Effect of hexafluoroisobutylene moieties on the structure and properties of copolymers of ethylene and chlorotrifluoroethylene

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(Received 13 July 1987; revised 28 September 1987; accepted 30 September 1987)

The thermal stress-cracking properties of ethylene–chlorotrifluoroethylene copolymer (E/CTFE copolymer, marketed as Halar® by Ausimont USA Inc.) has been improved considerably by using 2 to 6 wt% hexafluoroisobutylene (HFIB) as a termonomer. This improvement arises from the increased flexibility of the polymer molecule in the presence of HFIB units, which also reduces the average lamellar repeat from 300–400 Å for the copolymer to 135–185 Å for the terpolymer. We postulate that crystalline lamellae consist entirely of alternating units of ethylene and chlorotrifluoroethylene, while the HFIB substituted E/CTFE segments are segregated in the interlamellar amorphous regions. These structural features are used to explain the role of HFIB in enhancing the resistance of the terpolymer to environmental stress-cracking.

(Keywords: ethylene/chlorotrifluoroethylene copolymer; hexafluoroisobutylene termonomer; thermal stress-cracking resistance)

INTRODUCTION

The copolymer of ethylene-chlorotrifluoroethylene (E/CTFE copolymer) marketed under the trade name of Halar® by Ausimont, USA, is a mechanically tough polymer which is easily processible by extrusion, injection moulding, powder coating, blow moulding and roto moulding. Processed articles include wire insulation, fibres, films, and coated and moulded parts. At temperatures above 150°C, the E/CTFE copolymer becomes susceptible to thermal stress-cracking. It has been shown by Reimschuessel *et al.*[1,2] how the resistance to thermal stress-cracking in E/CTFE copolymer is improved by incorporating 0.5 to 4.0 mol% of units derived from perfluoroalkyl ethylenes with 4 to 8 carbon atoms in the alkyl groups. Since hexafluoroisobutylene (HFIB) has been used to modify E/CTFE copolymers, it was of interest to explore whether effects caused by HFIB incorporation can be explained by structural changes similar to those observed upon incorporation of perfluoroalkyl ethylene. We studied E/CTFE copolymers containing 2.5 to 6.0 wt% of HFIB.

EXPERIMENTAL

The modified E/CTFE polymers were prepared by terpolymerization of CTFE, ethylene and HFIB in an aqueous free-radical suspension polymerization initiated by a monomer-soluble organic peroxide[3]. Ethylene and HFIB were added to the reactor at a calculated rate throughout the duration of the polymerization reaction so as to maintain a fairly uniform composition of the terpolymer. Negligible HFIB was found in the unreacted monomers recovered upon completion of the polymerization run, suggesting that HFIB is almost completely reacted. Therefore, the concentration of HFIB in the terpolymer could be estimated from the total amount of HFIB fed into the reactor. An E/CTFE copolymer of approximately 50:50 molal composition was used as a control for comparing the properties with the terpolymer.

Polymers containing four different levels of HFIB were evaluated for stress-crack resistance by four different techniques. (1) Polymer was ground and sieved to give a fine powder with 35–100 μm diam. particles. This powder was electrostatically coated on 4 in × 1 in diam. threaded capscrews to a fused coating thickness of about 50 mils. The coated bolts were then heat-aged at 165°C for several days and the bolts inspected for hairline cracks every 24 hours. (2) Sieved reactor beads (particle size 18–60 mesh) were rotationally moulded to a 12 in cube in a McNeil–Akron Rotomolding Machine. Typically a 5 lb charge was heated at 282°C for 25 min, air cooled for 20 min and water cooled for 10 min. The moulded boxes were then inspected for warping, shrinkage, cracks and bubbles. Finally, 4 in panels were cut from the sides of the cube and tested for drop-weight impact strength. (3) Compression moulded strips (5 in × $\frac{1}{4}$ in × 50 mils) were subjected to mandrel wrap test (MIL-L-P-390C) at 150°C. This comes closest to simulating constant strain applications such as coated cable. (4) 5 in × 0.25 in × 50 mils strips were bent around a 0.25 in diam. bar and loaded with a 500 g weight. The specimen is thus subjected to a tensile stress of 44 psi. The time for the specimen to break at 180°C is taken as a measure of its stress-cracking resistance.

Wide-angle X-ray diffraction (WAXD) patterns were obtained on a Philips diffractometer in the parafocus mode using CuKα radiation. Small-angle X-ray scattering data were obtained using a position sensitive proportional counter on a Franks' camera[4]. The data on unmodified E/CTFE copolymer was also obtained at the National Center for Small-Angle Scattering at Oak Ridge National Laboratory. A measure of the degree of crystallinity was obtained by resolving parafocus scans

0032-3861/88/050829–04$03.00

between 2θ values of 10° and 28° into crystalline peaks and an amorphous halo, and by comparing the areas of the equatorial crystalline peaks and the amorphous halo. A crystallite size was determined using the Scherrer equation from the full-width at half-maximum of the equatorial peak at 18° (2θ). Lamellar repeat was calculated using Bragg's law.

Melting points of the terpolymers were measured using a Dupont 990 differential thermal analysis unit with a heating rate of 20°C min^{-1}. Tin was used as a calibration standard.

RESULTS

HFIB increases stress-cracking resistance in E/CTFE copolymer (*Table 1*), and it does so without affecting the tensile, flexural and impact properties of E/CTFE copolymer. It can be seen from *Table 1* that the higher the HFIB concentration, the better the resistance to stress cracking. The improvements in coated-capscrew test, bent-strip test and rotomoulding trials is dramatic up to 3.75% HFIB, but is small above 3.75%; only the 7% HFIB terpolymer passes the mandrel wrap test. Tensile test results given in *Table 2* show that the improvement in stress-cracking resistance is accomplished with only a slight decrease in tensile properties. The flexural properties (flexural strength$\approx$8200 psi; flex modulus$\approx$215 000 psi and notched Izod impact strength$\approx$1.7 ft lb/in notch) do not change significantly with HFIB concentration, while the drop weight impact strength increases from 114 ft lb at 2.5% HFIB to 190 at 7% HFIB.

Per cent alternation of ethylene and chlorotrifluoroethylene units remains at ~75% and does not change much as a function of HFIB content; the following values were obtained from infra-red spectra: per cent alternation 78 and 74 at 0 and 5% HFIB, respectively; block ethylene content ~7%; per cent ethylene content 46 and 44 at 0 and 5% HFIB, respectively. In many organic solvents (such as methylene chloride, trichloroethane, butanol, tetrahydrofuran, acetone, methyl ethyl ketone, glacial acetic acid, dimethylformamide, ethyl acetate, hexane and toluene) there was ~50% increase in the per cent weight gain at elevated temperatures as HFIB was increased from 0% to 4.5%. With NaOH (50% at 121°C) the per cent weight gain increased from 0.1 to 0.27%. The weight gain in acids remains essentially unaffected by the presence of HFIB. All terpolymers exhibited excellent resistance to hot and cold acids and bases: polymers containing up to 7% HFIB retained the same per cent elongation as the unmodified polymer in conc. HCl, conc. H_2SO_4, conc. HNO_3 and 50% NaOH at room temperature and at 250°C after 11 days of exposure. However, the per cent elongation does increase slightly in some organic solvents, such as methylene chloride, trichloroethylene, tetrahydrofuran, acetone, methyl ethyl ketone, ethyl acetate, hexane and toluene. The per cent elongation decreases in butanol, glacial acetic acid and dimethylformamide. The water vapour transmission rate over 24 h increases from 3.8 to 5.7 gms/m^2/s h (film thickness = 2 mils) as HFIB content increased from 0 to 4.5%.

Figure 1 shows WAXD scans of modified and unmodified E/CTFE copolymer. The corresponding data on crystalline index and crystallite size are given in *Table*

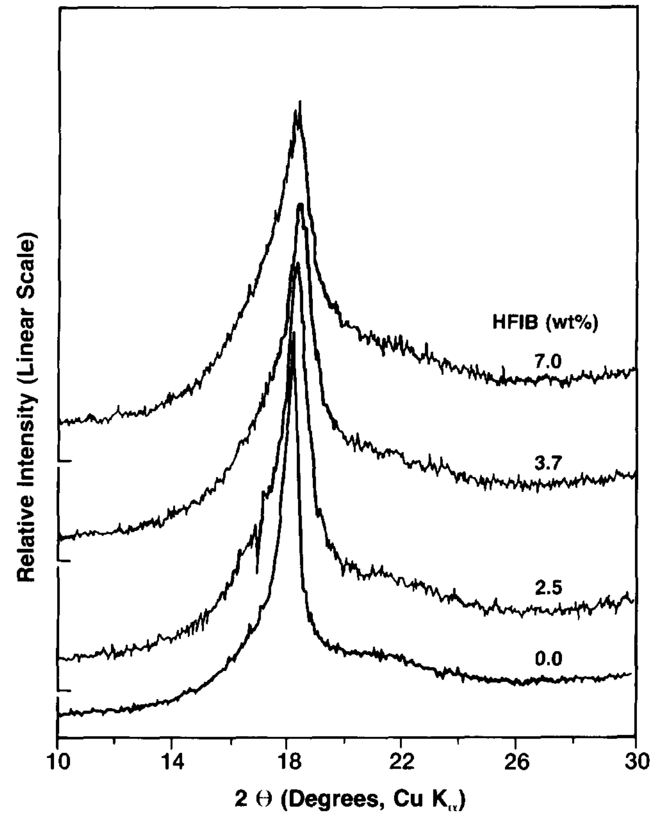

Figure 1 Wide-angle X-ray scattering curves of E/CTFE copolymer with 0%, 2.5%, 3.7% and 7.0% HFIB

Table 1 Stress-crack resistance at various HFIB concentrations

	Powder coated capscrews			Rotomoulding results		Mandrel wrap test result		Bent-strip test
HFIB (%)	Heat ageing temp. (°C)	Exposure time (days)	Number out of 10 cracked	Clarity	Appearance	Test duration (h)	Number out of 9 failed at 150°C	Result at 180°C time to break (min)
0	150	1	10	Opaque	Badly distorted and cracked	24	9	–
2.5	165	1	10	Translucent	Slight distortion and no cracks	24 120	7 9	10.8
3.75	165	2	3	Transparent	Very slight distortion	24 120	3 9	15.4
5.0	165	10	0	Transparent	No distortion	24 120	3 9	19.6
7.0	165	10	0	Transparent	No distortion	120	0	20.0

2. The diffraction patterns are very similar. In the unannealed films, however, the crystallinity of HFIB modified E/CTFE copolymer is lower than in the unmodified copolymer (23 vs. 37%). Also, the crystallite size, as determined from the intense equatorial 18° reflection, decreases from ~135 to 95 Å upon adding HFIB. *Figure 2* shows SAXS scans of modified and unmodified E/CTFE copolymer. The data on lamellar spacing are summarized in *Table 2*. Unlike the wide-angle patterns, these small-angle scattering curves show a dramatic change, even with as little as 2.5% HFIB. These changes, as discussed by Reimschuessel *et al.* on the effect of perfluoroalkylethylenes[2] can be summarized as follows. (1) The lamellar repeat is almost halved upon adding HFIB; in the unmodified E/CTFE copolymer, the typical lamellar repeat is ~350 Å, whereas in modified copolymer the value is 180 Å at 2.5% HFIB and 140 Å at 6.0% HFIB. (2) The small-angle peak is sharp in unmodified E/CTFE copolymer and is broad in the modified copolymer. (3) The modified E/CTFE copolymer has a distinct and intense small-angle peak, whereas this peak in the unmodified copolymer is smaller but sharper; more significantly, a second order of the lamellar repeat could be seen in the unmodified copolymer while no such higher orders were visible in the modified copolymer.

DISCUSSION

Since the position of the Bragg reflection does not significantly change upon the insertion of HFIB units, it is likely that HFIB does not alter the packing of the chains within the lamellae, although it induces disorder within the crystalline lamellae[2]. The small-angle X-ray scattering data show that the average repeat distance L between the lamellae in the HFIB terpolymer is one-half the corresponding value in the unmodified E/CTFE copolymer (*Table 2*). Also, the lamellae in the copolymer are more coherent (second order peak in the SAXS curve), and have a narrow distribution of both lamellar thickness and interlamellar separation (sharp SAXS peak) than the terpolymer. These results are consistent with the electron microscopy studies of the unmodified and modified polymer (*Figure 3*), which show that the lamellae in the E/CTFE copolymer are well defined and are arranged into bundles; this somewhat resembles spherulitic morphology. On the other hand, the lamellae in the modified polymer are not as well defined, are less coherent, and are fragmented.

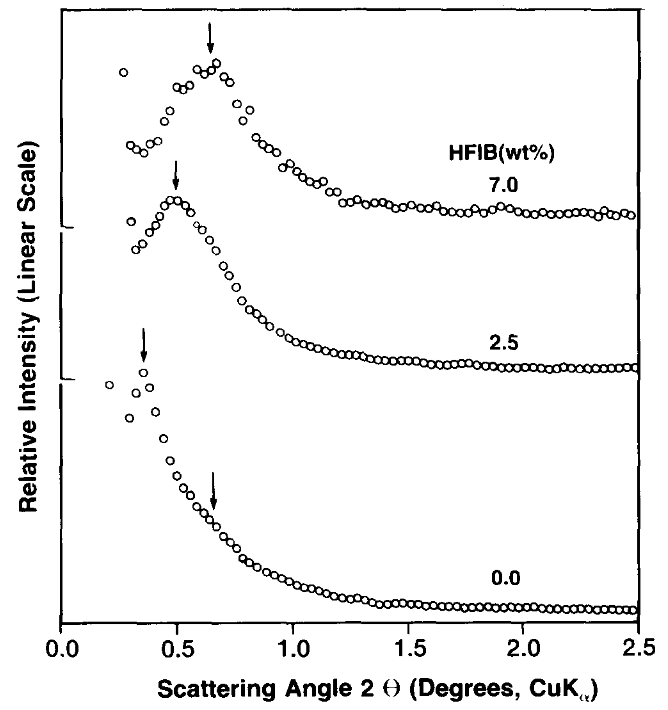

Figure 2 Small-angle X-ray scattering curves of E/CTFE copolymer with 0%, 2.5% and 7.0% HFIB

Table 2

HFIB (wt%)	L (Å)	Crystalline index (%)	Crystalline size (Å)	Melting point (°C)	Area of melting endotherm (cm^2 mg^{-1})
0	350–450	37	135	240	0.66
2.5	180	30	120	226	0.53
3.75	–	26	100	221	–
5	–	25	95	218	–
7	140	23	95	212	0.32

It is possible that while the polymer is crystallizing from the melt, a random encounter with the bulky HFIB units might cause the E/CTFE chain to make an excursion into amorphous regions, including interlamellar regions, and then re-enter the lamellae. This model is in agreement with the finding that the position of the crystalline reflections are not significantly different in modified and unmodified E/CTFE copolymer. It is likely that HFIB segments fragment the lamellae, impede their growth and organization during solidification, and also segregate the HFIB units into the interlamellar regions. Thus, kinetics of crystal growth might affect the stress-cracking behaviour. Other possible explanations will be discussed below.

Fragmentation of the lamellae by randomly placed HFIB groups along the E/CTFE backbone might account for the lack of coherence over long distances in the lamellae stacks, and also for the non-uniformity in the thickness and the separation of the lamellae. HFIB moieties in the interlamellar regions can cause the molecules in the amorphous regions to be packed less densely in the HFIB modified copolymer than in the E/CTFE copolymer, and thus enhance the electron-density contrast between the crystalline and amorphous regions[2]. This could contribute to the higher small-angle peak intensity in the modified copolymer. The effect of random placement of the HFIB units along the E/CTFE backbone is therefore to break up the lamellae into smaller fragments, to produce thinner lamellae, to produce a wider distribution of lamellar thickness/interlamellar spacing, and to reduce the density of the amorphous matrix. Because of these differences, as discussed in ref. 2, it is possible that an increased mobility of the crystallites in the terpolymer contributes to a better stress-cracking performance.

Despite the similarities in the crystal lattices of the modified and the unmodified C/CTFE copolymer, the melting-point of the terpolymer decreases from 240°C at 0% HFIB to 212°C at 7% HFIB (*Table 2*). Noncrystallizable HFIB–E/CTFE segments in the polymer backbone might contribute to the melting point depression[5]. The decrease in the chain-packing density can account for the sharper and longer β-relaxation peak although the β-relaxation temperature (78°C, glass transition temperature) remains unchanged[6]. As argued in ref. 2, the decrease in the α-transition temperature from

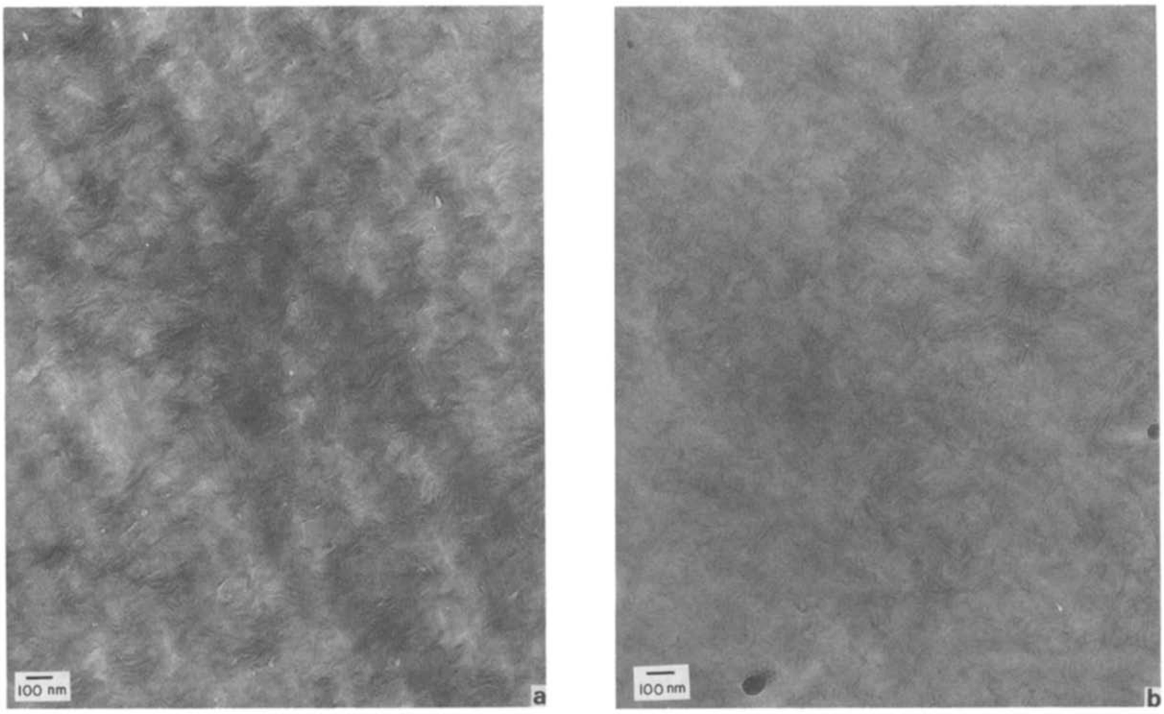

Figure 3 Electron micrographs of E/CTFE copolymer with (a) 0% and (b) 7% HFIB. The dark regions correspond to the crystalline lamellae, and the light regions represent the interlamellar amorphous regions

127°C to 105°C at 7% HFIB[6] could be due to the loose packing of the chains in the amorphous regions. This is in agreement with our SAXS results and, as pointed out in ref. 2, with the theoretical predictions of Manabe and Kamide[7]. However, since the α-transition occurs above the glass transition temperature ($\sim$75°C), it is possible that T_α is affected by changes in the relaxation of constrained amorphous molecules, which might, for instance, exist at the crystalline–amorphous interface. A decrease in T_α in the presence of HFIB could also be attributed to the decrease in the energy barrier for the conformational changes[8,9] in the fragmented, thinner lamellae in the modified copolymer. Finally, $\tan\delta$ at or above 150°C (at which stress-crack resistance measurements were made) is higher for material containing HFIB, again confirming that the viscous component (amorphous phase) plays a major role in determining the mechanical properties of the terpolymer at these temperatures.

Some of the data can be understood if we regard the semicrystalline polymer as a composite composed of rigid crystalline domains intimately linked and immersed in a flexible amorphous matrix. In the unmodified E/CTFE copolymer, the rigid domains are longer, thicker and well organized. In the modified copolymer, the rigid crystalline domains are shorter and thinner and their thickness and interdomain separation vary over a wide range. A more flexible amorphous matrix in the modified terpolymer enhances the mobility of the smaller lamellae. Further, the domains are more crystalline in the unmodified polymer than in the as-prepared, modified polymer, and the total volume fraction of these domains is higher in the as-prepared unmodified polymer. Finally, the growth of the crystalline domains is impeded by the HFIB-substituted segments. Each of these differences between the two polymers can be used to explain the improved resistance to stress-cracking of modified E/CTFE copolymer. We speculate that smaller lamellae and increased mobility of the amorphous matrix are the major factors contributing to the improved stress-cracking characteristics of the HFIB modified E/CTFE copolymer.

CONCLUSION

HFIB disrupts the crystallization of E/CTFE copolymer and is probably segregated in the interlamellar amorphous regions. The packing of the chains in the crystalline regions is very similar in the modified and the unmodified polymer. In the modified polymer the chains are less densely packed in the amorphous regions. The average lamellar repeat in the modified polymer is one-half of that in the unmodified polymer, the lamellae are less coherent and show a higher degree of non-uniformity. These structural features can account for the improved stress-crack resistance of the HFIB modified E/CTFE copolymer.

ACKNOWLEDGEMENTS

We thank H. B. Chin and N. K. Kundel, who carried out the synthesis of the terpolymer and measured the properties of the terpolymer, J. Marti and V. Kramer for electron micrographs, and J. P. Sibilia for his comments.

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