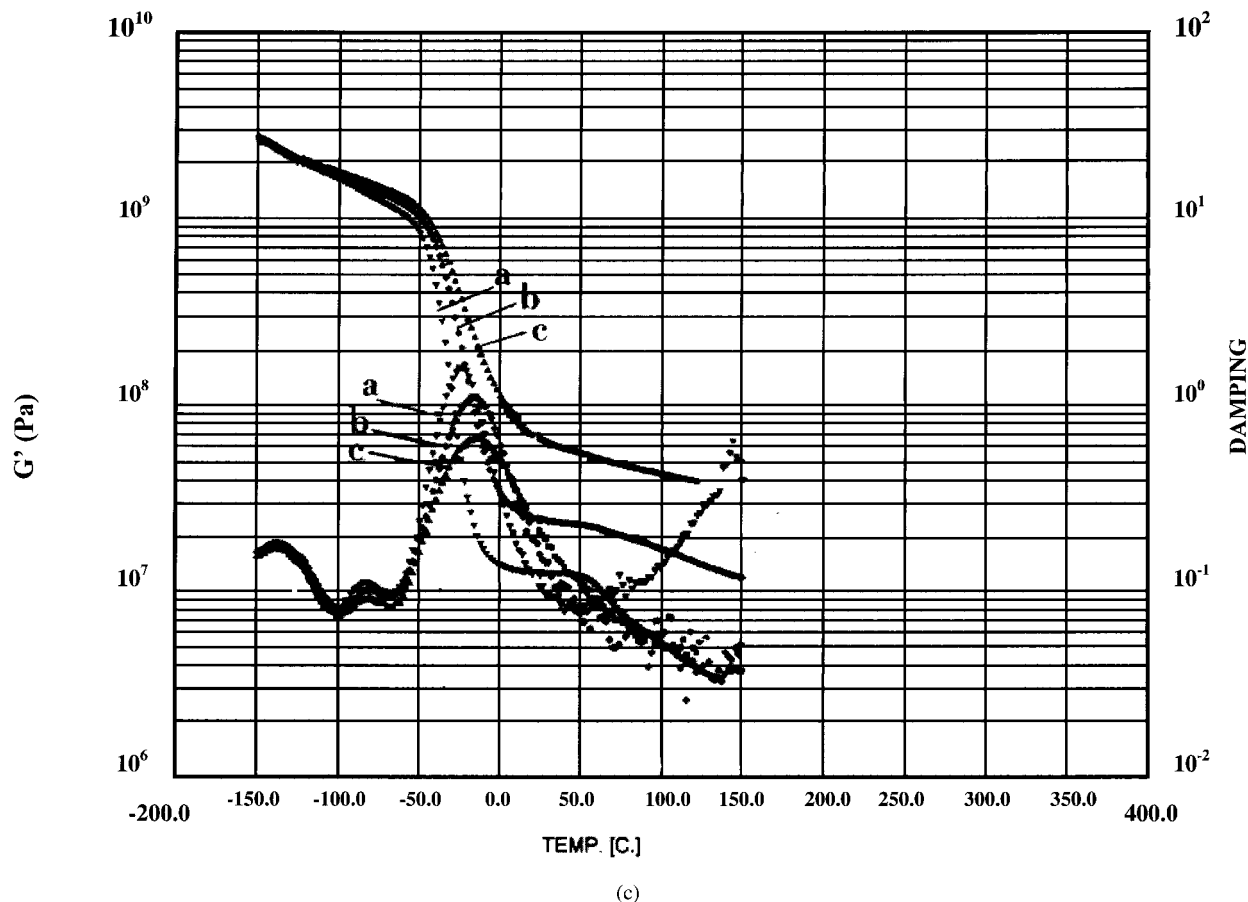


Figure 4 (Continued from the previous page)

the apolar and incompatible fluorinated segments, even if, in principle, it cannot be excluded that a higher fraction of long hard sequences, formed during the not completely homogeneous conditions of the fluorinated prepolymer synthesis, could contribute to the formation of higher melting domains. This trend was not observed when the soft chain was based on PBD; these PUs showed similar melting traces independently of the presence of PFPE segments (see Table II). Probably, in this case, the apolar hydrogenated soft segment was capable by itself of promoting a good self-organization of the hard domains, making the hard-phase segregation insensitive to the further addition of apolar fluorinated segments.

Generally, within each PTMEG series, T_m increased, as expected, with the nominal concentration of MDI units in the hard phase up to a given polymerization degree and then leveled off to a nearly constant value. Similar behavior was described in a previous work.³⁵ This trend was attributed to an artifact induced by annealing after casting carried out at a constant temperature, instead of a constant temperature difference becomes, with respect to the expected T_m ; this point will be clearer after the discussion on the second melting.

At the contrary, T_m of PBD-based PU_s was apparently insensitive, not only to the presence of PFPE segments,

but also to the hard-phase polymerization degree. One could conclude that in this case also, some inhomogeneous polycondensation had occurred, producing hard segments with larger polydispersity; thus, hard segments with higher T_m 's than those expected by stoichiometry were possibly present. However, this explanation could not justify the observed insensitivity of T_m versus the explored composition range. A second reason could arise from the ability of this apolar soft chain to promote a very efficient hard-phase segregation, which

TABLE IV
Relaxation Processes by Dynamic
Mechanical Spectroscopy

Sample	Soft Phase		G' at 23 °C (MPa)
	Fluorinated T_α (°C)	Hydrogenated T_α (°C)	
PTB-500-33	—	-25	13
PTB-500-39	—	-15	25
PTB-500-46	—	-16	65
FPTB-500-32	-104	-28	13
FPTB-500-37	-110	-28	60
FPTB-1000-22	-108	-50	8
FPTB-1000-30	-108	-56	12

T_α = glass transition

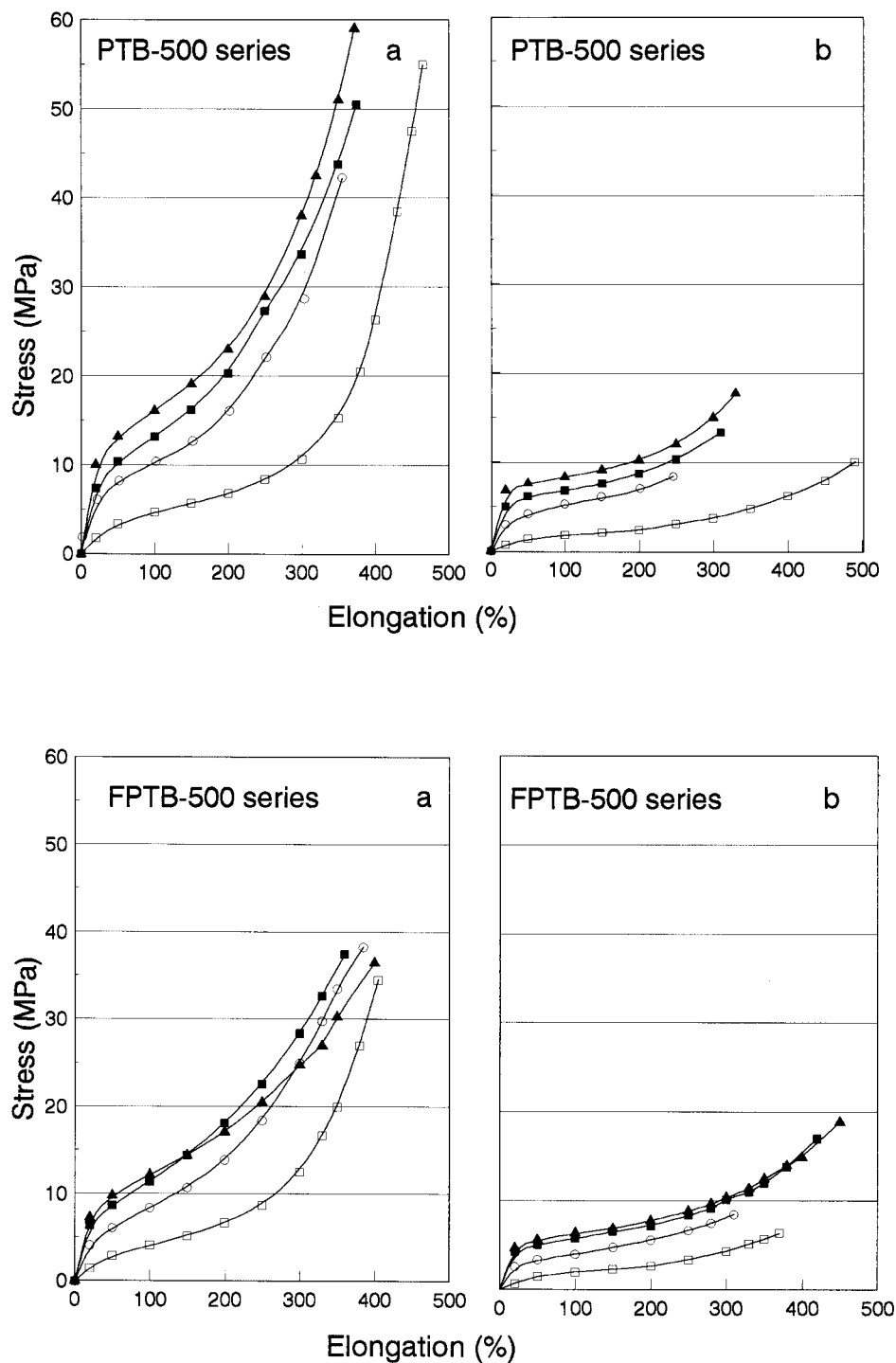


Figure 5 Engineering stress–strain curves at (a) 23 and (b) 100°C for the PTB-500 series [(□) PTB-500-33, (○) PTB-500-39, (■) PTB-500-44, and (▲) PTB-500-46] and for the FPTB-500 series [(□) FPTB-500-32, (○) FPTB-500-37, (■) FPTB-500-42, and (▲) FPTB-500-44].

would give a morphology in which large and well-organized domains were present.

Finally, the second melting and the difference with the first melting are considered. All series showed a large difference between the first and the second melting, which very often broadened over a large temperature range.

The second T_m is plotted against the number of MDI units in Figure 3(b). The unusual trend observed before disappeared, and a regular increase with hard-phase concentration occurred; in other words, the higher the hard-phase content was, the bigger and more perfect were the crystalline structures that were formed. Moreover, a better segregation between

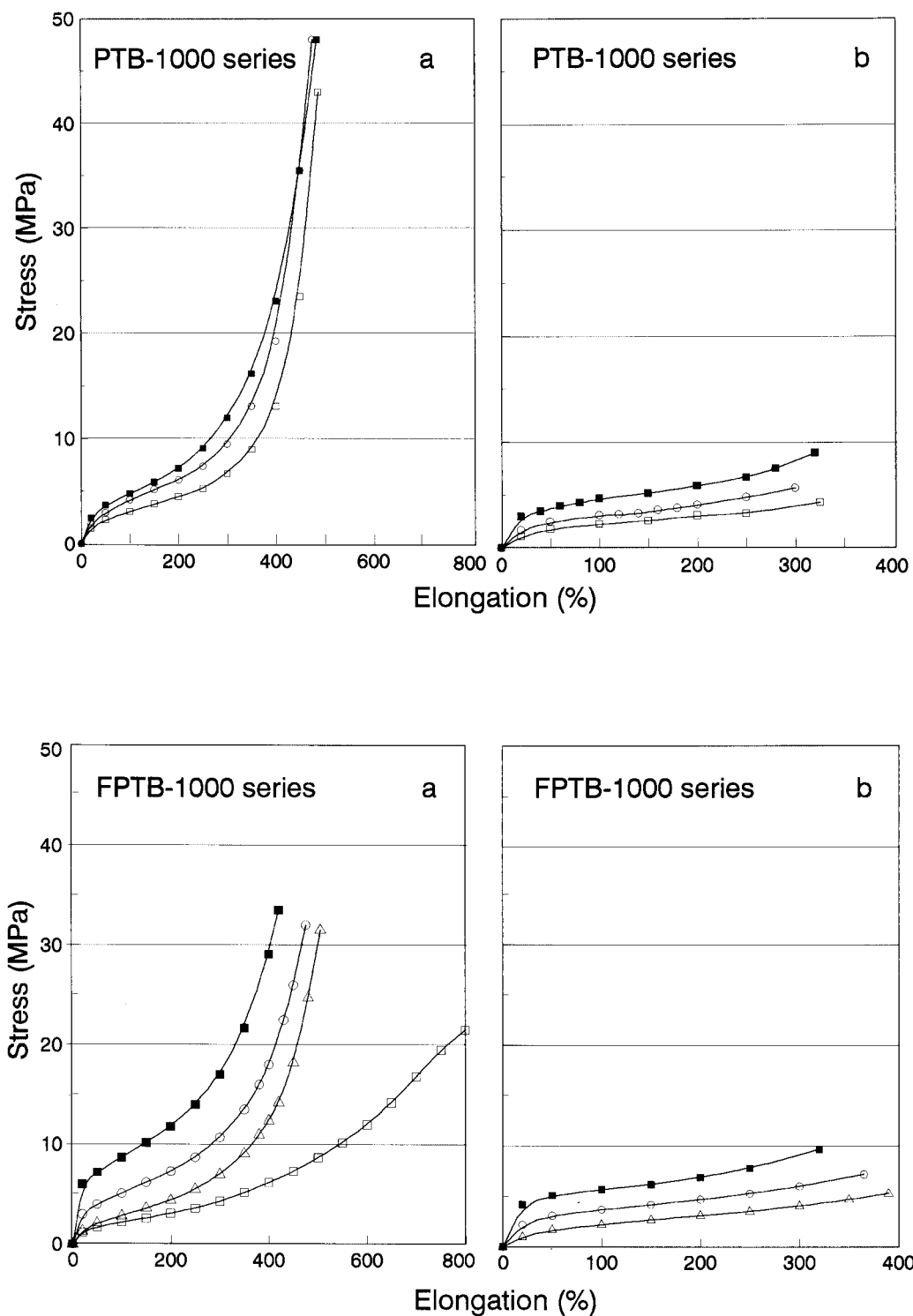


Figure 6 Engineering stress–strain curves at (a) 23 and (b) 100°C for the PTB-1000 series [(□) PTB-1000-20, (○) PTB-1000-24, and (■) PTB-1000-28] and for the FPTB-1000 series [(□) FPTB-1000-22, (△) FPTB-1000-23, (○) FPTB-1000-26, and (■) FPTB-1000-30].

phases, that is, a larger difference in the solubility parameters, improved the perfection of crystallites. As consequence, fluoro-modified PUs showed higher T_m 's than the corresponding unmodified PUs.

Miscibility of hydrogenated and fluorinated soft thermal step phases by capacity (ΔC_p) analysis

The experimental ΔC_p (ΔC_{p_e}) values for the fluorinated soft phase, measured after cooling at 80°C/min,

are reported in the first column of Table III and are compared with the theoretical values (ΔCp_t) predicted for the perfectly segregated model in the second column of Table III:

$$\Delta Cp_t = 6.93 \times 10^{-2} (1 - w_h)$$

where the value 6.93×10^{-2} (cal/g °C) corresponds to the ΔCp of the pure PFPE chain as determined in a previous work⁴¹ and w_h is the weight fraction of all hydrogenated components (soft and hard segments).

The data shown in the table must be carefully considered because the ΔCp measure of the PFPE phase, which was the minority component, could have been affected by a significant error. Nevertheless, a general trend was clearly evident that indicated the unique ability of the apolar PFPE segment to self-organize into segregated soft domains. This tendency was more pronounced for PTMEG 2000 (80–94% PFPE segregation efficiency) than for PTMEG 1000 fluoro-modified materials (67–92% segregation efficiency). This result agrees with the well-established findings that the miscibility of two different phases depends not only on the difference between the solubility parameters, according to the Flory–Huggins equation:

$$\chi_{s_1s_2} \approx 1/6(\delta_{s_1} - \delta_{s_2})^2$$

where $\chi_{s_1s_2}$ is the Flory–Huggins interaction parameter for the two soft phases and δ_{s_1} and δ_{s_2} are the corresponding solubility parameters,⁴² but also on the length of the considered segments. In fact, the critical condition for miscibility ($\chi_{s_1s_2}$)_{cr} can be defined as follows:

$$(\chi_{s_1s_2})_{cr} = 1/2(1/i_{s_1}^{1/2} + 1/i_{s_2}^{1/2})^2$$

where i is the degree of polymerization of the considered soft segment (s_1 or s_2).⁴³

The lowest the polymerization degree of the two considered segments is, the highest the χ_{cr} for miscibility is. The reduction of the chain length could thus make compatible components otherwise not mutually soluble because of their relatively high interaction parameter.

Dynamic mechanical properties

DMA was performed on cast materials with a fully hydrogenated or partially fluorinated structure and a hard-phase volume content ranging from 22 to 46%. In Figure 4, the spectra of PFPE-containing and hydrogenated materials are shown, and the relevant data about transitions are collected in Table IV.

Dynamic mechanical spectroscopy confirmed the two-phase nature of the soft domains; two glass tran-

sitions were actually present. The former was as low as $-104/-110^\circ\text{C}$. These temperatures were a little higher than those determined by DSC (see Table II), but in any case, the agreement was sufficiently good. Therefore, they could be unambiguously attributed to the segregated PFPE chain. The latter was located at a temperature range that depended on the MW of the hydrogenated macrodiol, specifically from -15 to -28°C for 1000 MW-based polymers and $-50/-56^\circ\text{C}$ for 2000 MW-based materials.

It is interesting to note that within each series, the storage modulus G' paralleled the hard-phase content of the considered PU (i.e., the hardness of the material). A general decrease in the G' modulus with increasing temperature was observed after the last T_g (the one corresponding to the hydrogenated phase). This phenomenon, more evident above 50°C , pointed out that the physical network, due to hydrogen bonding within the hard phase, became progressively less efficient. In fact, the fraction of free urethane groups, unable to participate to the physical crosslink formation, increased as the temperature increased. Finally, a large drop in modulus occurred at temperatures approaching the first melting peak observed in DSC traces for the first melting scan.

At room temperature, G' moduli, independently of the nature of the soft segments (hydrogenated or fluorinated) and of their MW (1000 and 2000), were mainly ruled by the hard-phase volume fraction (see the last column of Table IV).

Tensile behavior

Engineering stress–strain curves measured at 23 and 100°C are plotted in Figures 5–7, and numerical data are collected in Table V.

A comparison of the tensile behavior between hydrogenated and the corresponding fluorinated PUs highlights only minor differences. Specifically, similar moduli at 20 and 100% elongation (M20% and M100%, respectively) and elongation at break (E_b) were observed, whereas strain-hardening phenomena were more pronounced within the hydrogenated series; this brought about higher tensile at break (T_b) values. Strain-hardening phenomena were generally excluded for the PBD materials; in fact, in this case, the apolar soft phase, combined with the not perfectly regular chain structure, could not crystallize even under strain. Only sample FPBD-1200-40, which was rich in hard phase, showed strain-hardening characteristics.

As expected, all materials, independently of their hydrogenated or fluorinated structure, showed a strong dependence of the elongation properties on the temperature; at 100°C , stress properties were strongly reduced. Specifically, M20% and M100% were generally reduced about 20–40%, and T_b was 2–10 times lower. The T_b –temperature relationship was mainly

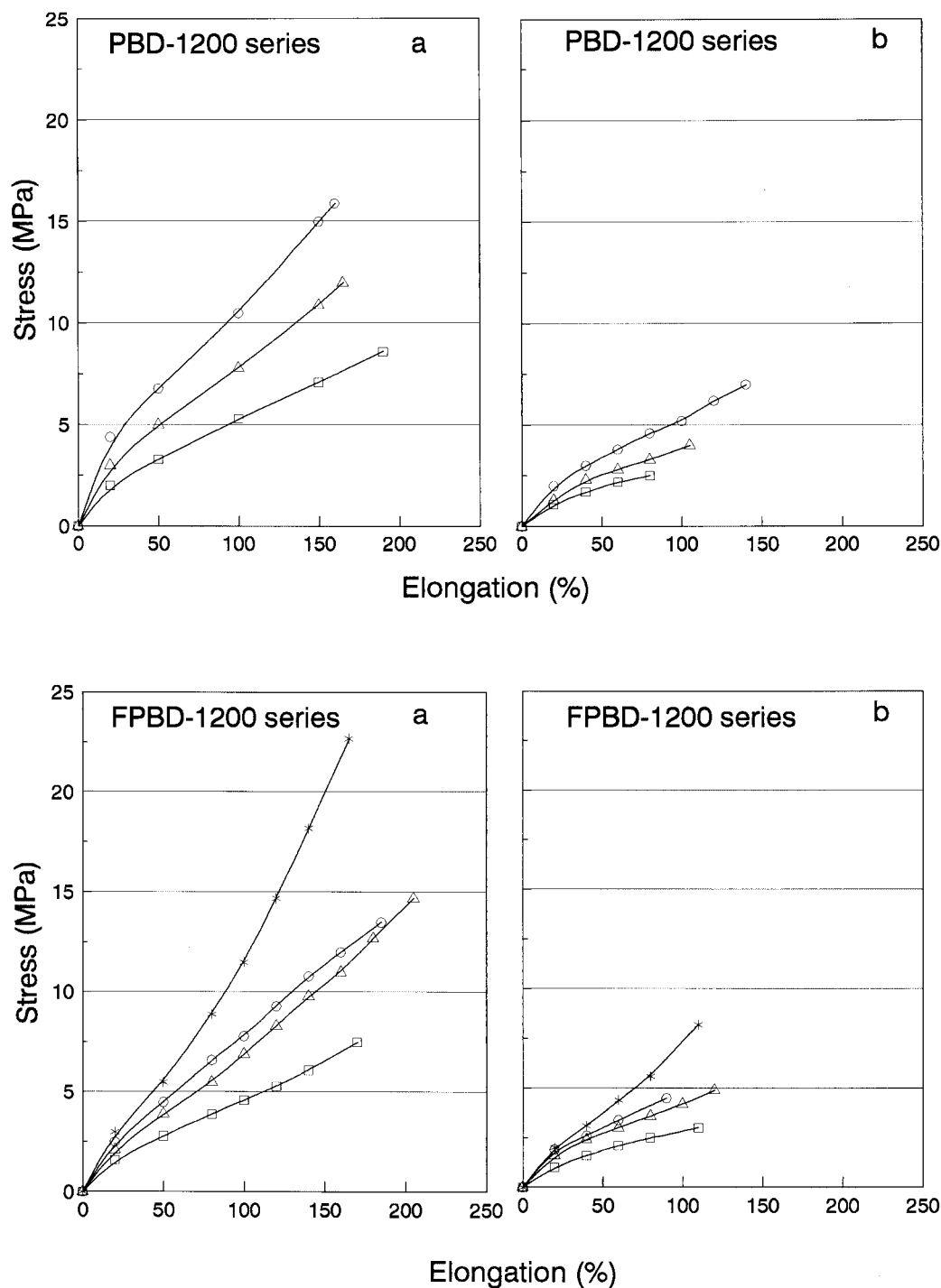


Figure 7 Engineering stress-strain curves at (a) 23 and (b) 100°C for the PBD-1200 series [(□) PBD-1200-23, (△) PBD-1200-29, and (○) PBD-1200-35] and for the FPBD-1200 series [(□) FPBD-1200-24, (△) FPBD-1200-30, (○) FPBD-1200-36, and (*) FPBD-1200-40].

ruled by the hard-phase weight fraction; that is, the higher the hard-phase content was, the lower was the T_b decreasing with temperature.

The dependence of Young's modulus measured at low strain (20%) on the volume fraction of the hard phase and the structural variables was another important feature. As shown in Figure 8(a,b), the mod-

ulus of PTMEG-based materials decreased with temperature but increased with the hard-phase concentration, as predicted by theories for two-phase polymers.⁴⁴

The modulus is related, in principle, to the number of crosslinks for unit volume, that is, to the chain length of the soft segment and to the functionality of

TABLE V
Tensile Properties

Sample	Room temperature				100°C			
	M20% (MPa)	M100% (MPa)	T_b (MPa)	E_b (%)	M20% (MPa)	M100% (MPa)	T_b (MPa)	E_b (%)
PTB-500-33	10.4	4.9	54.8	465	4.1	2.0	10.1	490
PTB-500-39	27.5	10.0	42.0	350	15.0	5.5	8.8	260
PTB-500-44	37.5	13.7	50.5	365	22.5	7.0	12.7	305
PTB-500-46	50.0	16.1	59.1	360	32.2	8.2	17.7	330
PTB-1000-20	6.5	3.1	42.7	492	5.2	2.2	4.3	320
PTB-1000-24	8.8	4.0	49.0	475	7.2	3.0	6.0	291
PTB-1000-28	9.5	5.0	48.3	480	8.9	5.0	9.3	310
FPTB-500-32	8.7	4.1	34.7	399	5.0	2.3	6.1	362
FPTB-500-37	18.2	7.8	38.3	385	13.1	4.2	9.6	315
FPTB-500-42	31.2	11.5	37.7	367	20.7	5.4	16.9	406
FPTB-500-44	36.8	12.3	35.9	397	22.5	5.8	19.8	452
FPTB-1000-22	5.5	2.1	21.2	600	—	—	—	—
FPTB-1000-23	7.0	3.0	31.5	505	5.0	2.2	5.2	390
FPTB-1000-26	14.6	5.0	32.0	470	10.4	3.7	7.1	368
FPTB-1000-30	30.0	8.8	33.5	420	21.7	5.8	9.6	320
PBD-1200-23	9.8	5.3	8.3	186	5.0	—	2.5	79
PBD-1200-29	15.3	8.0	11.8	166	6.5	4.0	4.1	105
PBD-1200-35	20.5	10.5	16.0	161	10.0	5.2	6.8	140
FPBD-1200-24	8.0	4.6	7.5	170	4.5	2.8	2.9	106
FPBD-1200-30	10.5	6.8	14.7	205	7.3	4.1	4.8	120
FPBD-1200-36	12.0	7.8	13.4	184	8.5	—	4.4	92
FPBD-1200-40	14.0	11.3	22.7	164	10.0	7.4	8.0	107

crosslinks. ZDOLTX had a shorter chain in comparison with PTMEG 2000 MW (40 carbon atoms and 110 carbon atoms, respectively), whereas its length was roughly the same of the PTMEG 1000 MW macrodiol. In light of these considerations, it was not surprising that all of the series, with exclusion of the FPTB-1000 series, gave M20% data, as a function of hard-phase volume fraction, lying within a single “muster curve,” whereas the FPTB-1000 series showed a more pronounced dependence of M20% on the hard-phase con-

tent. In fact, in this last case, a fraction of the soft hydrogenated segments was substituted by a shorted PFPE chain, thus contributing further to the hardness of the polymer (i.e., to the moduli).

Surface properties

To elucidate the effectiveness of the PFPE modifier to upgrade the surface properties of the polymeric ma-

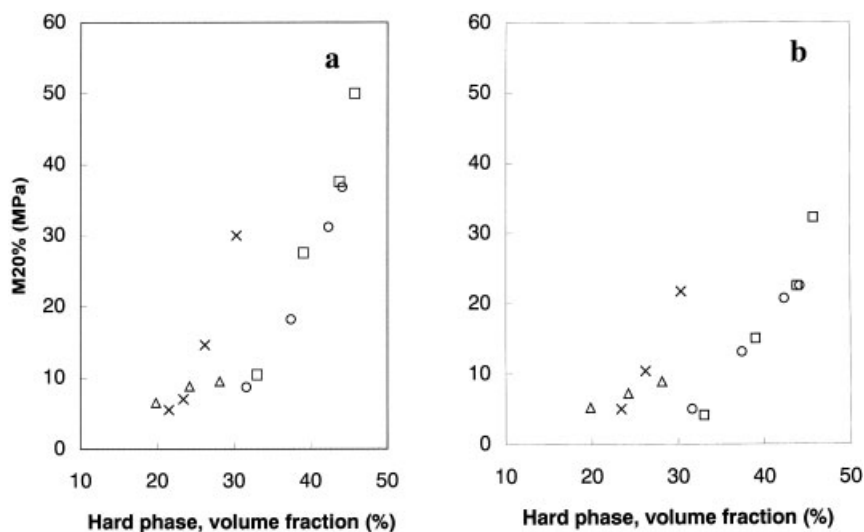


Figure 8 M20% at (a) 23 and (b) 100°C as a function of the hard-phase volume fraction for the (□) PTB-500 series, (○) FPTB-500 series, (△) PTB-1000 series, and (X) FPTB-1000 series.

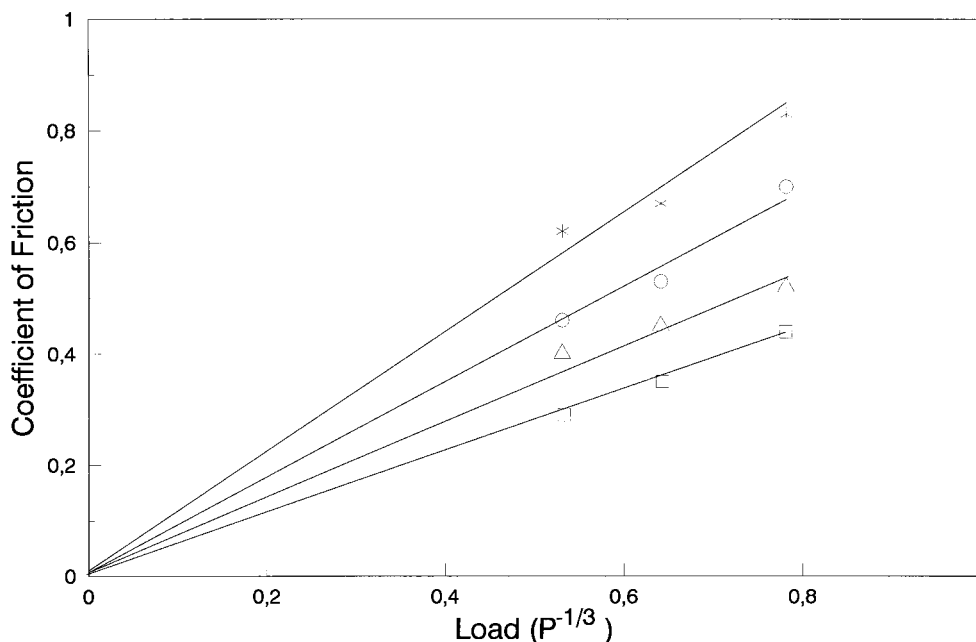


Figure 9 Coefficient of friction as a function of applied load for different PUs: (*) hydrogenated PU, (□) 1% (w/w) fluorine-containing PU, (O) 2% fluorine-containing PU, and (Δ) 5% fluorine-containing PU.

material, PTMEG-based PUs with a defined and low fluorine content (0–5%) were specifically synthesized.

Figure 9 shows the coefficient of friction dependence of these polymers as a function of fluorine content for different applied loads.

The hydrogenated material gave higher values of the coefficient of friction; whereas even very low amounts of PFPE chain introduced into the polymeric structure significantly lowered the coefficient of fric-

tion. The comparison of these PFPE-containing materials did not show any clear trend as a function of fluorine content. These findings seemed to be consistent with other experimental evidence, which suggests that, independently of the bulk composition, the surface behaved like a highly fluorinated one. This enrichment of fluorine to the surface, widely described in the literature, was thermodynamically and kinetically favored by the low surface energy and high mobility of the PFPE

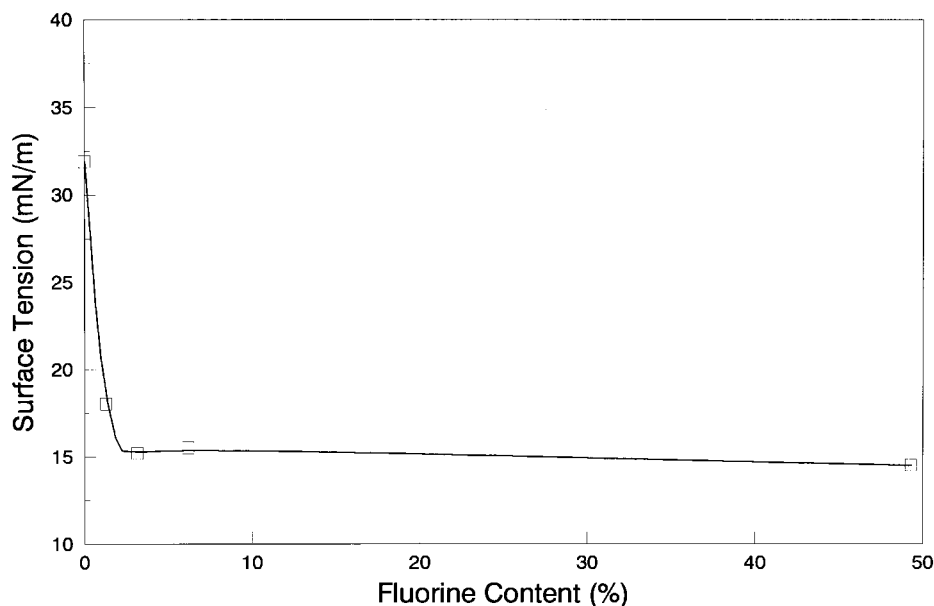


Figure 10 Surface tension as a function of fluorine content for different MDI–BDO-based PUs.

TABLE VI
Chemical Aging (23°C, 72 h)

Chemical	Sample (swelling, vol %)			
	PTB-1000-24	PTH-1000-29	FPTB-1000-26	FPTH-1000-31
MEK	213	75	69	53
Fuel C	82	59	48	47
Ethyl acetate	140	67	57	51
DMF	653	360	168	80
THF	695	234	196	127

chain, respectively. Also, the strong incompatibility of the apolar fluorinated chain toward the hydrogenated moiety played an important role.

This general characteristic of PFPE-containing materials was well represented by the data reported in Figure 10, which describes the relationship between the surface energy and the fluorine content. These data indicate that a slight modification of the bulk composition dramatically reduced the surface energy of the material to a minimum value that is that typically expected for perfluorinated PFPE-based polymers (ca. 15 mN/m).^{34,35}

Chemical resistance

The chemical resistance was definitely associated with the surface characteristics of PFPE-modified PU. In fact, the bulk composition analysis alone could not justify the strong increase in chemical resistance observed for the fluoro-modified polymers investigated in this work (Table VI). The PFPE chains were essentially inert and practically phobic with respect to all chemicals. This unique characteristic, combined with the selective enrichment of PFPE chains toward the surface, strongly increased the chemical resistance of the polymer, even if a hydrogenated continuous phase was present as dominant constitutive component. Table VI compares the chemical resistance of fluorinated and hydrogenated PUs with respect to different solvents. A dipper analysis of these data showed that both the hydrogenated structure and the fluorine content ruled the chemical resistance. In fact, the use of aromatic chain extenders (e.g., Hy) instead of linear BDO gave some advantages, but a further significant improvement of properties was achieved when PFPE chains were present. The combination of a proper selection of hydrogenated comonomers and PFPE modifying macromers offers a unique opportunity to design materials with good performances even in very severe conditions. Specifically, only minor swelling was observed by chemical aging with very strong solvents (DMF, MEK, ethyl acetate).

CONCLUSIONS

DSC, DMA, tensile properties joined with the coefficient of friction, and chemical resistance measure-

ments indicated that the fluoro-modified PUs of this work, despite their slightly modified composition (fluorine content in the range 3.3–15.8% w/w), presented unique characteristics. Namely, the surface properties were close to those expected for fluorine-rich materials, particularly in terms of improved chemical resistance and a reduced coefficient of friction. Moreover, some peculiar features were related to their bulk behavior. In fact, at constant hard-phase composition, higher first T_m 's were generally observed, suggesting an easier phase segregation. The presence of two well-defined T_g 's was an other unique morphological characteristic, never observed before in PUs (even those containing very different soft chains).

This profile of properties and the ease of the proposed bulk multistep synthesis will make the study of this new class of materials very interesting, not only for a strictly scientific point of view but also because they can be envisaged as candidates for special applications where improved surface characteristics must be carefully balanced with the maintenance of excellent mechanical properties.

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