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Influence of side branch on the elastic modulus of ethylene–tetrafluoroethylene terpolymers

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ABSTRACT

Influence of side branches on the storage modulus of ethylene–tetrafluoroethylene (ETFE) terpolymers has been investigated on the basis of dynamic mechanical analysis. The terpolymer containing short branches (CF_3) has been found to behave in a different manner from the case of long branches (C_4F_9). The storage modulus was found to depend sensitively on the content of branches and also the degree of crystallinity in the case of terpolymer with long branches, while the modulus did not change very much for the sample with short branches even when the crystallinity was changed remarkably. The storage modulus of the terpolymer with long branches was found to behave similarly to that of ETFE copolymer without any branch. These differences were successfully interpreted on the basis of mechanical series model of crystalline and amorphous phases, where the modulus of the bulk sample is dependent sensitively on Young's modulus of the crystalline region. The short branches (CF_3) are included in the crystal lattice and the crystal lattice is expanded with an increment of branch content, resulting in the remarkable decrease in Young's modulus of the crystal lattice. The long branches (C_4F_9) are on the other hand, excluded out of the crystal lattice and Young's modulus of the crystal region is not affected very much. This difference in Young's modulus of the crystal lattice reflects on the different behavior of the modulus of the bulk sample as mentioned above.

1. Introduction

Ethylene–tetrafluoroethylene copolymer (ETFE) is a melt-processable fluoropolymer having excellent weatherability, thermal and chemical stability [1]. ETFE is an alternating semi-crystalline copolymer, the crystal structure of which was investigated extensively [2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17]. Commercially available ETFE copolymers are terpolymers consisting of ETFE unit copolymerized with the termonomer for improving the practical properties, especially the anti-stress cracking and tensile elongation at high temperature [18]. For example, an introduction of 3,3,4,4,5,5,6,6,6-nonafluorohexene ($CH_2{=}CHC_4F_9$) or perfluoropropylvinylether ($CF_2{=}CFOC_3F_7$) to ETFE copolymer improves the tensile strength and the elongation behavior at high temperature [8,18]. However, the influence of the chemical structure and relative content of these termonomers on the physical properties of ETFE copolymer has not yet been revealed enough well. Especially, a clarification of the factors governing the elastic modulus is very important for the material design.

An influence of the side chain of termonomers on the elastic modulus of ETFE was reported in several papers [2,3,4,5, 8]. But almost no detailed and concrete interpretation was made concerning the relation between the structure and elastic modulus of the ETFE terpolymers. Funaki et al. reported the crystal structures of the terpolymers using X-ray diffraction data, where hexafluoropropylene ($CF_2{=}CFCF_3$; HFP) with CF_3 side chain and 3,3,4,4,5,5,6,6,6-nonafluorohexene ($CH_2{=}CHC_4F_9$; NFH) with C_4F_9 side chain were selected for termonomers [19]. The ETFE copolymer is known to show the crystal phase transition between the low-temperature and high-temperature phases at a transition point T_c. This T_c was found to shift to lower temperature side by introducing the CF_3 branches, whereas it does not change very much by introducing the C_4F_9 branches. In this way, the existence of side branches affects the behavior of the crystal phase. The unit cell size of ETFE copolymer increases by introducing the CF_3 branches and it changes to the pseudo-hexagonal high-temperature phase even at the room temperature. Contrarily the unit cell size does not change very much when the C_4F_9 branches are introduced in the ETFE

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Table 1
ETFE copolymer and terpolymers.

	Monomer content/mol%			
	E	TFE	Termonomer[a]	
			Monomer	Content
ETFE	50.0	50.0	–	0
$ET\text{-}CF_3$ 2.7	44.1	53.2	HFP	2.7
$ET\text{-}CF_3$ 4.6	44.0	51.4		4.6
$ET\text{-}CF_3$ 8.5	43.8	47.7		8.5
$ET\text{-}C_4F_9$ 0.8	45.6	53.6	NFH	0.8
$ET\text{-}C_4F_9$ 2.5	44.9	52.6		2.5

[a] HFP Hexafluoropropylene $CF_2{=}CFCF_3$; NFH 3,3,4,4,5,5,6,6,6-nonafluorohexene $CH_2{=}CHC_4F_9$.

copolymer chains. It was proposed that the CF_3 branches are included in the crystal lattice, whereas the longer branches (C_4F_9) are excluded to the amorphous region or the lamella surface [19].

In this way, the structure and elastic modulus change remarkably depending on the existence of termonomers and their types. Unfortunately, however, we do not know the reasons why these structural differences are related with the difference in physical properties of the bulk samples. This type of study was reported concerning the mechanical properties of grafted copolymers in Ref. [20]. In the present paper the viscoelastic behaviors have been compared between the ETFE copolymer and the corresponding terpolymers, from which the effects of side chains on the mechanical property are discussed by taking the above-mentioned structural characteristics into consideration.

2. Experimental

2.1. Samples

The copolymers were synthesized by the radical polymerization [21,22,23,24,25]. The copolymer compositions were estimated by fluorine-content analysis and melt-state NMR techniques. The composition of the copolymers is listed in Table 1. Hereafter these terpolymers are named $ET\text{-}CF_3$ *X* and $ET\text{-}C_4F_9$ *X*, where *X* is a mol% of termonomer unit. Unoriented films of 200 µm thickness were prepared by compression molding at 300 °C followed by quenching in a water-cooled press instrument (about 50 °C/min) or by slow cooling to an ambient temperature (about 0.4 °C/min).

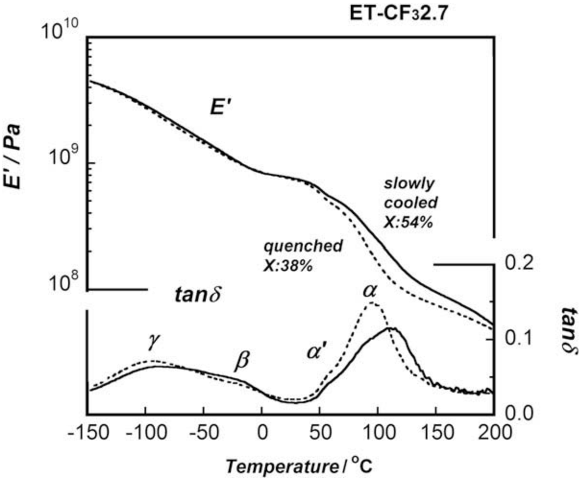


Fig. 1. Comparison in temperature dependence of the storage modulus and tan δ of ETFE terpolymer with 2.7 mol% HFP ($ET\text{-}CF_3$ 2.7) between the samples prepared under different conditions. The cooling rates were about 50 °C/min and 0.4 °C/min for the quenched and slowly cooled samples respectively.

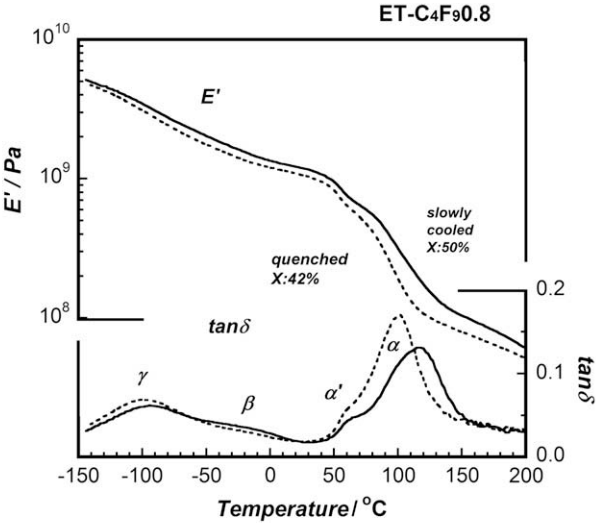


Fig. 2. Comparison in temperature dependence of the storage modulus and tan δ of ETFE terpolymer with 0.8 mol% NFH ($ET\text{-}C_4F_9$ 0.8) between the samples prepared under different conditions. The cooling rates were about 50 °C/min and 0.4 °C/min for the quenched and slowly cooled samples respectively.

2.2. Measurements

Dynamic mechanical behavior was measured by an IT instrument rheometer DVA200 at 10 Hz, where the heating rate was 6 °C/min from −150 °C to 200 °C. Degree of crystallinity of these samples was evaluated on the basis of the wide angle X-ray diffraction (WAXD) data taken with a Rigaku RINT2500 X-ray diffractometer at 25 °C.

3. Results and discussion

3.1. Influence of the thermal history on dynamic mechanical behavior

Figs. 1 and 2 show, respectively, the temperature dependence of the storage modulus (E') and the tan δ measured for the $ET\text{-}CF_3$ 2.7 and $ET\text{-}C_4F_9$ 0.8 samples prepared under different conditions. The crystallinity of the slowly cooled sample was higher than that of the melt-quenched sample as indicated in these figures. There are four relaxation peaks, α, α′, β and γ in the tan δ curves as already reported for a series of ETFE copolymers (without termonomers) [4,5,7,17]. These α and γ relaxations are related to the thermal motion of the chains in the amorphous region and the α relaxation corresponds to the glass transition. These relaxation peaks shifted to higher temperature side when the degree of crystallinity was increased by slowly cooling, and the corresponding tan δ peak height became lower as shown in Table 2. This comes from such

Table 2
Degree of crystallinity, T_g, tan δ and storage modulus of ETFE copolymer (50 mol% TFE content) prepared under different conditions.

Sample	Degree of crystallinity/%	T_g/°C	tan δ at T_g	Storage modulus at 25 °C/MPa
Quenched sample	49	132	0.16	1230
Slowly cooled sample	57	156	0.12	1340

Table 3
Degree of crystallinity, T_c and T_g of ETFE copolymer (50 mol% TFE content) and the terpolymers.

Sample	Degree of crystallinity/%	T_g°C	T_c°C
ETFE	49	132	60–70
ET-CF_3 2.7	38	97	−10
ET-C_4F_9 2.5	30	87	40

a reason that the chain mobility in the amorphous phase is depressed by the existence of crystalline phase.

In the temperature region below T_g (80–120 °C), the storage modulus (E') of ET-CF_3 terpolymer does not depend on the crystallinity, whereas the E' of ET-C_4F_9 terpolymer depends on the crystallinity. In the latter case, the E' is lower for the sample of lower crystallinity.

For some samples the temperature region to detect the α' relaxation is apparently close to the temperature region of the crystalline phase transition (T_c) where the low- and high-temperature phases show the transition [17]. The low-temperature form is a monoclinic phase consisting of planar-zigzag chains and the high-temperature form is a pseudo-hexagonal phase in which the conformationally disordered chains are packed in parallel to the chain axis [15]. On the basis of X-ray diffraction measurement in the heating and cooling processes, the transition temperature was found out as follows: the T_c was about 65 °C for the ETFE copolymer with 50–54 mol% TFE content, which was close to the α' transition peak. Similarly the ET-C_4F_9 0.8 shows almost the same T_c as that of ETFE copolymer as shown in Table 3 [19]. However, the α' transition peak detected for ET-CF_3 2.7 sample does not correspond to the phase transition temperature position, ca −10 °C, which was much lower than the α' peak position. In other words, it is more reasonable to consider that the T_c and α' peak position happen to overlap with each other, and the origin of the α' peak is not necessarily clear at the present stage.

3.2. Dependence of dynamic mechanical behavior on termonomer content

Figs. 3 and 4 show, respectively, the temperature dependences of the storage modulus and tan δ measured for ET-CF_3 and ET-C_4F_9 samples with the various termonomer contents. The α relaxation temperature or T_g shifted to the lower temperature side with increasing the termonomer content. The tan δ peak height at the α and γ transition temperatures increased with increasing the termonomer content. The degree of crystallinity (X) and T_g are plotted against the termonomer content as shown in Fig. 5. The degree of crystallinity and T_g of the ET-C_4F_9 are sensitively affected by the termonomer content. These values are lower than those of ET-CF_3. In the latter case, the X and T_g decrease gradually as the CF_3 content is increased.

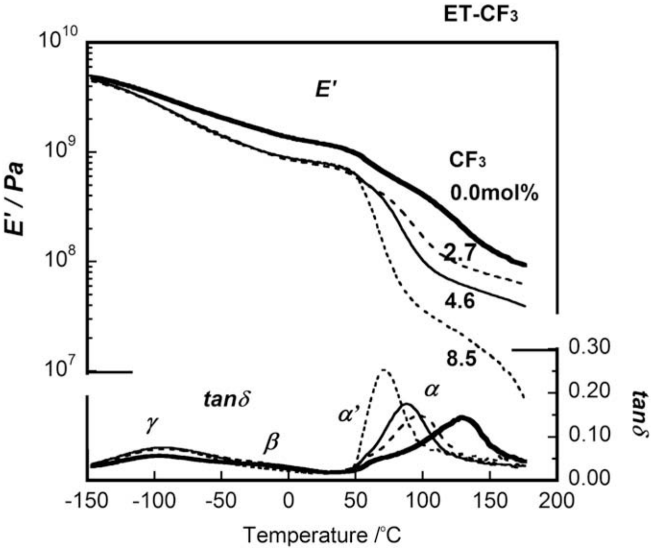


Fig. 3. Temperature dependence of the storage modulus and tan δ for the ETFE terpolymers with various HFP contents (ET-CF_3).

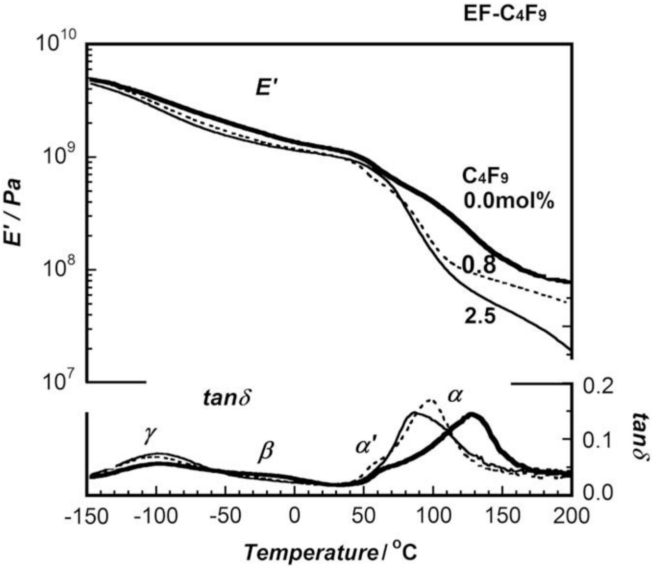


Fig. 4. Temperature dependence of the storage modulus and tan δ for the ETFE terpolymers with various NFH contents (ET-C_4F_9).

Fig. 6 shows the dependence of the storage modulus on the termonomer contents evaluated at 25 and 150 °C. In the case of ET-CF_3 sample, the storage modulus at 25 °C decreased steeply by introducing a small amount of HFP termonomer. But it was saturated beyond 3% of HFP content. On the other hand, the storage modulus at 25 °C decreased with increasing the C_4F_9 content. The value was higher than that of ET-CF_3 terpolymer. At

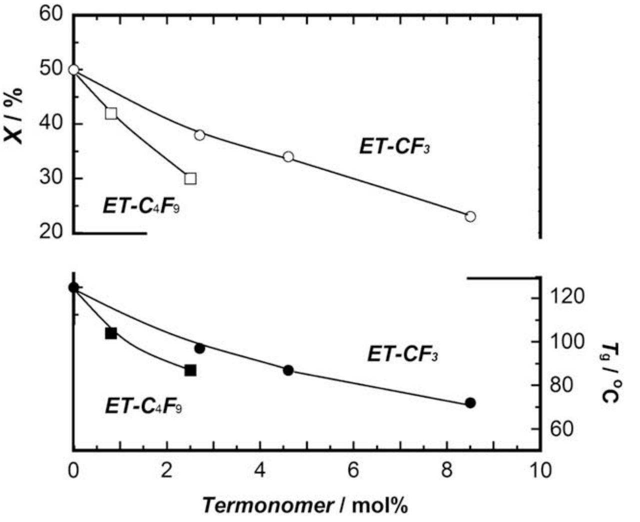


Fig. 5. Termonomer content dependence of the degree of crystallinity and glass transition temperature measured for ET-CF_3 and ET-C_4F_9 terpolymers.

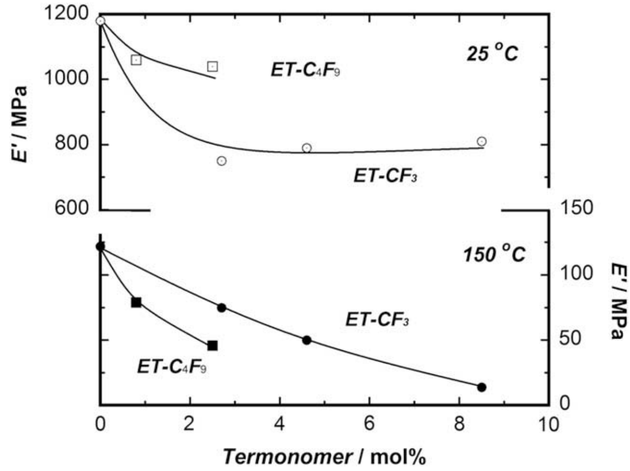


Fig. 6. Termonomer content dependence of the storage modulus at 25 and 150 °C measured for ET-CF_3 and ET-C_4F_9 terpolymers.

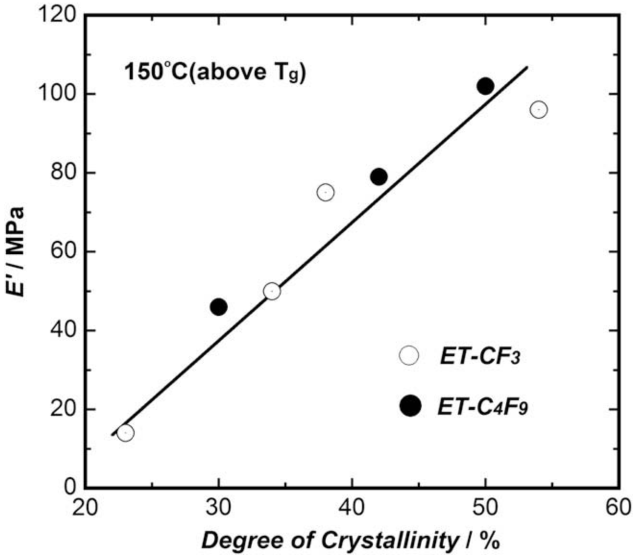


Fig. 8. Dependence of the storage modulus on the degree of crystallinity at 150 °C for ET-CF_3 and ET-C_4F_9 terpolymers.

150 °C (higher than T_g), the modulus of ET-CF_3 was higher than that of ET-C_4F_9. The storage modulus decreased steeply by introducing the termonomer component in both of these two cases. These behaviors at 150 °C are remarkably different from the behaviors observed at 25 °C.

Fig. 7 shows the dependence of the storage modulus at 25 °C on the degree of crystallinity. The modulus of ET-C_4F_9 increased as the crystallinity was increased, while that of ET-CF_3 did not depend on the crystallinity and was lower than that of ET-C_4F_9. Different behavior was observed for the E' at 150 °C as seen in Fig. 8, where the E' increased almost linearly with an increment of crystallinity and both the two kinds of copolymer showed the same tendency on a common line. In other words, the modulus depends only on the degree of crystallinity and does not depend on the side chain length, different from the case at 25 °C.

Fig. 9 shows the dynamic mechanical behavior of the terpolymers with almost the same content of side chains. Here the result of ETFE copolymer (without a termonomer) is also shown for comparison. In the temperature region of −50 to 100 °C, the storage modulus is lower in the order of ET > ET-C_4F_9 > ET-CF_3. The E' of ET-CF_3 is lower than that of ET-C_4F_9 in spite of higher crystallinity.

In this way, the mechanical property or the modulus E' changes sensitively depending on the type of side branches, their content and the degree of crystallinity. The characteristic points to be noticed are summarized as below.

(1) The E' at 25 °C or below T_g changes depending on the degree of crystallinity for the case of ET-C_4F_9, while it does not change very much for ET-CF_3.
(2) The E' at 150 °C, higher than T_g, changes linearly with the degree of crystallinity for both the ET-CF_3 and ET-C_4F_9 samples.
(3) The E' below T_g is lower for the ET-CF_3 sample than those of ETFE and ET-C_4F_9 cases.

These behaviors may be interpreted reasonably on the basis of a mechanical model as discussed in the next section.

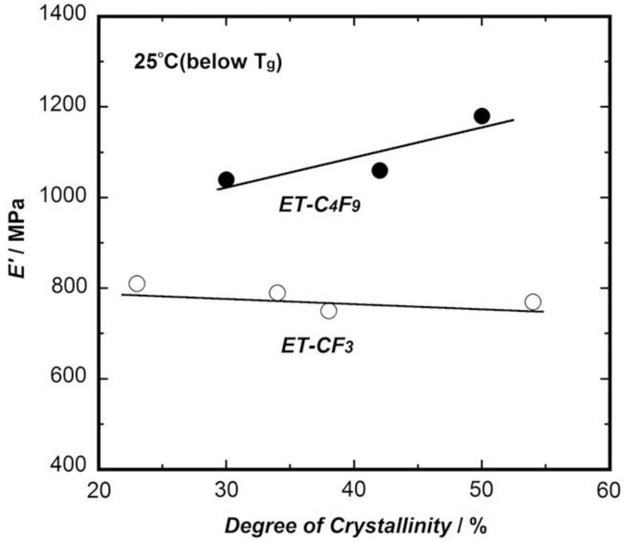


Fig. 7. Dependence of the storage modulus on the degree of crystallinity at 25 °C for ET-CF_3 and ET-C_4F_9 terpolymers.

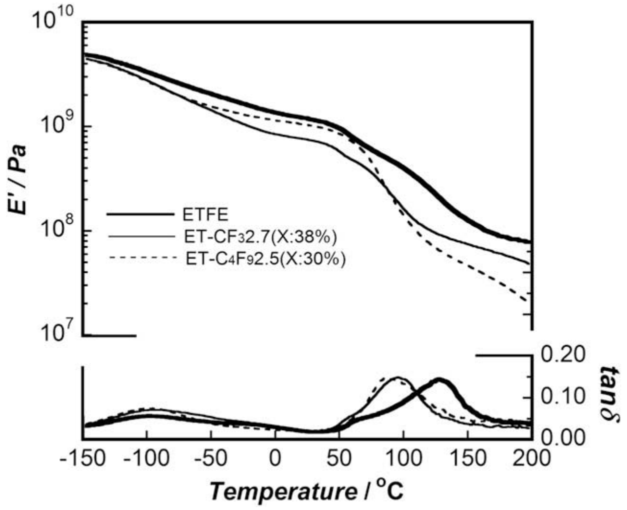


Fig. 9. Comparison in temperature dependence of the storage modulus and tan δ between the ETFE copolymer, ET-CF_3 2.7 and ET-C_4F_9 2.5 terpolymers.

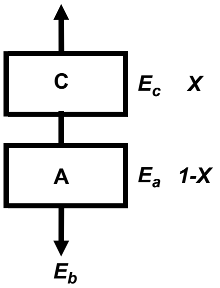


Fig. 10. Mechanical series model of semi-crystalline polymer.

3.3. The mechanical model

We assume here the mechanical series model consisting of the crystalline and amorphous phases as often used in a good approximation (Fig. 10).

Young's modulus E_b of the unoriented bulk sample is given as below.

$$1/E_b = X/E_c + (1-X)/E_a \tag{1}$$

where E_c and E_a are the modulus of the crystalline and amorphous regions, respectively, and X is the degree of crystallinity.

As pointed out above, in the case of ET-CF_3, the modulus below T_g does not depend on the degree of crystallinity. If the E_c is almost equal to E_a, the modulus does not depend on the degree of crystallinity as understood immediately from Eq. (1). The assumption of $E_c \approx E_a$ is reasonable below T_g since the E_c of the unoriented sample is expressed as given in Eq. (2).

$$3/E_c = 1/E_{\text{chain}} + 2/E_{\text{lateral}} \approx 2/E_{\text{lateral}} \tag{2}$$

where the E_{chain} or the modulus along the chain direction is much higher than the modulus in the lateral direction E_{lateral}. Since the E_a and E_{lateral} are in almost the same order below T_g [26],

$$E_c \approx (3/2)E_{\text{lateral}} \approx E_a \tag{3}$$

This relation was used to explain the mechanical behavior of the ET-CF_3 terpolymer below T_g.

At higher temperature, the E_a is remarkably lower than E_{lateral} and E_c. Since the first term in Eq. (1), X/E_c, is negligible the bulk modulus is expressed in Eq. (4). The E_b depends only on the X and E_a.

$$E_b = E_a/(1-X) \tag{4}$$

This equation can explain the experimental data given in Fig. 8. By applying the experimental data of E_b and X to Eq. (4), the E_a is estimated to be about 40 MPa at 150 °C.

On the other hand, the case of ET-C_4F_9 is different in situation. If the E_c or E_{lateral} is assumed to be equal to E_a below T_g, the E_b becomes constant ($=E_c=E_a$). This is not consistent with the experimental data shown in Fig. 7. Rather the E_c should be higher than E_a even below T_g. In the temperature region higher than T_g, the E_c is overwhelmingly higher than E_a and so the relation of $E_b \approx E_a/(1-X)$ can be applied also to the case of ET-C_4F_9 sample as supported by the data in Fig. 8.

In the case of ET-CF_3, the assumption of $E_c \approx E_a$ works reasonably to explain the constant E_b (or E') value shown in Fig. 7. The difference in these behaviors may come from the difference in the crystal structure of these terpolymers. In the case of ET-CF_3, CF_3 branches are included in the crystal lattice and the unit cell size expands largely with an increment of CF_3 content. Therefore the E_c decreases gradually and approaches the E_a value, resulting in $E_b \approx E_c$ ($\approx E_a$). (In this case the E_c is almost equal to E_{lateral} as shown in Eq. (2). The decrease in E_{lateral} with the expansion of the unit cell size can be seen in the case of orthorhombic polyethylene, for example [27].) In the case of ET-C_4F_9, the relation of $E_c > E_a$ is more reasonable because the C_4F_9 branches are excluded from the lattice.

Fig. 11 shows the summary of the discussion with some schematic illustrations of stacked lamella of ETFE terpolymers. The crystallinity dependence of E_b can be interpreted reasonably by taking the different relation of E_c and E_a between these two terpolymers into consideration. The mathematical model employed in the discussion seems reasonable for the interpretation of experimental data presented here, but it must be confirmed by more number of experimental data in future.

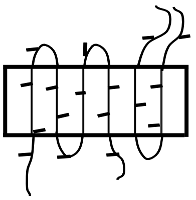
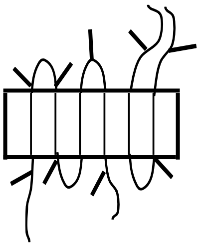
	ET-CF_3	ET-C_4F_9
Below Tg	$E_c \approx E_a$ E_b : constant (independent of crystallinity X)	$E_c > E_a$ E_b : proportional to X
Above Tg	$E_c \gg E_a$ $E_b \approx E_a/(1\text{-}X)$	$E_c \gg E_a$ $E_b \approx E_a/(1\text{-}X)$
Structure	CF_3 branches included in the lamella 	C_4F_9 branches excluded out of the lamella 

Fig. 11. Summary of the mechanical behavior and schematic illustration of stacked lamella estimated for ETFE terpolymers. In the case of ET-CF_3, the CF_3 branches are included in the crystal lattice and so the lattice is expanded. In the case of ET-C_4F_9, the long branches are excluded out of the crystal lattice, and the lattices do not very much expand.

4. Conclusions

In the present paper the effect of side groups on the dynamical viscoelastic property of ETFE copolymers has been investigated using a series of terpolymers. The important points may be described as below. Before summarizing them, however, it must be noticed here that the content of the third monomer is narrow (0–8%) and the conclusions deduced in the present study may be useful only in this relatively low range of the third monomer content. Ideally, of course, it is desired to increase the content to higher value, but the synthesis of terpolymer with higher content is quite difficult at present.

The behavior of the storage modulus of ETFE terpolymers below T_g is different, depending on the side chain length and its content. While the storage modulus of terpolymers with long side chains (C_4F_9) depends on the side chain content and the crystallinity, that of terpolymers with short side chains (CF_3) does not depend on the side chain content and the crystallinity. These behaviors have been found to be interpreted reasonably on the basis of simple mechanical series model of these terpolymers. The crystalline modulus E_c of ET-CF_3 terpolymers decreases when the CF_3 side chains are included into the crystal lattice. As a result, the E_c is almost equal to E_a, allowing us to understand the experimental data that the storage modulus does not depend on the degree of crystallinity. On the other hand, the crystalline modulus E_c of ET-C_4F_9 is considered not changed very much because the C_4F_9 side chains are excluded out of the crystal lattice. This characteristic feature can allow us to say that the storage modulus depends on the degree of crystallinity because E_c is higher than E_a.

In this way, the behavior of bulk mechanical property is affected remarkably by the existence of side chains. It should be noted that the inclusion and exclusion of side chains in the crystal lattice result in the remarkable difference in the mechanical behavior of ETFE copolymer sensitively.

In the present study the effect of side branches of C1 and C4 lengths was investigated. Of course it is important to study the effect of branches of intermediate carbon numbers (C2 and C3). But the introduction of these branches has not yet been tried, which should be an important theme to be challenged in a near future.

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