

Effects of equal-channel, multiple-angular extrusion on the physical and mechanical properties of glassy polymers

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ABSTRACT: Through the examples of polycarbonate and poly(methyl acrylate), the evolution of the structure and properties of glassy polymers processed by equal-channel multiple-angular extrusion (ECMAE) were studied. It was demonstrated that ECMAE allowed the substantial improvement of the set of strain–strength characteristics of these materials, regardless of the direction of loading applied. With the use of the data from scanning electron microscopy, differential scanning calorimetry, and dilatometry, we found that the simultaneous growth in the strength, plasticity, and impact resistance was related to the formation of a net of biaxially oriented polymeric chains, the decrease in the free volume, and the reinforcement of intermolecular interaction. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42180.

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INTRODUCTION

It is known that the molecular orientation in glassy polymers can substantially improve their physical and mechanical properties.¹ In addition, the methods of formation of the orientational order, namely, ram and hydrostatic extrusion, drawing, and rolling, form the orientational order along the extrusion direction only, and an increase in the degree of orientation is followed by a decrease in the cross section of the billet.

Equal-channel angular extrusion (ECAE) is a novel technique aimed at fabricating bulk polymers with precisely controlled molecular orientation.^{2–19} In addition to the constant dimensions of the extrudate maintained throughout the extrusion process, the uniqueness of the ECAE process is that multiple passes along the routes with systematically varied extrusion orientation provide the generation of many possible forms of molecular orientation. Prior research has shown that ECAE can tailor the molecular orientation of the macrometer or micrometer/nanometer scale through different extrusion routes.^{4,5,9–13,17}

In particular, in the case of route A (the extrudate is processed in the same orientation for a number of ECAE passes), the material can achieve a high molecular orientation at an angle differing from the extrusion direction. As a result, the mechanical properties of the extruded polymer become greatly enhanced

in the directions aligned with the extrusion direction and in the perpendicular direction, too. However, there is a drawback common to the case of conventional methods. Being parallel to the molecular orientation, weak planes are formed during the processing along route A. As the molecular orientation generally enhances the fracture resistance when the crack propagates perpendicular to the molecular orientation direction or at an angle to it, the fracture properties acquired after the processing along the A route become poor if the crack propagates parallel to the orientation direction.

In the case of route C (the sample is rotated by 180° around its axis at each even-numbered pass), the polymer chains are oriented at each odd-numbered pass and reverse their motion at each even-numbered pass. Therefore, the macroscopic scale of orientation is restored, and the localized molecular conformation remains highly oriented. In other words, the second pass seems to introduce an opposite local molecular orientation in addition to cancellation of the previous global deformation because of the first pass of the extrusion. This process results in a state of biaxial molecular orientation^{11,20} accompanied by the elimination of the weak planes and the mitigation of the brittle failure in nature.

In ref. 11, a series of 90° rotations in the ECAE processing was used to enhance the symmetry of the induced molecular orientations and to provide an increased impact strength of glassy

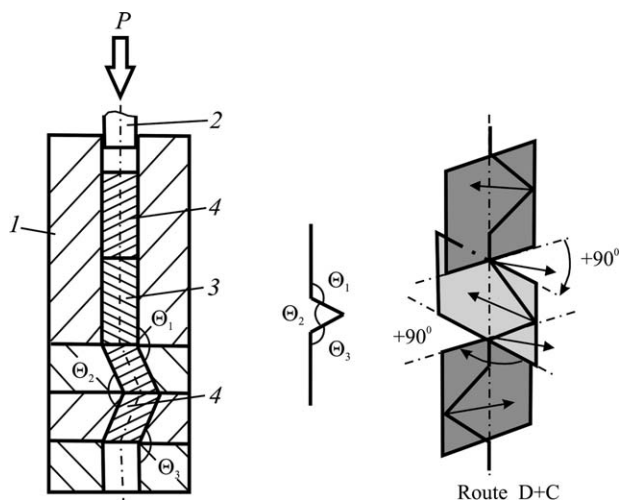


Figure 1. Scheme of the ECMAE process: (1) die, (2) punch, (3) polymeric billet, and (4) sacrificed billets.

polymers, regardless of the direction of the impact load. The solution of the problem becomes possible because of the use of a modified version of ECAE, equal-channel multiple-angular extrusion (ECMAE). ECMAE allows variation of the spatial orientation of the shear planes in the fixed increments, including the 90° rotations and variation of the intensity and the accumulated strain (ϵ) per one cycle.²¹ As compared to ECAE, an advantage of this method is that the billet stays inside the deforming channels in the course of extrusion. This fact allows one to avoid undesired relaxation processes related to the cooling and the succeeding heating of the deformed samples up to the optimum extrusion temperature or the equalizing at higher temperatures when the cycling is performed without an intermediate cooling of extrudates.

In this study, we examined the applicability of ECMAE for improving the physical and mechanical properties and reducing the dependence on the direction of the applied loading in glassy polymers with the examples of polycarbonate (PC) and poly(methyl acrylate).

EXPERIMENTAL

PC (PC 1000, Quadrant) and poly(methyl methacrylate) (PMMA; DuPont) were the objects of our research. Billets of the required size (diameter = 15 mm, length = 50 mm) were cut from cylindrical rods of 16 mm in diameter obtained by melt extrusion.

In Figure 1, the scheme of ECMAE is presented. A polymeric billet is pressed through a device composed by several pairs of channels of the same diameter intersecting at selected angles (θ_i). To maintain the direction of the motion of the billet, the inlet and outlet channels were vertically uniaxial. The oblique channels were located pairwise in the planes with the position in space to be varied by rotation about the vertical axis. The configuration allows the realization of different routes of deformation and the variants of the spatial evolution.

As a deformation route, the D+C route was selected. Detailed information on the D+C route is available in our previous work.²¹ Here, the pairwise combined oblique deforming chan-

nels were in the perpendicular planes to be rotated about the vertical axis in increments of 90° and separated by the vertical channels (Figure 1). The use of this route in the case of semi-crystalline polymers realizes the best set of properties.²¹ ECMAE was carried out at a deformation intensity ($\Delta\Gamma$) of 0.83, an extrusion rate of 0.6 mm/s, and extrusion temperatures of 393 K (PC) and 383 K (PMMA). The previous processing conditions allowed for the generation of a substantial level of molecular orientation in the polymer extrudate and minimized the molecular relaxation. They were registered with the method of microhardness (H), as reported in ref. 21. The temperature control was done with a universal measuring controller (TRM-151-01, Owen, Ukraine). The observational temperature accuracy was 0.1 K. The temperature of the deforming block within the container was maintained with an accuracy of ± 1 K. The value of ϵ was determined by the following formula:²²

$$\epsilon = 2 \sum_{i=1}^n \frac{\text{ctg } \theta_i}{\sqrt{3}}$$

where θ_i is the half-angle of channel intersection and n is the number of channel-intersection angles.

H was determined with an H tester of the PMT-3 type. For H , the relative error did not exceed 5%. The uniformity of H distribution over the sections of the extrudates was estimated by the value of dispersion (D_H), calculated as follows:

$$D_H = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (\bar{H} - H_i)^2}$$

where n is the number of measurements, H_i is the result of an individual measurement of the microhardness value, and \bar{H} is the average microhardness value. The anisotropy of microhardness (ΔH) was calculated as follows:²³

$$\Delta H = 1 - \frac{\bar{H}^\perp}{\bar{H}^\parallel}$$

where \bar{H}^\perp and \bar{H}^\parallel are the average microhardness values in the transversal and longitudinal sections of extrudates, respectively.

The dumbbell shaped specimens (head size diameter = 10 mm and length = 10 mm, working-part size diameter = 5 mm and length = 30 mm) were subjected to tensile tests. The specimens were cut along the direction of extrusion. The supporting platforms travelled at a velocity of 10 mm/min. The average values of the yield strength (σ_y), tensile strength, modulus of elasticity (E), yield strain (ϵ_y), strain at break (ϵ_b), and standard deviations were determined from the testing of five specimens of every sample.

The density of the specimens (ρ) was determined by hydrostatic weighing (AX200 type balance, Shimadzu Co.).

The differential scanning calorimetry (DSC) was performed with a thermoanalytical complex (DuPont 9900). The heating rate was equal to 10°/min, and the weight was 5 mg.

Changes in the linear dimensions of the specimens cut in the longitudinal and transverse directions with respect to the extrudate's axis were registered by a dilatometer (DIL 402 PC/4, Netzsch), and the heating rate was equal to 1°/min.

Table I. Effects of ECMAE on the H Values of the Polymers: Route D+C

ε	\bar{H}^{\perp} (MPa)	\bar{H}^{\parallel} (MPa)	ΔH	D_H
PC				
0	120	122	0.02	0.40
4.4	161	168	0.04	0.58
6.3	163	169	0.04	0.50
8.5	175	180	0.03	0.43
PMMA				
0	180	183	0.02	0.35
4.4	244	248	0.02	0.77
6.3	245	249	0.02	0.68
8.5	247	251	0.02	0.60

Scanning electron microscopy (SEM) was implemented with a JEOL JSM-6490 instrument at an accelerating voltage of 5 kV. A conducting layer (a golden layer 25–30 μm thick) was applied to the surface under investigation by a cathode sputtering method. The photographs were taken of the surfaces of the cross and longitudinal spallings of the original samples and the extrudates. The spalling was made at the liquid nitrogen temperature.

The notched (or unnotched) impact strength of the samples (a ; kJ/m^2) was calculated as follows:

$$a = \frac{A}{bS} \times 10^3$$

where A is the energy of the impact that went into the destruction of the notched (or unnotched) sample (J), b is the width in the middle of the sample (m), and S is the thickness in the middle of the sample (m).

RESULTS AND DISCUSSION

As shown in Table I, the results of H measurements of the original PC and PMMA and those after ECMAE are listed. We observed that as ε increased, H of the extrudates grew in both the longitudinal and transversal sections. In the case of PC, ΔH decreased to a value close to that of an undeformed polymer. ΔH in PMMA did not depend on the processing. At the same time, the PC extrudates were characterized by the comparatively low dispersion of H in the cross section. This fact was evidence of the sufficiently homogeneous distribution of deformation over the polymer volume. D_H decreased as ε increased in both polymers.

It is known that H of glassy polymers reacts strongly to the induced molecular orientation. In particular, H increased when the loads were parallel to the molecular orientation direction, and it was almost constant for loads perpendicular to the molecular orientation direction.²⁴ The registered behavior of H (the simultaneous growth of the absolute values of \bar{H}^{\parallel} , \bar{H}^{\perp} , and low ΔH) was related to either the formation of a uniaxially oriented structure where the polymeric chains are oriented at an angle of approximately 45° with respect to the extrudate axis or a biaxially oriented structure when the position of a part of the oriented macromolecules was perpendicular to the orienta-

tion of the second part in equal shares and/or the degree of molecular orientation. The results obtained in the course of ECMAE of semicrystalline polymers and dilatometric tests provided evidence in favor of the last suggestion.^{20,21} They demonstrated a net of interwoven fibrils of biaxial orientation in the extrudates.

As shown in Figure 2, the temperature dependences of the relative elongation [$\Delta l/l_0(T)$ where l_0 is the initial length of the specimen, l is the current length of the specimen during heating, T is the temperature] of the PC samples cut at varied angles about the extrudate axis are illustrated. Analogous dependences were observed in PMMA. The lengths of the original sample and the sample cut at an angle of 45° increased because of thermal expansion (Figure 2, curves 1 and 2). The samples cut at angles of 0, 20, 70, and 90° demonstrated a decrease in $\Delta l/l_0$ within the whole tested temperature range (Figure 2, curves 3–5). The absolute values of $\Delta l/l_0$ were determined by the competition of thermal expansion and the relaxation of oriented polymeric chains.^{8,17} The positive $\Delta l/l_0$ values were associated with the prevailing thermal expansion; the negative values were related to thermal shrinkage of the elongated macromolecules. As the largest decrease in $\Delta l/l_0$ at $T > 400$ K was observed in the samples cut at angles of 0 and 90° , a conclusion was made that the polymeric chains were the most elongated along and across the extrusion direction. At the same time, the dependences of $\Delta l/l_0(T)$ practically coincided to the directions of 20 and 70° and 0 and 90° . The reason can have been the fact that the elongated polymeric chains were uniformly distributed along these directions, and they were also of a comparable degree of the molecular orientation. Thus, the deformation along the D+C route resulted in the formation of a net of oriented polymeric chains. The direction of the preferred orientation of one part of the elongated chains forming the net coincided with the extrudate axis, and the second part was normal to it.

In the case of polymers processed by ECMAE and compared to the original material, the temperature range was extended where

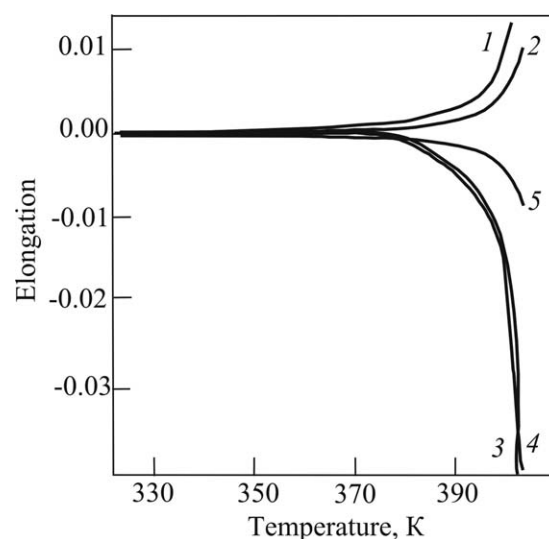


Figure 2. Temperature dependence of the elongation of (1) the initial PC samples and (2–5) the samples after ECMAE cut at angles of 45, 0, 90, 20, and 70° , respectively.

Table II. Effects of ECMAE on the Density and Mechanical Properties of the Polymers ($\varepsilon = 8.5$): Route D+C

Sample (treatment)	ρ (g/cm ³)	E (MPa)	σ_y (MPa)	σ_T (MPa)	ε_y (%)	ε_b (%)
PC						
Initial	1.198 ± 0.002	2100 ± 63	68 ± 2	70 ± 2	6.2 ± 0.4	98 ± 4
After ECMAE	1.214 ± 0.005	2600 ± 130	86 ± 3	87 ± 4	8.8 ± 0.4	106 ± 5
PMMA						
Initial	1.192 ± 0.004	2800 ± 84	58 ± 2	59 ± 2	2.7 ± 0.2	4.0 ± 0.2
After ECMAE	1.206 ± 0.005	3640 ± 175	74 ± 4	78 ± 3	3.1 ± 0.2	6.2 ± 0.3

the temperature did not modify the value of $\Delta l/l_0$ (the limit of the range was enhanced from 343 to 372 K and from 360 to 371 K in PC and PMMA, respectively). This fact was evidence that ECMAE resulted in an improvement in the molecular and/or segmental state packing. The observed increase in the density of PC and PMMA after ECMAE (Table II) confirmed the suggestion too. The secondary bonds (the van der Waal's forces) between the aligned adjacent chain segments was also effective during inhibition of the relative chain motion; this was confirmed by the results of DSC tests (Figure 3).

The DSC curve of the original PMMA was characterized by the step of ΔC_p and a small endothermic peak at the glass-transition temperature (T_g). In the case of PMMA processed by ECMAE, an additional endothermic peak was registered at a temperature higher than T_g by 10°. The additional peak was supplementary to the main endothermic peak at T_g shifted toward higher temperatures. The height of the peak increased as ε rose [Figure 3(a)]. According to ref. 25, the endothermic peak at $T > T_g$ is related to the input of heat required for the transition of macromolecules from the straightened state to the convoluted one, that is, the increase in the concentration of more energetic G-conformers. The same conclusion was made by the authors of ref. 26, who analyzed similar two-peak DSC curves

from the viewpoint of two T_g s, with the second T_g associated with the oriented polymer. The absence of exotherms in the DSC curves of the deformed polymers at $T < T_g$ pointed to the fact that ECMAE did not destroy the system of intermolecular interactions. The energy release occurred only at $T > T_g$ (small exo effect between two endothermic peaks). As the transformation of the convoluted T-conformers into the elongated G-conformers (so-called T→G transition) implied the input of the heat, the observed exothermic effect was probably determined by an increase (enhancement) in the energy of intermolecular interactions, not by this factor.

Analogous effects took place in the PC processed by ECMAE. However, in this case, the first small peak was observed, and the position of the second peak was shifted toward higher temperatures when ε increased [Figure 3(b)]. The ratio of the areas of the peaks confirmed that the G-conformers prevailed in the extruded polymer. This fact was indicative of the better orientation ability of the polymeric chains of PC compared to PMMA. Thus, on the basis of the data of the density measurements, DSC, and dilatometry, a conclusion was made that ECMAE facilitated intermolecular interaction, reduced the free volume, and modified the conformational composition of the polymer (toward high-energy G-conformers).

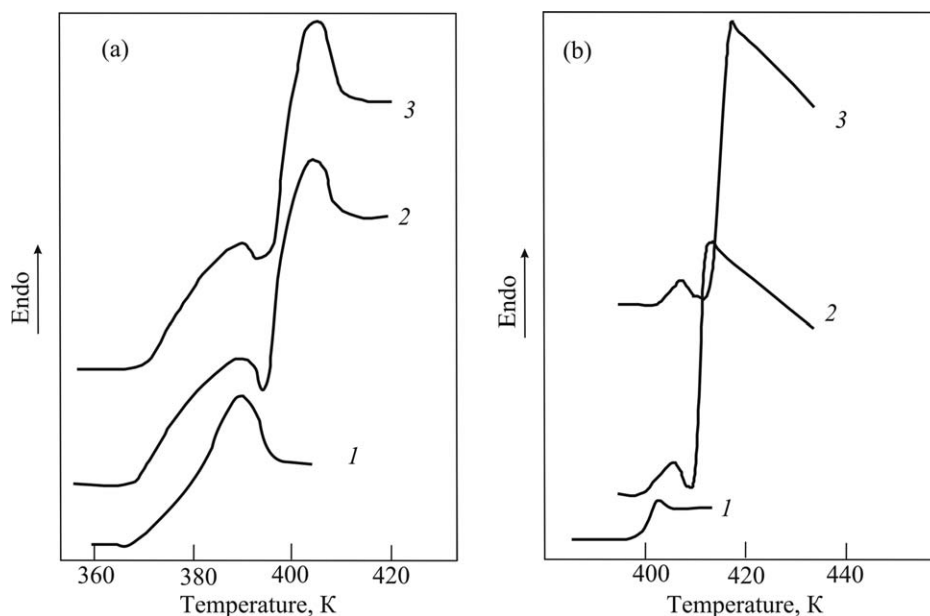
**Figure 3.** DSC traces for specimens of (a) PMMA and (b) PC: (1) $\varepsilon = 0$, (2) $\varepsilon = 4.4$, and (3) $\varepsilon = 8.5$.

Table III. Effects of ECMAE on the Impact Strength of the Polymers: Route D+C

ε	a (kJ/m ²)	
	Unnotched	Notched
PC		
0		8.2 ± 0.3
4.4	No break	13.0 ± 0.6
8.5		15.6 ± 0.8
PMMA		
0	16.2 ± 0.7	1.40 ± 0.04
4.4	23.2 ± 0.9	2.00 ± 0.06
8.5	26.9 ± 1.1	2.30 ± 0.07

ECMAE created increases in E , σ_y , and the strength of the tested polymers (σ_T) of up to 30% (Table II). The increases were clearly due to the alignment of the covalently bonded molecules parallel to the molecular orientation direction and the enhanced intermolecular packing along the maximum principal shear direction. At the same time, an increase in the plasticity (ε_y and ε_b) of the extrudates was registered. The increase of the plasticity due to the solid-phase orientation was related to formation of a net of oriented molecules restraining the development of the main crack.²⁷ In particular, this conclusion was confirmed by the data of the impact strength tests.

The impact test results are shown in Table III. We observed that ECMAE generated an increase in the fracture toughness (a) of PC and PMMA. As ε increased, the magnitude of a increased too. At the same time, the character of the crack propagation with respect to the extrusion direction was modified. The non-deformed PMMA exhibited brittle fracture behavior regardless of the crack propagation direction. This implied that a nearly isotropic state took place. When the load was applied, the crack propagated straight ahead, leaving few features on the fracture surfaces. This indicated that the fracture surfaces contained topographic irregularities smaller than the light wavelength. By contrast, once molecular orientation was introduced into the sample, complex fracture features were observed. The character of the crack propagation was determined by the value of ε . Contrary to the $\varepsilon = 4.4$ samples, the presence of a macroscopic weak plane was not observed in the samples characterized by $\varepsilon = 8.5$. As the direction of the crack propagation corresponded to the weak shear planes formed by the interfaces between the

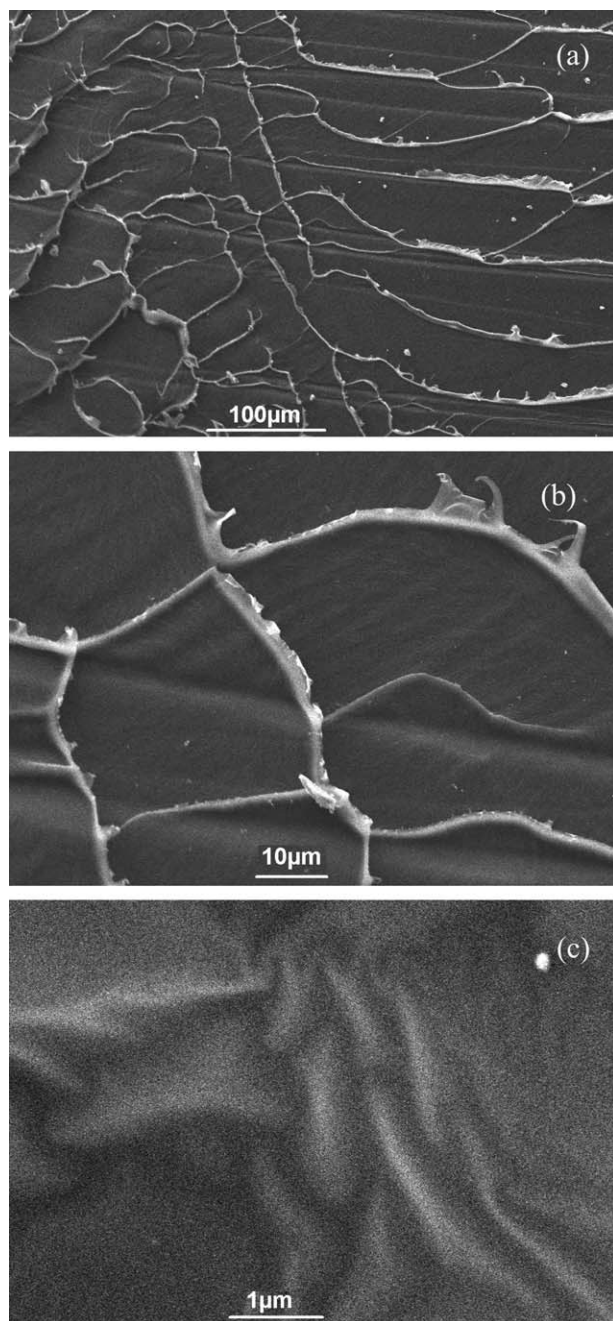
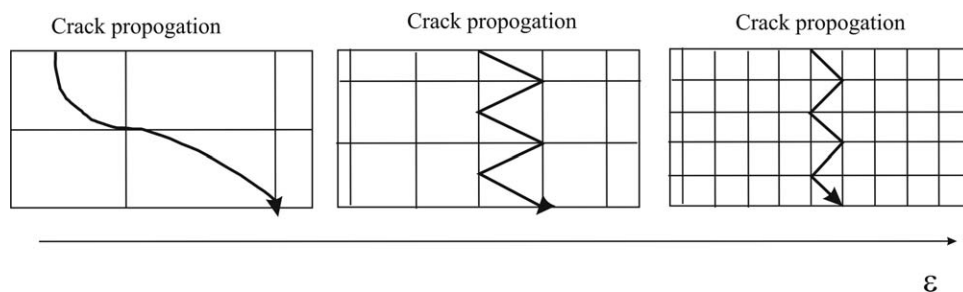
**Figure 5.** SEM images of (a,b) PC and (c) PMMA extrudates.**Figure 4.** Net effect on the character of the crack propagation (scheme).

Table IV. Effects of ECMAE on the Mechanical Properties of the Polymers ($\varepsilon = 8.5$): Route F

Sample (treatment)	E (MPa)	σ_y (MPa)	σ_T (MPa)	ε_y (%)	ε_b (%)
PC					
Initial	2100 ± 63	68 ± 4	70 ± 3	6.2 ± 0.2	98 ± 5
After ECMAE	2500 ± 125	80 ± 5	82 ± 4	8.7 ± 0.4	105 ± 5
PMMA					
Initial	2800 ± 76	58 ± 3	59 ± 2	2.7 ± 0.1	4.0 ± 0.2
After ECMAE	3590 ± 180	70 ± 5	70 ± 4	3.0 ± 0.2	6.0 ± 0.3

oriented molecules, this suggested that the accumulation of the elastic strain in the course of ECMAE generated the emergence of the system of mutually intersecting weak planes.

On the assumption that the magnitude of ΔH was insignificant at small ε and weakly varied together with the character of the $\Delta l/l_0(T)$ dependences of the extrudate samples cut along and across the extrusion direction when ε increased, we drew the conclusion that the net of oriented molecules was formed already at $\varepsilon \geq 4.4$. The scheme of the net effect on the character of the crack propagation is presented in Figure 4. The macromolecules oriented at a certain angle about the crack propagation prevented the crack development and generated a deviation from the direction of the impact loading. The strain accumulation increased the density of the net of oriented macromolecules and the degree of the molecular drawing. As a result, the scattering efficiency was enhanced, and the Z-shaped fracture pattern was formed (the fracture character).²⁸ This kind of the fracture character (the absence of a macroscopic weak plane) was evidence of an increase in the crack propagation resistance regardless of the direction of the impact load, that is, the state of the polymer characterized by the improved full fracture resistance.

The results of SEM also confirm the formation of biaxially oriented molecular chains in the PC and PMMA extrudates. Traces of the propagation numerous cracks along and across the extru-

date axis were clearly observed in the micrographs of the fracture surface of the PC extrudates [Figure 5 (a,b)]. The density of the net of the oriented macromolecules increased with ε . At the same time, the multilevel crack growth occurred, which was similar to the ECMAE processing, when a number of microcracks were initiated along the secondary weak plane (perpendicular to the main crack) between the oriented molecular chains. In other words, the sign-alternating deformation in the course of ECMAE formed a framework of mutually perpendicular weak shear planes with the cracks developed along them. The molecular chains oriented along these directions formed a net of physical nodes [Figure 5(c)], which were effective stoppers of the crack development. An increase in ε resulted in the enhancement of the concentration of the stoppers (the density of the net) and facilitated an increase in the impact strength of the extruded polymers.

As uniaxially oriented structures were associated with enhanced properties and the fracture toughness decreased at the approach to the orientation direction and vice versa, we supposed that the formation of a biaxial orientation allowed simultaneous increases in both the strength and impact characteristics of the glassy polymers, regardless of the direction of the loading. At the same time, a high reserve of plasticity was conserved. To confirm this assumption, samples of PC and PMMA were deformed along route F; this provided (see ref. 21) formation of a net of interwoven macromolecules set at an angle to the longitudinal axis of the extrudate. As a result, in this kind of the sample, the directions of tension and impact loads did not coincide with the orientations of the macromolecules. Tables IV and V report the results of the mechanical tests of PC and PMMA deformed along route F. We observed that the tensile strength, impact strength, rigidity, and plasticity of the extrudates exceeded those parameters of the original polymers. At the same time, they stayed below the corresponding characteristics of extrudates processed along route D+C (Tables II and III). The last result was related to the fact that the maximum mechanical properties were reached only along the directions of the preferable orientations of the macromolecules.

CONCLUSIONS

It was shown through the examples of PC and PMMA that ECMAE allowed the realization of the structural state and provided the enhancement of their stress-strain and impact characteristics in glassy polymers, regardless of the direction of the load. The observed effect was associated with the formation of a net of biaxially oriented molecular chains and the improvement of the intermolecular packing. An increase in ε resulted in a growth of the density of the net of the oriented macromolecules and the degree of the molecular drawing. As a result, higher mechanical properties of the extrudates and a reduction of the anisotropy of the properties were achieved.

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Table V. Effects of ECMAE on the Impact Strength of the Polymers: Route F

ε	a (kJ/m ²)	
	Unnotched	Notched
PC		
0		8.2 ± 0.3
4.4	No break	12.1 ± 0.6
8.5		14.9 ± 0.7
PMMA		
0	16.2 ± 0.7	1.4 ± 0.07
4.4	22.5 ± 0.8	1.9 ± 0.07
8.5	25.9 ± 1.1	2.2 ± 0.06

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