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EFFECT OF EQUAL CHANNEL MULTIPLE ANGULAR EXTRUSION ON THE MORPHOLOGY, MECHANICAL AND THERMAL PROPERTIES OF POLYMERIC BASED NANOCOMPOSITES

By the example of polymer composites, the abilities of the method of equal channel multi angular extrusion have been studied with respect to the modification of the structure and the properties of polymeric nanocomposites. With using Xray structure analysis, TEM, DSC and dilatometry, it has been demonstrated that this kind of processing provides an additional intercalation of the polymer into filler tactoids with the succeeding exfoliation, the increase in crystalline lamellar thickness and a decrease in the dispersion of the crystallite thickness, as well as the formation of biaxial orientation order in the polymeric matrix. The oriented nanocomposites were characterized by a reduced porosity and improved adhesion between the nanofillers and the polymer matrix. An increase in Young modulus, yield stress and strain at break was observed, being accompanied by a substantial decrease in the thermal expansion coefficient of the nanocomposites.

Key words: *polymer-matrix composites; microstructures; plastic deformation; electron microscopy; extrusion*

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ВПЛИВ РІВНОКАНАЛЬНОЇ БАГАТОКУТОВОЇ ЕКСТРУЗІЇ ПО МОРФОЛОГІЮ, МЕХАНІЧНІ ТА ТЕПЛОВІ ВЛАСТИВОСТІ ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ

На прикладі полімерних композитів було вивчено здатність методу рівноканальної багатокутової екструзії щодо модифікації структури і властивостей полімерних нанокомпозитів. За допомогою рентгенівського аналізу, ТЕМ, ДСК і дилатометрії, було показано, що цей вид обробки забезпечує додаткову інтеркаляцію полімеру в тактоіди наповнювачів з подальшою ексфоліацією, збільшення товщини кристалічних ламелей і зменшення дисперсії товщини кристалітів , а також формування двухосної орієнтації в полімерній матриці. Орієнтовані нанокомпозити характеризуються зниженою пористістю і поліпшеною адгезією між нанонаповнювачами і полімерною матрицею. Спостерігається збільшення модуля Юнга, границі плинності при розриві, істотне зниження коефіцієнта теплового розширення нанокомпозитів.

Ключові слова: *полімер-матричні композити; мікроструктура; пластична деформація; електронна мікроскопія; екструзія*

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ВЛИЯНИЕ РАВНОКАНАЛЬНОЙ МНОГОУГЛОВОЙ ЭКСТРУЗИИ НА МОРФОЛОГИЮ, МЕХАНИЧЕСКИЕ И ТЕРМИЧЕСКИЕ СВОЙСТВА ПОЛИМЕРНЫХ НАНОКОМПОЗИТОВ

На примере полимерных композитов была изучена возможность метода равноканальной многоугловой экструзии для модификации структуры и свойств полимерных нанокомпозитов. С помощью рентгеновского анализа, ТЕМ, ДСК и дилатометрии, было показано, что этот вид обработки обеспечивает дополнительную интеркаляцию полимера в тактоиды наполнителей с последующей эксфолиацией, увеличение толщины кристаллических ламелей и уменьшение дисперсии толщины кристаллитов, а также формирование двухосной ориентации в полимерной матрице. Ориентированные нанокомпозиты характеризуются пониженной пористостью и улучшенной адгезией между нанонаполнителем и полимерной матрицей. Наблюдается увеличение модуля Юнга, предела текучести при разрыве, существенное снижение коэффициента теплового расширения нанокомпозитов.

Ключевые слова: *полимерно-матричные композиты; микроструктура; пластическая деформация; электронная микроскопия; экструзия*

1. Introduction

Polymeric nanocomposites are of substantial scientific and practical interest due to possible formation of an enhanced level of physical and mechanical properties at extremely low content of a nano-filler [1]. The reason is creation of nano-scale structures where the filler particles are well stratified and dispersed within the polymer matrix. The efficiency of property enhancement is determined by the filler shape, strain-strength characteristics, the aspect ratio, volume fraction and interfacial adhesion. A special attention is attracted by layered nanofillers like montmorillonite, zirconium phosphate and graphene, that are composed by thin (~1 nm) plate-like structures characterized by high surface area and aspect ratio. Being used as the second phase, they allow increase in the elasticity modulus and the yield strength, the heat distortion temperature, enhancement of gas barrier properties, flame retardancy and UV resistance of polymeric composites. Besides high electrical and thermal conductivity of such nanofillers like graphite nanoscale platelets (GnPs) and carbon nanotubes (CNTs) can be useful when creating functional materials characterized by electric and thermal conductivity, thermal stability etc.

Common fabricating methods of the polymer nanocomposites include solution mixing, in situ polymerization and melt blending [2]. Solution mixing method is the most effective with respect to the composites based on soluble polymers, but in any case, it cannot be applied to a number of insoluble polymer based ones. In situ polymerization allows substantial improvement of the fillers dispersion and the intensified interaction between the nano-filler and the polymeric matrix. However, the most universal and wide-spread method of production of the polymer composites including those based on thermoplastic polymers is melt blending. Here, exfoliation and dispersion of the fillers are mostly controlled by the shearing force in the course of mixing. In turn, the shearing force is determined by the blending parameters (temperature, pressure etc.), and the polarity of the polymeric matrix. For instance, in the case of weakly-polar polymers, extremely weak interaction between the reinforcement and the matrix is registered. As a result, a weak reinforcing effect is observed.

One of the methods aimed at an increase in the shearing force in order to intensify the exfoliation and dispersion of the reinforcement can be processing of the polymer composites in the solid phase when the viscosity of the polymer matrix is several millions of the polymer viscosity in the melt. In [3], promising application of a method of severe plastic deformation of solid polymers is presented, that is equal channel angular extrusion used for structural modification of the polymeric nanocomposites. In particular, it has been shown that in semicrystalline polymer-based nanocomposites, the alignment of nano-sized clay layers by ECAE has an effect on the nanoscopic orientation of crystalline lamellae, structural parameters of the nanoclay and the polymer in nanocomposites [4-9]. After processing the one-pass ECAE, the nanoclays were shortened, well-aligned and closely packed, and the crystalline lamellae were compressed and diagonally well oriented. The two-pass ECAE process with a 180^0 rotation between passes results in a random dispersion of the nanoclay particles, and the recovery of the packed nanoclay interlayer spacing and the compressed lamellar long period. Creasy et al. [4] found that ECAE can control the fiber orientation and the length of glass fiber/polyacetal composites, depending on the processing routes. Li et al [9] also noticed that controlled nanoparticle orientation and effective exfoliation could be easily achieved through ECAE. As a result, the processing allows achievement of a better set of physical and mechanical characteristics.

Equal-channel multiple-angular extrusion (ECMAE) is a new method of processing of solid-phase polymeric materials [10]. The method is extrusion of the sample through a die composed by several pairs of channels of the same cross-section. In the plane of intersection of two channels, a huge shearing force is realized, resulting in plastic deformation of the polymeric material. By varying the number of the intersecting channels, a required level of the accumulated plastic strain can be achieved, and a change in the spatial position of the planes of the intersecting channels (deformation route) allows change of the direction of the shearing force and formation of varied oriented states within a polymeric matrix [11].

The present paper is aimed at the test of abilities of ECMAE application to the modification of the structure and the properties of polymeric nanocomposites. The relationships between the parameters of nanofillers, composite morphologies, the type of the polymeric matrix, mechanical reinforcement, and electrical properties have also been studied.

2. Experimental

2.1. Materials. Isotactic PP (Moscow Naphta Processing Plant, Russia) with a melt flow index of 0,6 g/10 min (2,16 kg, 230 °C, ASTM D1238), $M_w = 6{,}3 \times 10^5$ g/mol, $M_w/M_n = 3{,}5$ and PE (Lupolen 5261 ZQ 456) with a melt flow index of 2,0 g/10 min, (21,6 kg, 230 °C, ASTM D1238), $M_w = 4{,}8 \times 10^5$ g/mol were used as the polymers matrix. xGnPs Grade C were supplied by XG Sciences Company (USA, MI, EastLansing). xGnPs were prepared by the microwave expansion of graphite oxide. The modified montmorillonite (Cloisite 20A) produced by Southern Clay Products, with the particle size within the range of 6–8 μm, was also used as the filler.

2.2. Sample preparation.

Preparation of the nanocomposites. The composites were prepared by the melt mixing in a two-roller mixing chamber at 433K (PE- matrix) и 463 K (PP-matrix) and with a rotor rotation speed of 90 rpm. First, PP or PE was melt-blended with stabilizers of the thermooxidative degradation (0,3 wt. % of topanol and 0,5 wt. % of dilauriltiodipropionate) for 3 min. Then the xGnPs were added slowly over 3 min, and the mixture was compounded for 15 min. The nanoparticle loadings were 10 and 20 wt. %.

The PP-OMMT composites were prepared by the melt mixing in a two-roller mixing chamber at 453K and with a rotor rotation speed of 90 rpm. First, PP was melt blended with stabilizers of the thermooxidative degradation (0.3 wt.% of topanol and 0.5wt.% of dilauriltiodipropionate) for 3 min. Then the OMMT was added slowly over 3 min, and the mixture was compounded for 10min. The filler concentration was 10 wt.%, permitting obtaining the original composites characterized by the dispersion of the OMMT particles within the polymeric matrix and the optimum combination of stress-strain characteristics.

Procedure of pressing of the ECMAE billets. PE and PP-based composites were heated up to 433К in a closed mould of 15 mm in diameter (PE matrix) and to 463 К (PP matrix). The temperatures were kept stable for 10 minutes, and then the pressure of 10 MPa was applied for 10 minutes. Air cooling down to 323 K was performed under the pressure of 10 MPa in the mould. The cooling rate was 1,1–1,3 deg./min.

Solid state extrusion. ECMAE was performed to achieve the orientation of the polymer matrix and xGnPs nanoparticles. The detailed description of ECMAE is presented in [10]. ECMAE was carried out at the deformation intensity ΔΓ=0,83, the accumulated strain $\varepsilon = 8{,}5$, at the extrusion temperature of 383 K (PE matrix) and 413 K (PP matrix) and at the extrusion rate of 0,6 mm/s. As a deformation route, route D+C was selected. Here the pairs of oblique deforming channels are located in perpendicular planes rotated through the vertical axis in increments of 90^0, and separated by vertical channels [11]. This configuration allows realization of simple shear in the planes perpendicular to the extrusion axis and in the planes arranged at an angle of ±67,5° to the extrusion axis. At the same time, the shift vector is rotated by an angle of 180° and depending on the deformation zone - by an angle of 90°. As shown in [11], the above processing condition allows for the generation of the maximal orientation of macromolecules of the polymer matrix parallel and normal to the extrudate's axis. Both the extrudates and the original billets were shaped as cylinders of 15 mm in diameter and 50 mm in length.

2.3. Characterization.

2.3.1. Transmission electron microscopy (TEM). TEM was performed with using JEM-200A by "JEOL" under the accelerating voltage of 200 kV. The replica of the fracture surface was obtained as follows. The roentgen film (the matrix) was wetted by acetone and sticked on the fracture surface. After the drying, the film was separated and a thin carbon layer was applied on the obtained pattern. The test of the carbon replica was made after the separation from the matrix.

2.3.2. Wide-angle X-ray scattering (WAXS). WAXS investigation were done by using a X-ray diffractometer. Mn-filtrated FeK_α-radiation was used in this case. The patterns were taken in the diffraction mode (the Bragg-Bretano focusing). To estimate the function of space orientation of crystallites, the scanning was accomplished in increments of 5^0 by the sample rotation in the azimuthal direction from the angle corresponding to the direction normal to the extrudate axis (these are angles of 90^0 and 270^0). The detector was fixed at the scattering angle corresponding to the top of the diffraction maximum (in the case of PE, PP and xGnP, it was the maximum with the index of 200 with the top at $23{,}8^0$, the index of 110 with the top at $14{,}14^0$, the index of 002 with the top at $26{,}4^0$, respectively). As a measure of the total share of oriented material, the ratio of integral intensities of azimuthal scanning, I_{max}, within the angle range from 0^0 to 180^0 was used, being separated from isotropic scattering to the total integral intensity.

2.3.3. Scanning electron microscopy (SEM). SEM was implemented by using the JEOL JSM-6010LA instrument at the accelerating voltage of 10 kV. The samples were coated with a fine gold layer by ion sputtering (JEOL JFC-1200). The photographs were taken of the surfaces of cross and longitudinal spallings of the original samples and the extrudates. The spalling was made at the liquid nitrogen temperature. The 'Image-Tool' and 'Excel' application package was used to process the results of quantitative analysis of the agglomerate size distribution. The lateral size and thickness of 200 GnP agglomerates were measured.

2.3.4. Differential Scanning Calorimetry (DSC). The thermal characteristics were analyzed by a scanning calorimeter («Netzsch», Germany, model DSC-204 F1). DSC experiments including heating and nonisothermal crystallization were carried out in the range of 300–450 K at the rate of 5 K/min. The specific heat flow from the melting peak (W/g) was corrected for the mass of PP or PE in the nanocomposite. The degree of crystallinity χ_c of the nanocomposites is calculated as: $\chi_c = \frac{\Delta H_s}{(1-\phi)\Delta H_0}$, where ΔH_s is the heat of fusion of the measured sample (obtained by integration of the melting peaks), ϕ is the weight fraction per unit of mass of the nanofiller, and ΔH_0 is the value of melting enthalpy of 100% crystalline PP and PE, taken as 209 J/g and 294 J/g, respectively.

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

2.3.6. Tensile Testing. Tensile measurements were performed according to the GOST (State Standard) 11262 (an analogue of ASTM D638-02). The samples before and after ECMAE processing were machined into dimensions: the length of the test section was 32 mm, the diameter of the test section was 5 mm, the bending radius was 6 mm (GOST11262, type 4). The samples oriented along the extrusion directions were prepared and tested at room temperature (294 К) with using universal testing machine "JJ Instruments T5K". The deformation rate was 1% min^{-1}.

3. Results and discussion

The modification of the GnP morphology by the action of orientation of the polymeric matrix chains was characterized by using SEM. It was found that in composites produced by melt mixing, the agglomerates were not dispersed into individual plates, however they were relatively well distributed within the matrix. In fig.1 a,b the structures of the PP composite containing 10 wt.% GnP(5) are presented. The composites characterized by the highest nanofiller content contain more and bigger xGnPs agglomerates than those observed in sample with a lower GnPs amount. The shear-induced orientation promotes a higher dispersion degree of the agglomerates (fig.1 c-d). At the same time, at the filler concentration of 10 wt.%, formation of aggregates composed by 2-5 graphite plates is registered. An analogous situation takes place in the case of extruded PE-based composites. The dramatic dispersion of the agglomerates is related to the possible accumulation of a substantial equivalent plastic strain (ε=8,5), and to the alternating-sign character of the deformation (the shear direction is alternated in every next deformation zone [11]), that facilitates dispersion of the agglomerates of the nanofiller.

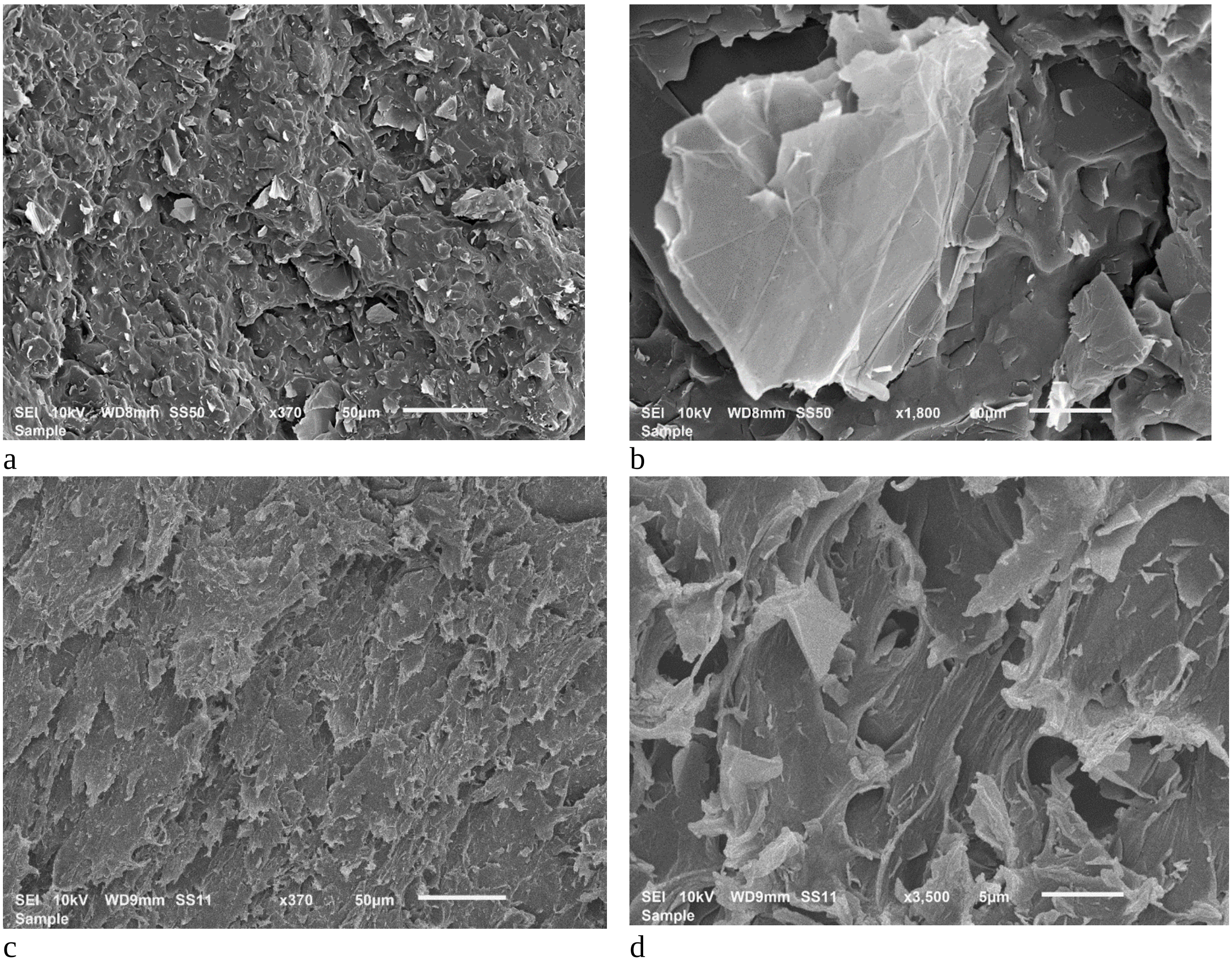
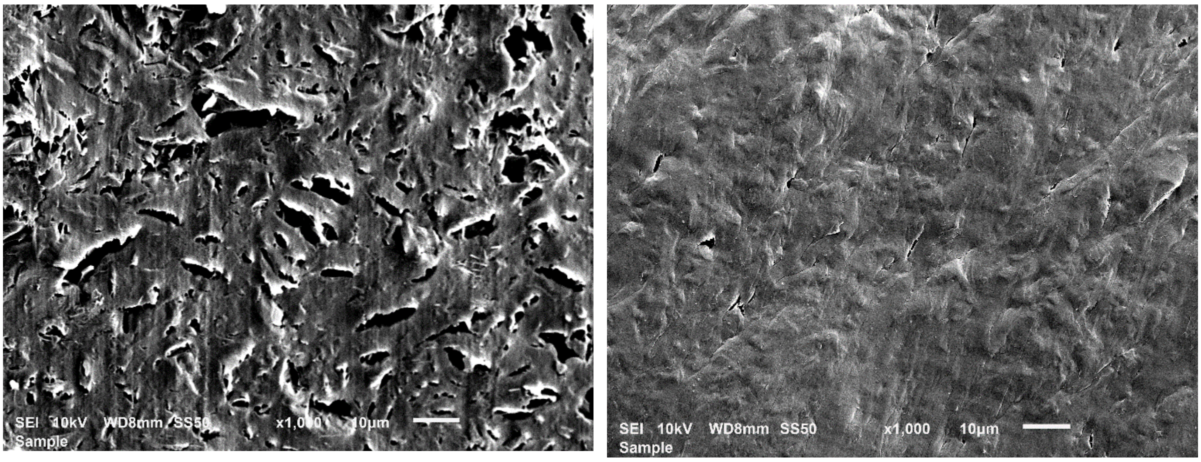


Fig.1. **- Cryogenically fractured surface of PP-5%GnP(5),** ***a, b*** **– melt mixing,** ***c-d*** **–ECMAE.**

A similar regularity is observed in the case of a PP–OMMT composite. The main specific feature of the curve of OMMT wide angle scattering is the existence of an intensive maximum with the peak at the scattering angle of 3.2 degree that corresponds to the periodicity of 2.76 nm. Besides the crystal maximums typical of PP, the PP–OMMT composite produced by melt mixing is characterized by a substantial low angle diffusion component in the angular range from the minimal registered angle to approximately 7 degrees, and the diffraction maximum of OMMT at 2.3 degrees associated with the periodicity of 3.84 nm. The presence of the above component is not characteristic of the neat PP, being related to the presence of nano-dispersed material of the filler. In the case of ECMAE, a substantial (two- or three-fold) reduction of the integral intensity of the low-angle contribution of the nano-filler and the vanishing diffraction maximum of OMMT are registered, that can be the results of the succeeding increase in the inter-layer periodicity of OMMT and the shift of the maximum to the low-angle region out of the reach of the used diffractometer, respectively. The observed changes in the form of the wide-angle diffraction patterns of the tested materials areevidences of the fact that the melt mixing determines the intercalation of the fragments ofpolymer molecules to the inter-layer space of OMMT, and the succeeding ECMAE results in thefurther increase in the degree of intercalation and facilitates to the effective exfoliation of the tactoids of the nano-filler. The last statement is confirmed by the results of TEM studies.TEM images indicating the nanoclay structures of the initial and ECMAE-processed nanocomposites demonstrate that in the original PP–OMMT composite, the thickness of the layer of the filler particles is about 60 – 90 nm. ECMAE processing results in the reduction of the thickness down to 15 – 30 nm.

The nanocomposites produced by melt mixing include a large number of big pores related to a poor dispersion of the nanofiller in the matrix and a weak interfacial interaction. Fig. 2 shows an example of the structure of the PE- 5% GnP(5) composite before and after ECMAE. Exfoliation of the xGnPs determines an increase in the specific contact area of the matrix and the filler, and orientation under high pressure is responsible for a partial healing of the pores at the filler-matrix interface. These processes can be reasons of an increase in strength of the interface between the xGnPs and the polymer matrix.



a b

Fig.2. - **The structure of the PE- 5% GnP(5) composite before (a) and after (b) ECMAE.**

The results of the measurement of the microhardness of nanocomposites correlate to the data of their tensile tests. It has been found that as compared to melt mixing, ECMAE determines an increase in the Young modulus (an enhancement of the reinforcement effect) and provides higher yield stress of the composites. For instance, in the PP–10wt.%GnP(10) composite, the Young modulus rises from 400 to 650 MPa, and the yield stress increases from 20 to 25 MPa; in PE–10wt.%GnP(10), the abovementioned characteristics increase from 360 MPa to 500 MPa and from 20 to 24 MPa, respectively. The ductility of the extrudates rises too: the strain at break ε_b is increased by a factor of 1,5 to 2,0. The best result is achieved when the exfoliated graphite nanoplatelet xGnP(10) is used. In particular, in the PP–20wt.%GnP(10) composite, an increment of ε_b from 5% (melt mixing) to12% (ECMAE) is registered.

In melt mixing produced composites, low yield stress is determined by the formation of weak interfacial layers because of weak adhesion between the filler particles and the polymeric matrix. An increase in the filler concentration results in emergence of bigger GnPs agglomerates, weakened interaction between the filler and the matrix followed by a lower fall down of yield stress. Formation of the orientational order during ECMAE provides a rise of yield stress as well as the Young modulus. When the content of the filler increases, this contribution decreases because of a worse dispersion of the particles of the nanofiller that form larger aggregates. Formation of weakened interfacial layers characterized by a lower stretch-induced orientation ability and a reduced volume fraction of the oriented (strengthened) polymeric matrix facilitates this effect, too. The highest increment of yield stress is achieved in the case of the PE matrix, contrary to the PP one. The reason is better ability to the molecular alignment. Besides, the use of the xGnP(10) characterized by a larger aspect ratio in comparison with xGnP(5) provides better adsorption interaction.

It is known [12] that low ductility of the composites is determined by formation of large agglomerates of GnP, that restrict deformability of the polymeric chains between them. The dispersion of the xGnPs or OMMt agglomerates depresses the restricting effect. An improvement of the ductility can be also related to partial healing of pores in oriented composites.

In the case of semicrystalline polymers, the formation of the molecular orientational order–can also affect the polymer matrix morphological features, such as crystalline lamellar thickness and crystallinity [13]. The degree of crystallinity χ_c of the non-deformed polymer matrix remains unaffected by an addition of xGnPs (Table 1). The facts also demonstrate that xGnPs-PE or xGnPs-PP interfacial layers does not significantly affect the melting process. A similar behavior was also observed in other thermoplastic/nanofiller composites [14,15], which was explained in terms of a weak particle-matrix interface and nanofiller agglomeration. There is also no change in the melting temperature upon addition of a nanofiller, which was also associated with weak particle-matrix interface and nanofiller agglomeration. ECMAE results in an increase of χ_c, accompanied by a shift of the melting peak toward the higher temperatures and a reduction of the half-width (Table 1). An increase in χ_c can be related to the strain induced crystallization [13]. A rise of the onset temperature T_{onset}, the melting peak temperature $T_{\max}$, the position of the right shoulder of the melting peak at higher temperatures, a reduced half-width of the melting peak ΔT are the evidences of formation of larger and more perfect crystallites and a decrease in the dispersion of the crystallite thickness. The observed effects can be associated with destruction of thinner crystallites and the succeeding crystallization and injection of the defects into the inter-crystallite space.

Table 1

Structural and thermal characteristics of PE, PP and the related composites

Sample	χ_c	T_{onset}	$T_{\max}$	ΔT
			K	
PE	54/65	393,0/-	405,8/-	10/-
PE–10wt.%GnP(5)	54/59	393,0/396,4	405,6/410,2	10/8
PE–20wt.%GnP(5)	54/61	393,4/396,5	406,4/410,6	10/7
PE–10wt.%GnP(10)	54/59	393,2/396,7	405,6/411,2	10/8
PE–20wt.%GnP(10)	54/62	393,6/397,1	406,4/411,4	10/8
PP	46/56	404,3/-	437,4/-	13/-
PP–10wt.%GnP(5)	46/50	404,2/408,0	436,3/439,5	13/9
PP–20wt.%GnP(5)	46/52	404,3/408,4	437,4/439,7	13/8
PP–10wt.%GnP(10)	46/50	405,6/409,5	436,5/442,2	13/9
PP–20wt.%GnP(10)	46/52	406,3/409,4	437,3/444,4	12/9
PP-10wt.%OMMT	48/52	397,0/418,0	439,0/442,0	17/10

melt mixing/ ECMAE

From the above discussion, we can suggest the following deformation mechanism of the crystal structure evolution during ECMAE. The original crystal structure of the polymeric matrix is a set of isotropic lamellae. Under simple shear deformation, lamellar blocks are formed with the succeeding unfolding of the chains and orientation of partly confined chains and released chains. With an increase in the accumulated strain, the amount and the degree of orientation of the fibrillar crystallites increase too. Two populations of the oriented polymeric crystallites are formed (so-called α and β crystallites [16]). The last fact is due to ECMAE determining formation of a biaxial orientation, not a uniaxial one. In general, the melting curve of such extruded polymers displays double melting peaks that indicate two existing types of the crystal structure with different perfection degree and thermal stability. The low-temperature peak is close to the one of undeformed polymer and related to the formed lamellar blocks. However, the high-temperature peak is that of the oriented crystals in the fibrillar structure. Therefore, it is probable that these two types of the crystal structure exist in the case of GnP or OMMT-based nanocomposites subjected to ECMAE, too, and they generate the effect of combination of two peaks. The presence of a nanofiller results in formation of more defective and less oriented fibrillar crystals that bring an overheating effect into the melting of lamellae blocks. An increase in the filler concentration facilitates the growth of the amount of the oriented crystallites (according to the data of X-ray structure analysis). This fact can be related to a fast orientation of more defective crystals as compared to more perfect crystallites at the same value of the accumulated plastic deformation. In turn, a faster orientation leads to a faster strain-induced crystallization that is confirmed by the results of the measurements of the crystallinity degree of the oriented composites.

In paper [8], it is demonstrated in the course of ECAE of the clay-based nanocomposites that the chain orientation angle is always slightly smaller than the clay orientation angle which suggested that the orientation of the clay layers has induced the chain orientation. As reported in [8], this fact could be attributed to the existence of some thousands of clay layers (about 1 nm thick and about 50-500 nm long) inside the spherulites. In the course of deformation and realignment, the orientation of crystal lamellae lags behind that of the macromolecular chains, which is almost oriented along the direction of the clay layers. An analogous situation is observed in the case of the GnPs or OMMT-based composites: the angles of the preferred orientation in the filler crystals exceed that of the polymeric crystals. However, this mechanism of deformation is valid in nanocomposites when the nanofiller is distributed over the polymeric matrix in a perfectly uniform way and the dispersion minimizes the size of the non-reinforced polymer domains [17].

At the beginning of the deformation, the presence of large filler aggregates and their weak bond with the molecular chains determines sliding of the filler layers and the orientation of the polymeric matrix that is not connected to the filler crystals. At the same time, the mechanism of the chain-induced filler crystal orientation can take place. To the extent of dispergation and improvement of the contact between the filler layers and the polymeric matrix, the filler layers can play an active role in inducing the orientation of the molecular chains and the crystal lamellae (the slip of the filler crystals will stretch the molecular chains and crystal lamellae), i.e. the activation of the filler-induced chain orientation mechanism. One can suppose that in the case of the PE matrix, these processes are more effective because a smaller difference in character of the orientation distribution in the filler and polymeric crystals is registered.

The presence of an oriented molecular structure can result in realized invar effect in semicrystalline polymers [18]. It is characterized by very low and weakly varied relative elongation of the samples under heating in a wide temperature range. An addition of layered nanofillers is also a method of reduction of the coefficient of linear thermal expansion (CLTE) of the polymeric matrix. However, the platelet shape of the nanofiller particles determines a decrease in CLTE by about 25% and by 15 – 20% parallel to the direction of orientation of the filler particles and perpendicular to it, respectively. The maximum reduction of CLTE (by 65%) was achieved when carbon fibers were used that are characterized by a high degree of alignment and the highest rigidity as compared to other carbon fillers [19]. It is seen that CLTE of the extruded composites is less by 300 – 380% in comparison with the original ones. This effect is mostly associated with the orientational order of the polymeric matrix, not with the modification of the aggregate size, the orientation of the GnP particles or the magnitude of the interfacial interaction between the filler and the matrix.

4.Conclusions

The performed investigation has shown that the implementation of the shear induced solid state orientation process under pressure is favorable with respect to the structure transformations responsible for the reinforcement effect in polymer nanocomposites. The reinforcement is determined by a substantial modification of the morphology of the nanofiller and the structural transformations of the polymeric matrix (molecular orientation, an increase in the crystallinity degree, formation of more perfect oriented crystals). In the case of composites subjected to ECMAE, the fracture of large agglomerates of the nanofiller is observed, accompanied by the formation of the layers composed by a few of individual plates. An increase in the specific contact area between the nanofiller and the polymeric matrix provides stronger interfacial interaction and activation of the nanofiller-induced chain orientation. The highest effect is achieved when the polymeric matrix is used that is characterized by a better ability to the molecular alignment and the filler of the highest aspect ratio. In the tested systems, the shear induced reinforcement process allows a substantial increase in ductility of the nanocomposites at the moderate increase in rigidity and strength, the realized invar effect.

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