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Mechanochemical Method for Producing Polymer Powder Composites and Films Based Thereon

V. A. POLUBOYAROV, Z. A. KOROTAEVA, A. A. ZHDANOV, M. A. MIKHAILENKO, L. K. BERDNIKOVA, A. V. KADIMOVA

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

E-mail: sanych@solid.nsc.ru

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Abstract

An efficient mechanochemical method for producing composites based on LLDPE 6101RQ polyethylene and inorganic additives was investigated. Films with improved barrier and mechanical properties were produced therefrom. In obtaining films without master-batches, the content of additives (TiO_2, $CaCO_3$, SiO_2, or Na-montmorillonite) was 0.01–5 %. Herewith, gas permeability reduced to 30–50 %; modulus of elasticity (along) increased by 24–60 %, strength - by 15 %.

Keywords: mechanochemical treatment, inorganic ultrafine additives, polymer composites, polyethylene

INTRODUCTION

Currently, to obtain composites, there are used three main procedures for mixing polymers with ultrafine (including nanodispersed) particles: 1) dispersion in solutions; 2) joint polymerization *in situ*; 3) mixing in melt. Polar polymers are readily mixed with nanoparticles via three ways, and for non-polar or slightly-polar ones, such as polyolephines, the second alternative is preferable, though examples of obtaining these composites by other methods are known. Nanocomposites of polyamide-6 and nanolayered silicates with improved thermal and physicomechanical properties, and also as polyethylene and polystyrene, were obtained by *in situ* polymerization.

The third method of mixing in the melt is very common due to commercialization simplicity and easiness. It is used for mixing polyethylene oxide with nanosilicates, polystyrene, polypropylene, biodegradable polylactides, maleic anhydride, high-density polyethylene, and ethylene-vinyl acetate copolymer/nanoscale montmorillonite particles. Its application for mixing hydrophobic polymer matrices, such as polyolephines with hydrophilic particles, is complicated, on the one hand, by poor dispersion and adhesion of hydrophilic nanoparticles in hydrophobic polymer matrices, and on the other hand, by a trend of high surface energy nanoparticles towards agglomeration.

Polymers are usually reinforced with nanoparticles in the quantity of 2–6 %, though nanocomposites with their higher contents (in master-batches of polyolefins, the fraction of calcium carbonate, titanium dioxide, and silicon oxide nanoparticles reaches 70 %) have been developed.

Properties of the resulting two-phase composites are determined by two main factors: 1) dispersion and distribution of nanoparticles in the polymer matrix; 2) interaction between polymer chains and nanoparticles. The first affects the barrier, and the second – on physical and mechanical properties of packing materials.

Apart from research in the area of the development of nanocomposites based on polar polymer matrixes, the modification of properties of nonpolar polymers, primarily, polyolefins broadly used in industry and household is being extensively explored. Their portion in the world production of plastic material goes beyond 50 %. Alongside with that, nanocomposites with nonpolar or slightly-polar polymers do not have such good performance characteristics, as materials based on polar polymers.

Natural layered silicates are most often used as an inorganic component, the hydrophilic surface of which prevents the uniform distribution of the inorganic component in the polymer. The ability of polymers to intercalate into clay with diverse layer structures has not been fully explored [1].

Furthemore, numerous methods for the preparation of nanocomposites [2–11] suggest using one or several laminating additives, complex ways introducing inorganic particles into melt or solution, obligatory preparation of preliminary composites, such as inorganic nanoadditive/organic modifier, and complex multicomponent compounds.

Mechanochemical methods for obtaining powder compositions of polymers and ultrafine (including nanodisperse) inorganic particles [12] are deprived of these disadvantages, though being rarely used in practice.

This paper considers the preparation of powder composites of polyethylene and ultrafine inorganic additives using mechanochemical techniques, production of films from these composites, and investigation of properties of powder composites and films.

EXPERIMENTAL

To produce polymer powder composites, there were used linear low-density polyethylene (LLDPE) and diverse inorganic additives (TiO_2, SiO_2, $CaCO_3$, and sodium montmorillonite (bentonite)). Table 1 gives the performance (commercial grade, specific surface area, and particle size) of the initial powders. The average particle size of powdwes was determined by the method of laser light scattering (LLS) and calculated using the values of specific surface area (S_{sp}) if the true density of the material was known.

Mechanochemical treatment (MT) of powder materials was carried out in AGO-2 activators for 1–5 min with 60g (loading into one drum: 5 g of work material and 200 g of steel balls) or in AGO-3 for 20–60 s with 60g (loading into one drum: 100 g of work material and 1800 g of steel balls (900 g of balls with a diameter of 5 and 10 mm)).

Inorganic additives content in polymer was varied within 0.01–70 % (by mass). Diverse water-and organic-based oil wetting agents, artificial waxes based on polyesters, maleic acid, water, and isopropyl alcohol (to 10 %) were used as surfactants.

TABLE 1

Properties of initial powder

Powder	Grade	Average particle size d, μm	Method of determination of particles size	S_{sp}, m^2/g
Polyethylene	Exxon Mobile™ LLDPE 6101RQ	N. d.	N. d.	0.06
TiO_2(1)	TE-92 (rutile)	~3	LLS	17.14
		0.08	S_{sp}	17.14
TiO_2(2)	R-FC5 (rutile)	0.18	GOST	6.84
	(for polymers)	0.21	S_{sp}	6.84
Bentonite powder for casting (Na-Bent)	P1T1 (GOST 28177–89)	N. d.	N. d.	17.36
$CaCO_3$	GOST 4530–76	0.63	S_{sp}	3.54
Rosil-175 (SiO_2)	TU 2168-038-00204872–2001	0.015	GOST, S_{sp}	155

Note. N. d. indicates a value was not determined.

Composites with low contents of inorganic additives (≤5 %) were produced via diverse methods: direct mixing in activators, pre-mixing in mixers followed by treatment therein, dilution of more concentrated compounds using a mixer and an activator.

Afterwards, using diverse methods, powder composites yielded films with a thickness of 40–500 μm. This paper considers 500 μm LLDPE 6101 RQ polyethylene-based films and inorganic additives produced *via* the hot extrusion method.

The average theoretical density of composites (polymer + inorganic additive) was computed by the formula:

$$\rho = 1/(X_1/\rho_1 + X_2/\rho_2)$$

where X_1 and X_2 are mass fractions of polymers and inorganic additives, respectively; ρ_1 and ρ_2 are densities of polymer and inorganic additive, respectively.

RESULTS AND DISCUSSION

Powder compositions

The material treated in the mill had the appearance of powders, flakelets, flakes, and fibres. Table 2 gives the composition of composites and their preparation conditions.

TABLE 2

Powder compositions for production of films

Sample	Composition					S_{sp}, m^2/g	Note	
	Polymer, g/%	Inorganic additive		Surfactant				
		Type	Quantity, g/%	Type	Quantity, g/%			
Initial	100/100	–	0/0	–	–	0.06	LLDPE 6101 RQ	
4-60″	50/50	TiO_2(1)	50/50	–	–	0.50	–	
6-60″	30/30	TiO_2(1)	70/70	PEGS	6/6	0.30	–	
11-60″	40/40	TiO_2(2)	60/60	–	–	0.22	–	
12-60″	50/50	TiO_2(2)	50/50	–	–	0.04	–	
14-60″	30/30	$CaCO_3$	70/70	G	8/8	2.67	–	
15-60″	80/80	SiO_2	20/20	–	–	0.18	–	
16-60″	30/30	TiO_2(1)	70/70	–	–	0.34	–	
17-60″	30/30	$CaCO_3$	70/70	–	–	2.12	–	
21-60″	70/70	Na-Bent	30/30	–	–	1.54	–	
23-20″	95/95	$CaCO_3$	5/5	G	0.9/0.9	0.06	Dilution	14-60″
24-20″	95/95	TiO_2(2)	5/5	–	–	0.10	»	12-60″
27-20″	95/95	SiO_2	5/5	–	–	0.06	»	15-60″
28-20″	95/95	Na-Bent	5/5	–	–	0.18	»	21-60″
30-20″	90/90	SiO_2	10/10	–	–	0.02	»	15-60″
32-20″	75/75	TiO_2(1)	25/25	–	–	0.08	»	4-60″
45-20″	95/95	TiO_2(1)	5/5	PEGS	0.4/0.4	0.02	»	6-60″
43-20″	50/50	TiO_2(2)	50/50	–	–	0.83	–	
44-40″	50/50	TiO_2(2)	50/50	–	–	0.08	–	
45-60″	50/50	TiO_2(2)	50/50	–	–	0.13	–	
61-20″	99/99	TiO_2(2)	1/1	–	–	0.05	–	
65-20″	99/99	SiO_2	1/1	–	–	0.13	–	
68-20″	99.90/99.90	TiO_2(2)	0.10/0.10	–	–	0.01	Dilution	61-20″
69-20″	99.90/99.90	SiO_2	0.10/0.10	–	–	0.10	»	65-20″
73-20″	99.99/99.99	TiO_2(2)	0.01/0.10	–	–	–	»	68-20″
74-20″	99.99/99.99	SiO_2	0.01/0.10	–	–	–	»	69-20″

Notes. 1. Here and in Tables 3 and 4: in sample cipher 20″–60″ indicates treatment time in activator, s. 2. Surfactant additional amount is indicated as percentage of polymer–inorganic additive composition. 3. PEGS is polyethylene glycol secabate, G is organic-based waterproofing agent. 4. Dash refers to missing.

Determining polymer resistance to MT conditions was preliminarily carried out. For this purpose, LLDPE 6101RQ grades were treated in AGO-2 for 1–5 min. Figure 1 gives X-ray diffraction patterns of the initial polyethylene also after MT. There are no significant changes in X-ray spectra. The specific surface area varies from 0.02 to 0.04 m^2/g (S_{sp} = 0.06 m^2/g for the initial polyethylene).

Figure 2 gives X-ray diffraction patterns of samples of the initial polyethylene, titanium oxides, and composites produced by joint treatment in with TiO_2 (1) and TiO_2 (2) additives in the amount of 50–70% in AGO-2 for 1–5 min.

The reflections corresponding to titanium oxide are clearly seen therein. In samples with the addition of 50 % TiO_2 (2) and treatment in the activator for 20–40 s (curves *4*, *5*), the crystalline phase of polyethylene is still recorded in the X-ray diffraction patterns, and upon MT of 60 s (curve *6*), its reflections are absent. With titanium dioxide additive in the amount of 60 and 70 % and MT for 60 s, the reflections corresponding to titanium dioxide were found, and there were practically no reflexes corresponding to polyethylene. Only titanium dioxide additive in the amount of more than 50 % and 60 s of MT contribute to a high degree of polyethylene amorphization.

It was found experimentally that TiO_2 grades did not have an effect on the properties of composites.

The reflections corresponding to titanium dioxide with TiO_2 content of 0.05–1 % were not found in X-ray diffraction patterns; their intensity is insufficient with titanium dioxide concentration of 5 %. For example, TiO_2 additive to 5 % does not have an effect on polyethylene crystallinity degree and MT duration.

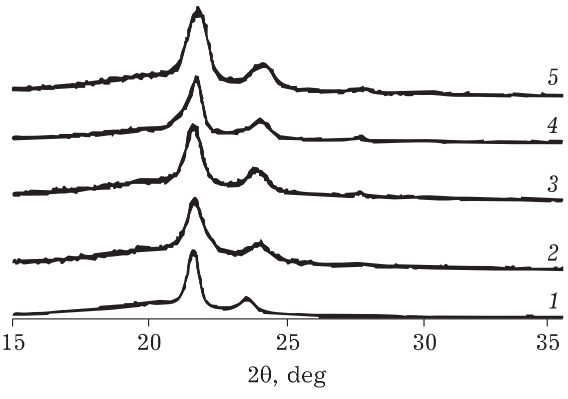


Fig. 1. X-ray diffraction patterns of LLDPE 6101RQ powders: *1* – initial; *2*–*5* – treated in AGO-2 for 1 (*2*), 2 (*3*), 3 (*4*), and 5 min (*5*).

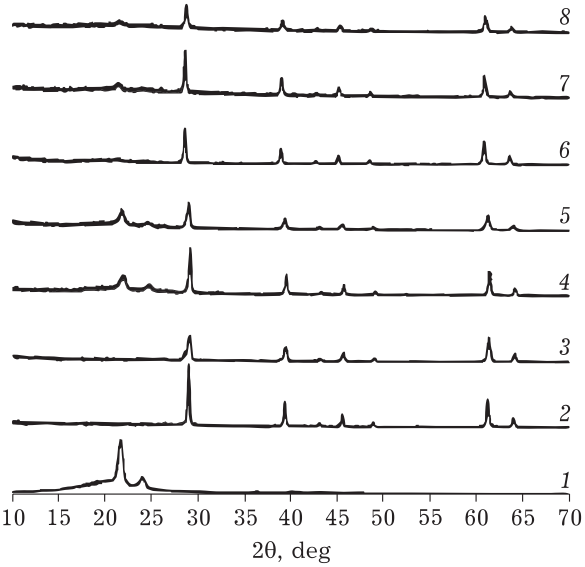


Fig. 2. X-ray diffraction patterns of powders: *1* – initial 6101RQ LLDPE polyethylene; *2*, *3* – TiO_2 (1), TiO_2 (2), respectively; *4*–*6* – composites with additives of 50 % TiO_2 (2) (samples 43-20″, 44-40″, 45-60″, respectively); *7* – with 60 % TiO_2 (2) additive (11-60″); *8* – with 70 % TiO_2 (1) (16-60″).

In case of $CaCO_3$ addition from 0.05 до 5 %, its reflections are absent in X-ray diffraction patterns. In these amounts, it does not affect polyethylene crystallinity degree and MT duration. The crystal phase of polyethylene has been detected with $CaCO_3$ concentrations to 60 %. The specific surface area of the composite with $CaCO_3$ concentration of 50 % and MT duration of 20–60 s is reduced from 0.75 to 0.19 m^2/g.

The X-ray diffraction patterns of samples of polyethylene treated with SiO_2 additives (Rosil-175) in the amount of 0.05–20 % and MT duration of 20–60 s are similar to those of the initial polyethylene; only with 20 % of SiO_2, the intensity of the reflections corresponding to polyethylene decreases.

A similar picture is also observed for samples with sodium bentonite additives in the amount of 5–30 % and MT duration of 20–60 s (there is a decrease in the intensity of the reflections of polyethylene with Na-Bent content of 30 %). Surfactant additives (to 10 %) do not have a significant effect on polyethylene crystallinity degree but contribute to a more uniform distribution of inorganic powders in the polymer, reduce powder composite delamination, especially with high concentrations of the inorganic component.

TABLE 3

Extruder parameters for film production

Sample	Temperature, °C			Filter, μm
	extruder	melt	rollers	
LLDPE 6101RQ	190	182	95	20
15-60″	215	206	95	Absent
17-60″	215	205	95	«
23-20″	215	205	95	«
24-20″	215	206	95	«
28-20″	215	205	95	«
30-20″	215	204	95	«
35-20″	215–225	214	95	«

Films

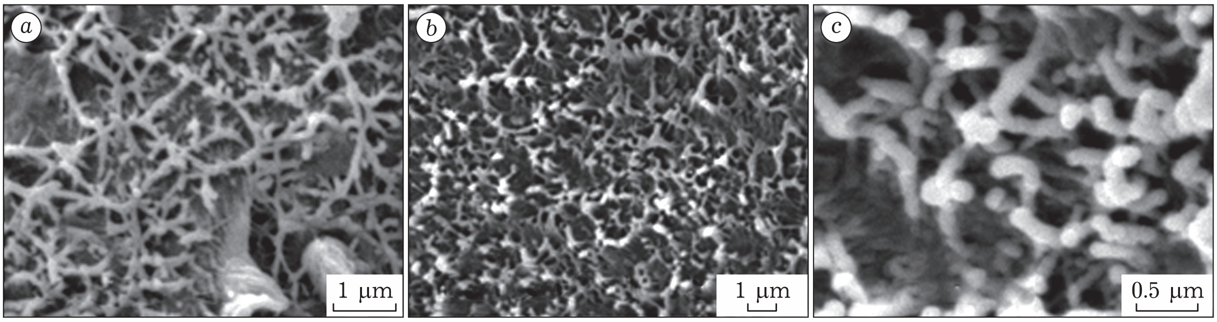
There were preliminarily determined the maximum concentrations of inorganic additives. Composites containing large amounts inorganic powders and, as a rule, fairly developed specific surface area (over 1 m^2/g) do not melt. Samples with high contents of surfactants also poorly melt. Preparation technique for films with surfactant additives has not yet been worked out. It has been noted that samples with surfactants change the initial colour and contain more gels than those without them.

Fairly firm composites are produced with the following additive content, %: TiO_2 70, $CaCO_3$ ≤50–70, sodium montmorillonite ≤30–40, and SiO_2 (Rosil-175 grade) ≤20. These composites and their production techniques can be recommended for manufacture of granular master-batches.

Table 3 gives extrusion parameters of some composites to produce films. It has been determined that the optimum concentration of inorganic additives for extrusion of films without master-batches is 5–10 %.

Scanning electron microscopy (SEM) examination of films. There have been presented micrographs (Fig. 3–6) of samples of films made of unmodified polyethylene (see Fig. 6, *c*) and composites with additives: 28-20″ (5 % Na-Bent, see Fig. 3, *a*), 24-20″ (5 % TiO_2, see Fig. 3, *b*, *c*); 23-20″ (5 % $CaCO_3$ with addition of organic hydrophobizator, see Fig. 4); 61-20″(1 % TiO_2, see Fig. 5, *a*), 65-20″ (1 % SiO_2, see Fig. 5, *b*); 73-20″ (0.01 % TiO_2, see Fig. 6, *a*); 69-20″ (0.1 % SiO_2, see Fig. 6, *b*). Even particle distribution in polymer matrix has been recorded. As can be seen with a magnification of 20 000–70 000×, the composite is crystallized as volume grids with a certain size of the crystal cell or seed.

Film density investigation. Table 4 gives determination results of film density by hydrostatic weighing. Experimental and theoretical densities of samples with a content of inorganic additives of 0.01 % (samples 74-20″ and 24-20″) correspond to the density of the control sample (polyethylene LLDPE 6101RQ without additives). Experimental densities of the remaining samples with the content of additives 1–25 %,



×20 000 ×10 000 ×40 000

Fig. 3. SEM image of samples of films: *a* – 28-20″ (5 mass % of Na-Bent), *b*, *c* – 24-20″ (5 mass % TiO_2 (2)).

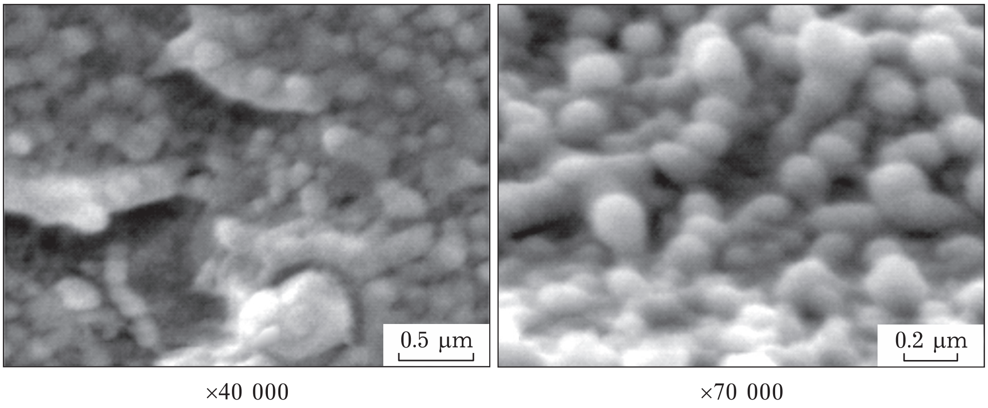


Fig. 4. SEM image of sample of film 23-20″ (5 mass % of $CaCO_3$ + organic-based oil wetting agent).

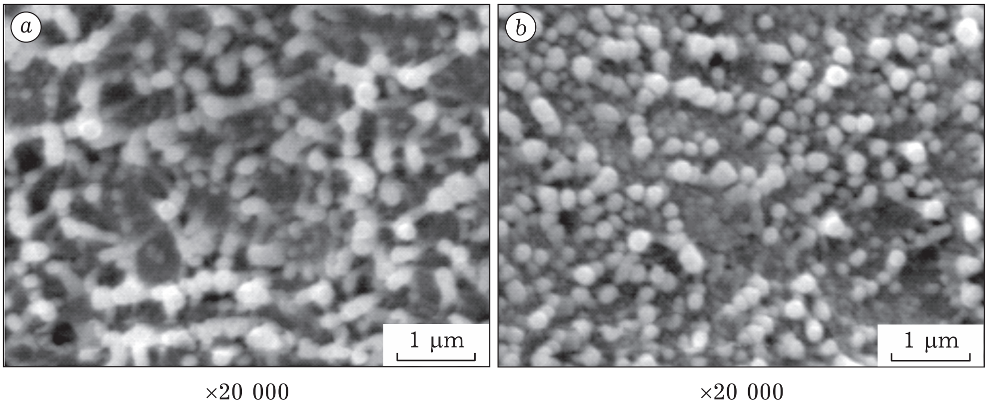


Fig. 5. SEM image of samples of films: *a* – 61-20″ (1 % TiO_2 (2)), *b* – 61-20″ (1 % SiO_2).

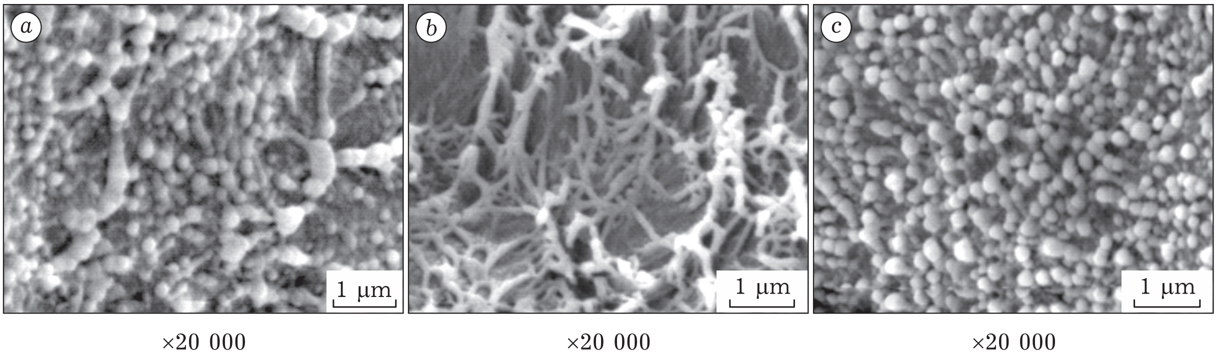


Fig. 6. SEM image of samples of films: *a* – 73-20″ (0.01 % TiO_2 (2)), *b* – 69-20″ (0.1 % SiO_2), *c* – LLDPE 6101RQ.

with the exception of the sample 65-20″ are lower than the theoretical due to the formation of mesh structures. Perhaps, for sample 65-20″, the number of dispersed particles and MT conditions correspond to the maximum dense filling of all voids of the polymer matrix.

An X-ray phase examination of films. It can be seen from Fig. 7, as in case of powder composites, that TiO_2 additive in the amount of 0.01–5 % (curves *2–4*) does not affect polyethylene crystallinity degree in films. In case of a sample with TiO_2 additive to 25 % (curve *5*), the intensity of reflection corresponding to the crystalline phase of polyethylene decreases.

A similar picture is also observed in case of additives to 10 % of SiO_2 (Fig. 8, curves *2–5*), to 5 % of $CaCO_3$ and Na-Bent (Fig. 9, curves *2* and *3*).

Exploration of physical and mechanical characteristics of films. Figure 10, a gives the data on the tensile strengths of the films along and across (the average of five measurements). It can be seen that the strength characteristics

TABLE 4

Data on film density

Sample	Additive		Composite density, g/cm ^{3}		Δ_1, %	Δ_2, %
	Type	Content, %	Experimental	Theoretical		
LLDPE 6101RQ	–	–	0.927	0.927	–	–
73-20″	TiO_2(2)	0.01	0.927	0.927	0	0
61-20″	TiO_2(2)	1	0.937	0.934	1.07	0.75
24-20″	TiO_2(2)	5	0.966	0.965	4.04	3.94
32-20″	TiO_2(2)	25	1.05	1.152	11.71	19.51
74-20″	SiO_2	0.01	0.929	0.927	0.22	0
65-20″	SiO_2	1	0.956	0.933	3.94	0.64
27-20″	SiO_2	5	0.952	0.956	2.63	3.03
30-20″	SiO_2	10	0.980	0.986	5.41	5.98
23-20″	$CaCO_3$	5	0.957	0.959	3.13	3.34
28-20″	Na-Bent	5	0.950	0.958	2.42	3.24

Note. Δ_1 and Δ_2 signify increasing experimental and theoretical densities, respectively, in relation to reference sample LLDPE 6101RQ.

of all modified samples are improved insignificantly (maximally by 15 %) compared with the initial sample of polyethylene.

Gas permeability of a sample containing 25 % TiO_2 (measurements were carried out at 23 °C and 50 % of RH, an area of samples of 50 cm^3) decreases by 43 % (see Fig. 10, *b*, sample 2), for a sample with 5 % TiO_2 (sample 4) at 34 %, with 5 % $CaCO_3$, SiO_2 and Na-montmorillonite (samples 3, 5, and 6, respectively) – by 27–29 %. For samples containing inorganic additives such as TiO_2 and SiO_2 from 1 to 0.01 %, gas permeability is reduced by 22–50 % (samples 7–11).

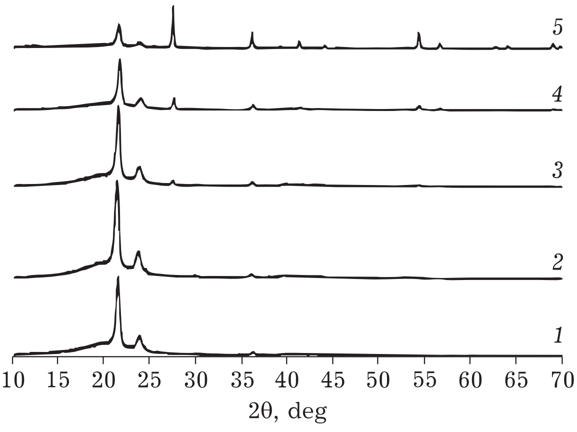


Fig. 7. X-ray diffraction patterns of films: *1* – from unmodified polyethylene; *2–5* – with TiO additives 0.01 (*2*), 1 (*3*), 3 (*4*), and 25 % (*5*).

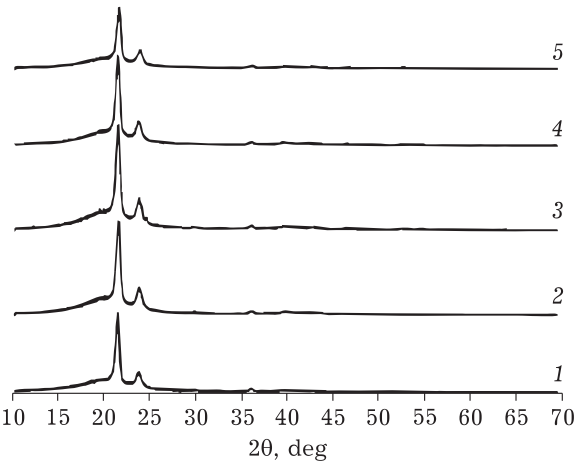


Fig. 8. X-ray diffraction patterns of films: *1* – from unmodified polyethylene; *2–5* – with TiO additives 0.01 (*2*), 1 (*3*), 3 (*4*), and 10 % (*5*).

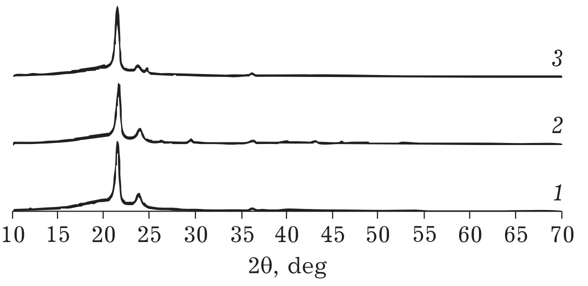


Fig. 9. X-ray diffraction patterns of films: *1* – from unmodified polyethylene; *2*, *3* – with additives of 5 % CaCO + oil wetting agent (*2*) and 5 % of Na-Bent (*3*).

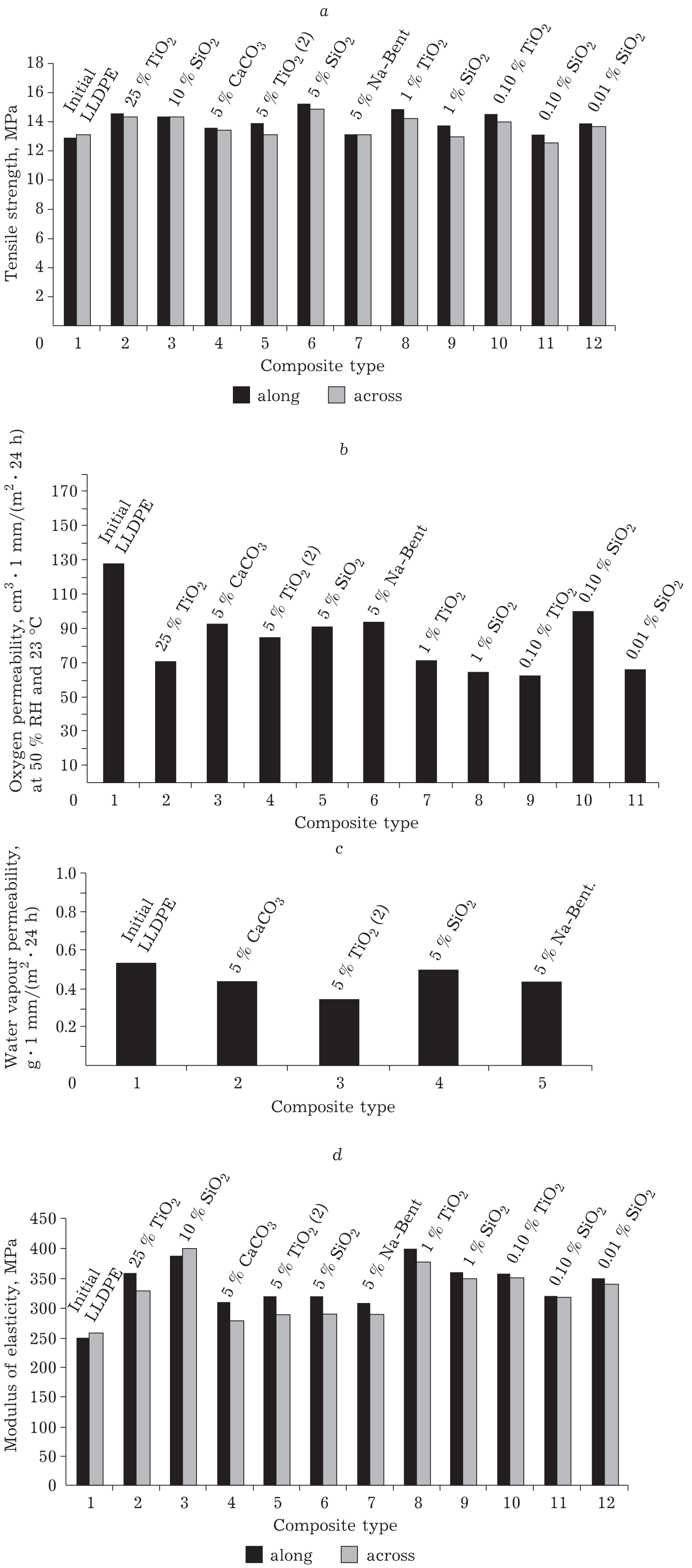


Fig. 10. Tensile strength (*a*), gas permeability (*b*), vapour permeability (*c*), and modulus of elasticity (*d*) of film samples.

Vapour permeability (see Fig. 10, *c*) (at 38 °C, 50 % of RH) of samples containing 5 % $CaCO_3$, Na-montmorillonite, or TiO_2 is reduced by 19–35 % (samples 2, 3, and 5, respectively), for the remaining samples, it is comparable to vapor permeability of the unmodified sample.

Plastic properties (see Fig. 10, *d*) change in a significantly higher degree for samples with low contents of TiO_2 and SiO_2 additives. With the introduction of 0.01–1 % of additives (samples 8–10, and 12) modulus of elasticity along and across increased by 40–60/31–46 (percentage), with 5 % (samples 4–7) – 24–28/8–12; 0.1 % SiO_2 (sample 11) – 28/23; 10 % SiO_2 (sample 3) – 56/54; 25 % TiO_2 (sample 2) – 44/27.

CONCLUSION

The mechanochemical method allows mixing non-polar hydrophobic polymers (polyethylene) and various hydrophilic inorganic particles as powders, thereby expanding the range of inorganic additives used and their concentration range (from 0.01 to 70 %). With this compositions preparation method, it is not required to use additional dispersing agents.

It is worth noting the high degree of homogenization of the inorganic component in the polymer matrix, which is unachievable with other methods of mixing. The dispersion process takes from a few seconds to 1 min (when dispersing in the melt – a few hours). When films obtaining, one may accelerate extruding processes (for mixtures that have passed mechanochemical treatment, as a rule, one run through the extruder is sufficient).

The maximum concentrations of the explored grades of inorganic additives for master-batches are the following, %: TiO_2 70, $CaCO_3$ 70, Na-montmorillonite 40, SiO_2 20.

Linear low-density polyethylene (LLDPE) based films 6101RQ with improved barrier and mechanical properties have been obtained. It is found that composites crystallize as volume grids with a certain size of the crystallization cell.

The amount of inorganic additives (TiO_2, $CaCO_3$, SiO_2, or Na-montmorillonite/bentonite) in preparing films without master-batches is 0.01–5 %. Herewith, gas permeability decreases to 30–50 %; modulus of elasticity (along) rises by 24–60 %; strength increases maximally by 15 %.

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