Study of the Thermal Properties and Relaxation Transitions in Tetrafluoroethene-Ethene Copolymers

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ABSTRACT: Copolymerization of tetrafluoroethene (TFE) with ethene (E) in water-alcohol medium initiated by 2,2′-azo-bis-izobutyronitrile (AIBN) at 338 K and 4.2 MPa was conducted in an autoclave by employing a semiflow procedure to feed the comonomers. The thermal properties of the copolymers under both the static and dynamic conditions of thermal treatment in air (ageing) were studied. The most pronounced changes in the initial temperature of destruction were observed for the compositions containing more than 42 mol % TFE, which corresponded to the formation of alternating copolymers. The reaction of thermal degradation was found to follow the first order kinetic equation, with the activation energy 174 kJ · mol^{-1}. The higher thermal stability of the alternating TFE-E copolymers was proved by IR spectroscopy and DTA analysis. Both the melting and crystallization DSC scans of copolymers of various compositions were analyzed. Monomodal peak of melting (and respectively, crystallization) was observed in both scans for the alternating copolymer, whereas the second peak appeared for the copolymer fractions with the higher content of ethylene block fragments and 30–40 mol % TFE units. The dynamic-mechanical analysis showed three relaxation transitions (γ, β_1 and β_2, α) in the temperature interval from 173–433 K, related to the mobility of structural units of different type in the copolymers prepared. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2626–2632, 2001

Key words: tetrafluoroethene-ethene copolymers; heterophase polymerization; thermal properties; phase and relaxation transitions

INTRODUCTION

Copolymers of tetrafluoroethene (TFE) with 1-alkenes are known to represent alternating polymers, and the corresponding sequence of the comonomer units is the least pronounced with ethene (E).[1] Any deviation from the alternation in the copolymer chain results in the composition heterogeneity of the product. The composition and the configuration arrangement of the different structural units in the fluorine-containing co-polymers have a significant influence on their thermal and chemical properties, particularly those concerning both the phase and relaxation transitions.[1,2]

Copolymers of TFE and E represent melt-processable fluoroplastics. Therefore, their processing can be conducted by using "conventional" equipment. This advantage, combined with their outstanding thermal, chemical, and radiation stability, plus good mechanical and dielectric properties, determine their application as materials in various technical fields.[1,2]

By using DTA analysis, Loginova et al.[3] have studied the thermal stability of poly(vinylidene fluoride) (PVDF) and TFE-E copolymers of

equimolar composition as a function of the alternation of the methylene and difluoromethylene structural units. The dependence of the apparent activation energy of thermooxidative destruction (E_d) on the structure of the copolymers was also discussed on the basis of DTA data obtained. Modena et al.[4] have explored the relationship between both the melting temperature (T_m) and initial temperature of thermooxidative destruction (T_{d0}) and the copolymer composition. The authors found that T_{d0} did not depend on the copolymer composition if TFE content was below 46 mol %, however, it gradually increased above this values. On the other hand, T_m became higher as TFE content in the copolymer increased up to 50 mol %, and at higher values of the latter, the opposite trend was observed. Surprisingly, these dependencies were not directly associated with the microstructure of the copolymer.

Yamabe and coauthors[5] have found a nonlinear relationship between T_m and the copolymer composition. The increase of the TFE content from 53 to 63 mol % led to the corresponding change of T_m from 537 to 550 K. The disruption in the order (i.e., the mutual sequence of arrangement of the structural units in the copolymer chain) resulted in the change of T_m within the wider limits.[6]

A few experimental details only, associated with the kinetical analysis of the thermal decomposition of TFE-E copolymers, have been available in the literature. Morisaki[7] has found that at TFE content of 49.52 mol % the copolymer decomposed randomly in an inert medium. The corresponding kinetic parameters of destruction were as follows: the reaction order amounted to 0.94 and the apparent activation energy of thermal degradation, E_d, was found to have a value of 194.3 kJ · mol^{-1}.

The data on the glass transition temperature (T_g) of TFE-E copolymer have been rather contradictory. EPR analysis of alternating copolymer compositions conducted by Bobileva et al.[8] indicated T_g values that were close to 326 K. On the other hand, Tanigami and coauthors[9] have employed the dilatometry method for the evaluation of oriented films of TFE-E copolymer, crystallized in bulk, to find that T_g amounted to 355 K.

There have also been only a few studies devoted to the viscoelastic properties of TFE-E copolymers.[10–13] Basically, three relaxation transitions with copolymers of various comonomer composition were discussed. These changes were determined as α- and γ-transitions for the amor-phous regions and β-transitions for the crystalline ones.

In our previous work, the copolymerizations of TFE with E in both the bulk[14] and suspension[15] were studied. Depending on the starting comonomer composition and the reaction conditions, copolymers of various degrees of alternation were obtained. TFE content within 65–80 mol % in the starting comonomer composition was found to result in highly alternating copolymers. Some of the thermal properties of the products prepared by the copolymerization in bulk were discussed earlier.[16]

The present work is a continuation of our previous studies, and its objective is to study the effect of the copolymer compositions of some products prepared by suspension copolymerization on the copolymers' thermal properties and also on the corresponding phase and relaxation transitions.

EXPERIMENTAL

Copolymers prepared by suspension copolymerization of TFE with E according to methods described previously[15] and containing from 30.2–54.6 mol % TFE were studied. The copolymerization conditions were as follows: initial comonomer mixtures of various compositions; water-tert BuOH as a reaction medium; 2,2′-azo-bis-izobutyronitrile (AIBN) as an initiator; the temperature and the pressure were 338 K and 4.2 MPa, respectively; stirring speed was 17.5 s^{-1}, and inert atmosphere. The reaction pressure was maintained at almost constant value by continuously introducing TFE/E, feed of molar ratio of 50/50, into the reactor (semiflow procedure). The composition of the copolymers obtained was determined on the basis of the elemental analysis data by using the Erba Science 1108 analyzer (Italy) for C and H, whereas the fluorine content was analyzed by employing ion-exchange chromatography with the Dionex Series 200 (USA) instrument.

The DSC scans were recorded with the DSC-111 (Setaram, France) instrument while heating and/or cooling the sample at a rate of 10 K · min^{-1}. The thermogravimetric scans were recorded by using the OD-102 derivatograph (MOM, Hungary) at a heating rate of 6 K · min^{-1} within the temperature interval from 293 to 873 K.

The kinetic parameters of the thermooxidative destruction for the copolymers were determined
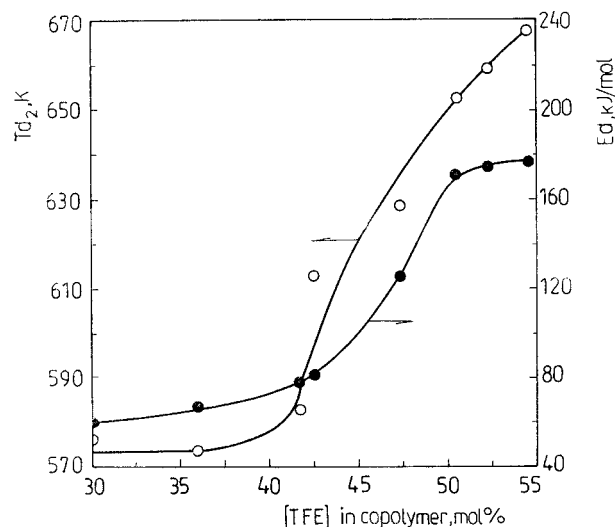
Figure 1 Dependence of the initial temperature of thermal destruction T_{d2} (○) and the apparent activation energy of thermooxidative destruction E_d (●) on TFE content in the copolymer.

from the change of the sample mass during the nonisothermal heating (dynamic thermogravimetry) within the 303–873 K temperature range and at a heating rate of 10 K · min^{-1}.

The thermal stability of the copolymers was assessed by the observed mass loss (%) resulting from the thermal treatment of the samples in air at 548 ± 5 K for 5 h under static conditions. The study on the thermal ageing was also conducted under the static (temperature of 573 ± 2 K, duration of exposure of the samples 1 h, air medium) and dynamic conditions (five consecutive extrusions performed on the instrument for the determination of the melt index, temperature of 573 ± 0.1 K, pressure of extrusion 105 N). The changes in the copolymer that occurred after the thermal ageing were registered by means of the differential infrared (IR) spectrometry.

IR spectra of the copolymers were obtained with film samples on the Specord M80 (Carl Zeiss, Germany) instrument, operating in absorption mode within the 3800–400 cm^{-1} interval.

The dynamic-mechanical spectra were obtained on a free oscillation pendulum operating at low frequency (3.5 Hz) within the temperature range from 93–673 K.

RESULTS AND DISCUSSION

Thermal Properties of TFE-E Copolymers

The mode of arrangement of the comonomer units along the macromolecular chain determined the thermal stability of the copolymers obtained, and the corresponding kinetic parameters of destruction were associated with the thermal stability of the copolymers' chemical structure. These parameters were measured according to the method developed by Reich[17] under nonisothermal conditions, i.e., by employing dynamic thermogravimetry.

The initial temperature of destruction at 2% mass loss (T_{d2}) and the apparent activation energy of thermooxidative destruction were found to increase as TFE content in the copolymer became higher. The most pronounced changes in this respect were observed within the interval from 42–50 mol % TFE, as shown in Figure 1. Alternating structures of the highest heat resistance were predominantly formed as the content of TFE in the copolymer increased to 45–55 mol %.

The thermal destruction of the TFE-E copolymer within the temperature range of 298–773 K took place in accordance with the first-order reaction kinetics. The values of the parameter E_d were within those obtained for the corresponding homopolymers (Table I). These results were in accor-

Table I   Parameters of the Structure of TFE-E Copolymers and the Corresponding Homopolymers

No.	Polymer	Monomer Unit	Reaction Order	E_d, kJ · mol^{-1}	T_{d50}, K
1	PE[a]	(—CH$_2$—CH$_2$—)	1.4	145	406
2	PVDF[b]	(—CH$_2$—CF$_2$—)	—	201	446
3	TFE-E[c]	(—CF$_2$—CF$_2$—CH$_2$—CH$_2$—)	1.04	174	470
4	PTFE[d]	(—CF$_2$—CF$_2$—)	1.0	308	509

[a] Poly(ethene).
[b] Poly(vinylidene fluoride).
[c] Tetrafluoroethene-ethene.
[d] Poly(tetrafluoroethene).

dance with the increase of the thermal stability of PE as more TFE units were introduced into the macromolecular chain. Thus, the order of increase of the thermal stability as discussed above can be expressed as follows: $(-CH_2-CH_2-)$ $< (-CH_2-CF_2-) < (-CF_2-CF_2-CH_2-CH_2-)$ $< (-CF_2-CF_2-)$

The low degree of thermal destruction for the alternating TFE-E copolymers was also confirmed by the mass loss ($> 0.5\%$) observed at temperature 548 ± 5 K for 5 h, as compared to the copolymers containing more ethylene block fragments. In the latter case, the corresponding mass loss recorded under the same conditions was within 2–4%.

The initiator (AIBN) employed for the copolymerization of TFE with E in the water-alcohol medium was found to produce more regular microstructures. For example, degree of alternation exceeding 85% was achieved at initial molar ratios of TFE and E, amounting to 75–80/25–20, respectively. This result concerning the degree of alternation was significantly higher than that obtained with ammonium peroxydisulfate[4] (70%) and with β-oxyethyl-tert-butylperoxide[18] (75%) as initiators for the copolymerization. These experimental facts are difficult to account for, because with AIBN as an initiator, various factors seem to have been superimposed. On the one hand, AIBN is known to be a powerful generator of radicals during the initial stage of copolymerization, with half-time decomposition of around 70 min at 353 K, and accordingly, it is believed to suppress the possible side reactions, such as crosslinking, grafting, etc. On the other hand, both the higher solubility and efficiency (the value of the latter exceeded 0.7) of AIBN in the reaction medium sharply reduced the time necessary for the initial homogeneous stage of the reaction, and determined the heterogeneous chain propagation within the copolymer particles formed. These effects restricted the mobility of the growing macroradicals and facilitated the nascent formation of crystalline structure. In other words, the copolymerization and crystallization took place simultaneously. These processes favored the formation of more regular structure, which, in turn, affected the thermal stability of the TFE-E copolymers. As a result, the difference between the decomposition and melting temperatures exceeded 100 K.[15]

IR spectra of alternating TFE-E copolymer samples subjected preliminarily to thermal age-
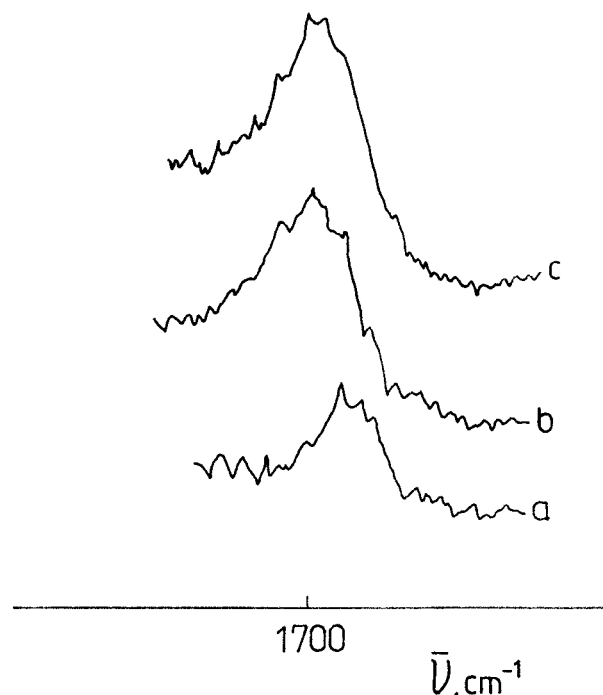
Figure 2 Differential IR spectra of TFE-E copolymers: (a) initial (nontreated) sample; (b) sample subjected to the thermal ageing under the static conditions; and (c) the same under the dynamic conditions.

ing under both static and dynamic conditions did not indicate any significant changes in the corresponding chemical structure. This confirmed the higher thermal stability of the alternating copolymer (Fig. 2). The differential IR spectra indicated absorption bands at 1755 cm^{-1} [ν(C=O)], corresponding to a carbonyl group. This characteristic band was shifted towards the "standard" one (1716 cm^{-1}), which resulted from the influence of fluorine atoms, adjacent to the carbonyl functional groups.

The intensity of the band at 1755 cm^{-1} increased after the process of dynamic thermal ageing took place, as compared to the "static" ageing process, which is believed to prove the occurrence of thermooxidative destruction to a somewhat higher degree. No other changes in the IR spectra were observed, which indicated that the functional groups, such as —C(O)F, —COOH, —CF=CH—, etc., typical for the thermal destruction of the fluoropolymers, were not formed. Similar trends were observed with the study of the mechanical characteristics of alternating copolymers after the exposure to thermal ageing under static or dynamic conditions.[15]
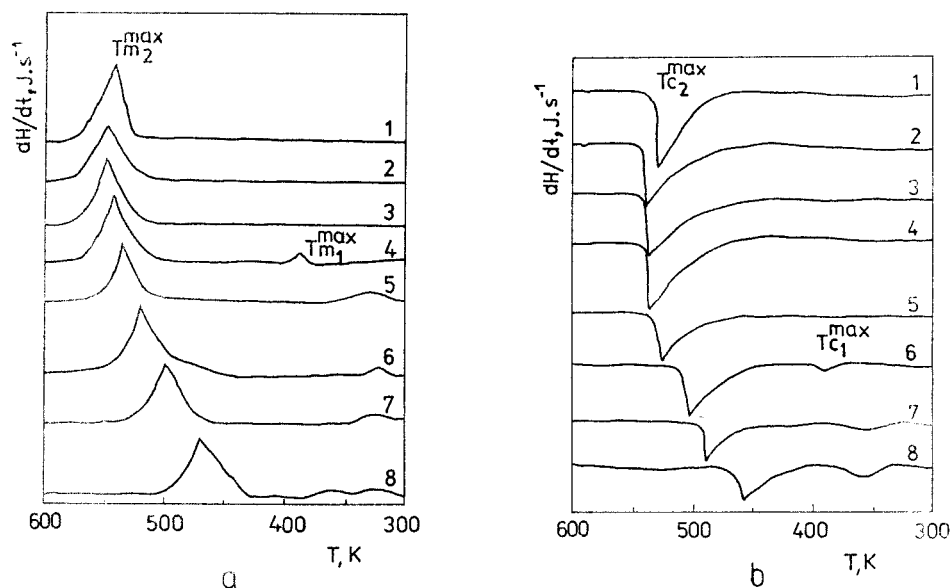
Figure 3 DSC scans obtained under the conditions of heating (a) and cooling (b) samples of TFE-E copolymer prepared by suspension copolymerization with different TFE content in the polymer (mol %). (1) 54.6; (2) 52.4; (3) 50.5; (4) 47.2; (5) 42.5; (6) 41.8; (7) 36.0; (8) 30.2.

Phase and Relaxation Transitions in TFE-E Copolymers

The phase transitions under the conditions of both heating and cooling the TFE-E copolymer samples prepared by suspension polymerizations were studied by employing the DSC method.

Both the melting and crystallization DSC scans of TFE-E copolymer samples of various compositions are shown in Figure 3(a,b). With samples of TFE content above 50 mol %, the melting scans [Fig. 3(a), curves 1–3] indicated strong monomodal endotherm with the corresponding melting temperature ($T_{m2}^{\max}$). The increase of ethylene content in the copolymer (samples corresponding to curves 4–8) produced the appearance of the low-temperature endotherm ($T_{m1}^{\max}$) within the 325–390 K range, which could be assigned to the melting of copolymer fractions with higher content of ethylene block fragments. A similar mode of the DSC scans was observed with the subsequent cooling of the molten sample, as shown in Figure 3(b). The copolymer samples containing 30–40 mol % TFE (curves 6–8) only indicated the low-temperature exotherm ($T_{c1}^{\max}$), whereas the second main exotherm ($T_{c2}^{\max}$) actually corresponded to the alternating TFE and E fragments in the copolymer. The latter formed the new crystalline structure that was determined by the well-known characteristic recurring structural sequences ($-CF_2-CF_2-CH_2-CH_2-$).

Therefore, the monomodal peaks, corresponding to the melting and crystallization of the alternating TFE-E copolymer samples prepared by suspension polymerization served as additional evidence for the higher degree of the structural and chemical homogeneity of these samples, as compared to the copolymers synthesized in bulk.[16]

The dependence of $T_{m2}^{\max}$ and the corresponding enthalpy of melting (ΔH_{m2}) on the TFE content in the copolymer (Fig. 4) indicated that the maximum for the melting temperature was observed with copolymer samples of nearly equimolar composition. On the other hand, ΔH_{m2} was found to increase as the content of ethylene fragments in the macromolecular chains became higher.

The decrease of the melting temperature with the copolymers containing 45–70 mol % ethylene fragments, according to the Flory's theory,[19] could serve as a useful tool for the calculation of the equilibrium melting temperature (T_m^o) for the copolymer of an "ideal" comonomer alternation. Thus, the value of the parameter $T_m^o = 588$ K was obtained, which was close to that for the copolymers prepared in bulk.[14]
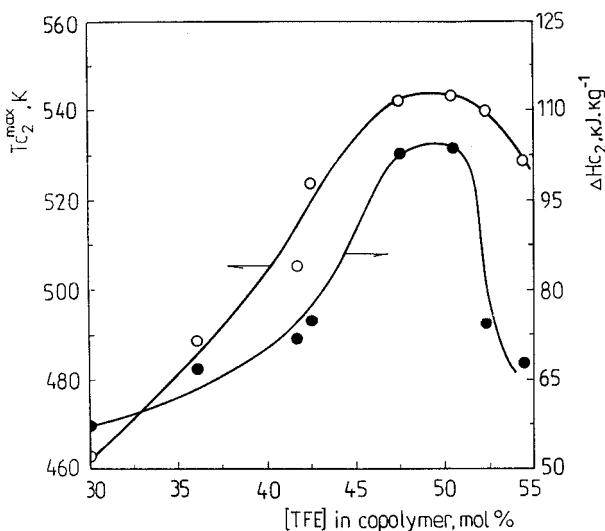
The dependence of the crystallization temperature $T_{c2}^{\max}$ and the enthalpy of crystallization (ΔH_{c2}) on the composition of the "suspension" copolymer (Fig. 5) showed that the maximum values for both parameters corresponded, approxi-
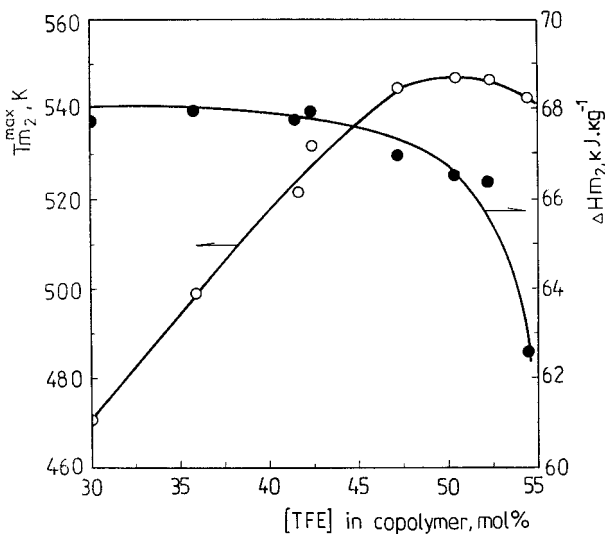
Figure 4 Dependence of temperature $T_{m2}^{\max}$ (○) and enthalpy ΔH_{m2} (●) of melting on TFE content in the copolymer.

mately, to the equimolar ratio of the comonomers in the polymer product.

The relaxation transitions in the alternating TFE-E copolymers were studied by using the dynamic-mechanical analysis ($tg\ \delta/T$ dependence, Fig. 6). On the whole, three transitions were registered for the copolymer. The first (γ-) transition was observed within the temperature range 153–173 K, which was similar to the glass-transition state II in the case of poly(tetrafluoroethene), and

Figure 5 Dependence of temperature $T_{c2}^{\max}$ (○) and the enthalpy ΔH_{c2} (●) of crystallization on TFE content in the copolymer.
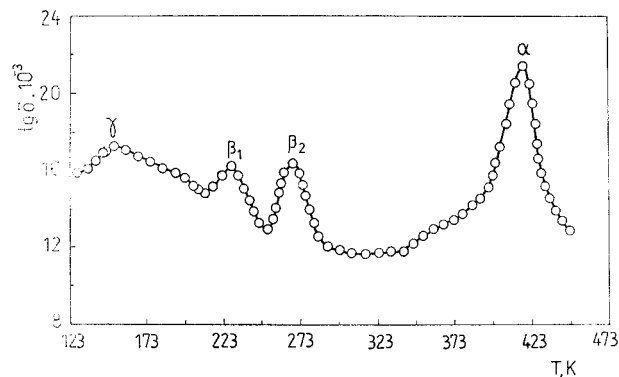
Figure 6 Dynamic-mechanical spectrum of internal friction of TFE-E copolymer at a frequency $\nu = 3.5$ Hz.

could be assigned to the mobility of the short-chain segments of the macromolecules in the amorphous regions.[20] The complex β-relaxation transition consisted of two subprocesses (β_1 and β_2), which reflected the mobility of the segments in the crystalline regions. The α-relaxation, corresponding to the glass transition in the amorphous regions with the characteristic temperature (T_g) was accompanied by the sharp change of the torsion modulus in the temperature interval from 393–433 K. The T_g temperature did not represent an additive parameter with respect to the homopolymers (PE and PTFE), and was actually shifted towards the higher temperatures (415 K), probably as a result of the stronger intermolecular interactions involving hydrogen bonds.

CONCLUSIONS

The copolymerization of TFE with E in the presence of AIBN as an initiator has been found to produce highly alternating copolymers, due to the heterophase copolymerization and crystallization, which take place simultaneously.

The thermal stability of the products synthesized shows that the alternating copolymers have a low degree of thermal destruction, i.e., the corresponding mass loss is below 0.5% at temperature 548 ± 5 K for the exposure time of 5 h. Thus, the level of the thermal stability of TFE-E copolymers is intermediate between PVDF and PTFE homopolymers. Moreover, the IR spectra recorded after thermal ageing under both the static and dynamic conditions does not indicate any significant changes in the functional groups of the alternating copolymers.

The DSC scans of TFE-E copolymers obtained in suspension show the presence of monomodal melting (and crystallization) peaks in the alternating region of the copolymers. This corresponds to the existence of a new crystalline structure, which has been determined by recurring structural sequences, such as $-CF_2-CF_2-CH_2-CH_2-$.

The mechanical tg δ/temperature dependence indicates three peaks (γ, β_1 and β_2, α) within the temperature interval 173–433 K. The α-relaxation transition (T_g) does not represent additive parameter with respect to the corresponding PE and PTFE homopolymers.

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