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ВИСОКОМОЛЕКУЛЯРНІ СПОЛУКИ ТА (НАНО)КОМПОЗИЦІЙНІ МАТЕРІАЛИ

N. V. Chopyk[1], V. M. Zemke[1], V. V. Krasinskyi[2], I. Gaydos[3], B. V. Levytskyi[1]
[1] Lviv Polytechnic National University,
Department of Chemical Technology of Plastics Processing
[2] Łukasiewicz Research Network – Institute for Engineering of Polymer Materials and Dyes
[3] Technical University of Košice,
Department Technologies, Materials and Computer Aided Production
viktoriia.m.zemke@lpnu.ua

RESEARCH OF POLYMER BLENDS PROPERTIES CONTAINING ADDITIVES OF THE DIFFERENT STRUCTURE

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The properties of blends filled with polymers of a different structure and low molecular weight additives were analyzed. Additives selection is grounded. It was established that three-component polymer blends have a sufficient fluidity value, which ensures the ability of obtained materials to be processed. The influence of the composition and nature of the components on the physical and mechanical properties of obtained compositions was studied. The adding of mineral filler into the polymers blend helps to increase dispersion and thus expands of application of mentioned polymer owning to their possibility to be processed.

Key words: filling; polyvinylchloride; polyolefins; relative elongation; polymer additives; yield point.

Introduction

The quality of polymer blends depends on that how mutually compatible their components are, as well as on the conditions of their mixing and crystallization. One of the main tasks of mixing is to obtain blends that combine the valuable properties of each component. On the other hand, the distribution uniformity affects the physico-mechanical characteristics, and as a consequence allowing assessing the homogeneity degree of blends which are based on their physico-mechanical properties.

However, most of the studied polymer pairs until today are thermodynamically “incompatible” [1]. At the same time, it has been proven that there are no absolutely immiscible polymers. The limit of mutual solubility of polymers depends primarily on their molecular weight and temperature. If the solubility of polymers increases with a decrease in molecular weight [2] than the rising solubility with temperature is typical for most polymers of a homogeneous structure. For the softening the components which being blended, the process is carried out at an elevated temperature corresponding to the viscous state of polymers namely, to the state of highly viscous liquids. Mixing insoluble in each other liquids leads to the formation of emulsion. A low-molecular emulsion without an emulsifier is not stable and instantly delaminates, and the blend of polymers, due to its high viscosity, is quite stable over time. So, regardless of the polymers compatibility, we can get an externally homogeneous blend, in which even over time the delaminating will not be observed.

The largest group of industrial thermoplastics makes a polyolefins, which are the basis of many compositions [3]. Compositions based on polyethylene and polypropylene was the most widely applied. The use of polyethylene in compositions is due to its rather valuable complex of properties: high impact strength, non-toxicity, resistance to aggressive environments and the ability to keep properties in a wide range of compositions. At the same time, ultrahigh molecular weight polyethylene possesses substantially high melt viscosity, which complicates its processing.

In previous works, the authors established a positive effect of polypropylene as a third additive on the fluidity of polyethylene blends [4]. Consequently, taking into account the increased strength of blends of ultrahigh molecular weight polyethylene with polypropylene, interest was discovered in three-component blends both from the technological point of view and from the point of operational properties view. Mentioned above also includes physical and mechanical properties as a determining factor for obtaining materials with the desired properties and evaluating operational stability compositions. Mixing ultrahigh molecular weight polyethylene with polyolefines via the different mechanisms leads to the formation of compositions with different structural changes due to various affinities of the components. However, it should be noted that the processing of ultrahigh molecular weight polyethylene and the compositions based on it, as can be seen from the given data [5], is complicated. Therefore, it is fully grounded to conduct research in the direction of creating technological compositions based on ultrahigh molecular weight polyethylene, which would possess the high strength and resistance properties appropriate characteristic of this polymer and, simultaneously, would be characterized by the ability to be processed through the traditional, high-performance methods, such as injection molding or extrusion.

The aim of research – study of the influence of the homogeneity degree of ultrahigh molecular weight polyethylene blends with other polymers and additives as well as the composition and component's nature and, as a result their influence on the physical and mechanical properties.

Materials and research methods

Ultrahigh molecular weight polyethylene (UHMWPE) of 7047 brand with melt flow index of 0.24 g/10 min, density 920–950 kg/m^3, melting temperature 408 K, relative elongation during stretching 100 %.

Low-density polyethylene (LDPE) of 15803-020 brand with a melt flow index of 1.97 g/10 min, density 900–939 kg/m^3, melting temperature 378–398 K, relative elongation during stretching – 160 %.

High-density polyethylene (HDPE) of 21008-075 brand with a melt flow index of 6.4 g/10 min, density 948–959 kg/m^3, melting point 403–418 K, relative elongation at stretching – 105 %.

Polypropylene (PP) of 21060 brand with a melt flow index of 12.52 g/10 min, density 900–910 kg/m^3, melting point 433–445 K, relative elongation at stretching – 18 %.

Copolymer of ethylene with polypropylene (CEP) of 23201-003 brand with a melt flow index of 0.4 g/10 min, density 907 kg/m^3, melting temperature 393–398 K, relative elongation during stretching 700 %.

Polyvinyl chloride (PVC) of E-74P brand is emulsion resin with a Fikentcher constant of 74, bulk density >0.45 g/cm^3, content of volatile substances <0,3 %, particle size (residue on sieve is 63 μm) – < 3 %, relative elongation at stretching – 10–50 %.

Polyethylene terephthalate (PETPh) of 030110 brand with a density of 1090–1110 kg/m^3, melting point 523–538 K, relative elongation during stretching 2–4 %.

Calcium carbonate ($CaCO_3$): density 2600–2750 kg/m^3, melting point 1612 K at 1025 MPa, destruction temperature 1173 K, specific heat capacity 0.84–0.90 J/kg ×K.

Methods of obtaining samples. Polymer blendes were obtained mechanically by blending ultrahigh molecular weight polyethylene with additives at room temperature in a drum with a capacity of 3 liters. The resulting blend was heated in a vertical plunger injection cylinder at T = 463 K for 15 min. with further extrusion of the melt through a nozzle. The rod was cooled and crushed applying a rotary knife device. The resulting granulated blend was loaded into a casting machine Kuasy 25×32 II/1 (Germany). Blending in the plasticizer of the casting machine was carried out with in the cylinder zones at the temperature: 463, 473, 493 K for 90 seconds, to obtain a more homogeneous system after further pressing into the mold at t_f = 323–343 K the samples in the shape of blades were obtained. Derived samples afterward were used for testing.

Physico-mechanical testing, for instance, yield point, destructive tensile stress, maximum tensile stress, relative elongation at yield point, relative elongation at break were determined according to ISO 527-2:2012 [6]. The Rockwell hardness of the materials was determined according to ISO 2039/2-87 [7].

Results and discussion

The authors in previous works [4] studied three-component polymer blends. The polypropylene was added in an amount from 5 to 20 % by weigh to the UHMWPE: LDPE and UHMWPE: HDPE compositions (50:50 of content). For dual compositions containing low-density polyethylene, during the forming samples by injection molding at T = 503 K, the values of the plasticity limit of ternary blends are somewhat higher, but the deformability has decreased. Analyzing the properties of the ternary compositions among themselves, we can conclude that the blend containing 5 % of polypropylene has satisfactory physical and mechanical properties. Dual compositions with high-density polyethylene were similarly studied. It was established that mentioned blends have approximately the same maximum tensile stress values, but differ in deformability. The blend containing 10 % of polypropylene has the highest deformability index, the relative elongation of which exceeds other compositions by 2–3.5 times.

The study of structural changes of ternary blends shows that a sufficiently homogeneous blend with stable properties can be obtained with a polypropylene content of 5 % by weigh. When increasing its content in the range of 6–15 % by weigh. an inversion of phases is observed, which leads to anomalous behavior of blends.

During the experiment, a blend based on ultrahigh molecular weight polyethylene was filled with polymers of different structure, in particular: copolymer of ethylene with propylene, a block of ultrahigh molecular weight polyethylene – polypropylene, polyethylene terephthalate, polyvinyl chloride, as well as a powdered mineral additive – calcium carbonate. The properties of newly created compositions were investigated.

The choice of additives was due to the following reasons: copolymer CEP and block (UHMWPE -PP) [10] the possibility of improving the compatibility and properties of blends; PETPh – in order to solve the problem of waste disposal [8]; PVC – the effect of powdered polymer and the possibility of strengthening compositions; $CaCO_3$, based on its properties - low abrasiveness during processing, availability, and also gives composites increased thermal conductivity and the ability to be dyed with pigments in a wide range of colors and printing [9].

Table 1 illustrates the physical and mechanical properties of blends of ultrahigh molecular weight polyethylene filled with polyethylene terephthalate, depending on the content of the latter. The polyethylene terephthalate used in the work is a waste product from the manufacturing of bottles that have been finely ground.

Table 1

Physical and mechanical properties of polymer blends

Indicators	Content of PETPh, %					
	5	10	15	25	50	75
Plasticity limi, s_{pl}, MPa	9.0	10.6	10.5	13.0	9.1	8.8
Breaking point, s_p, MPa	8.6	10.2	10.1	12	8.4	7.9
Relative elongation at break, e, %	15	27	25	18	9.4	20

The introduction of polyethylene terephthalate into ultrahigh molecular weight polyethylene leads to a decrease in strength properties of the blends. The values of yield point and relative elongation of ultrahigh molecular weight polyethylene are being decreased in 2 and 5 times correspondingly.

Fig. 1 demonstrates tensile curves of double and triple compositions derived on basis of ultrahigh molecular weight polyethylene containing emulsion polyvinyl chloride. To obtain samples, the polymer granules were dusted with powdered PVC in the amount of 3 % of the total weigh of the blend.

Analyzing the obtained results, it can be concluded that the introduction of polyvinyl chloride to ultrahigh molecular weight polyethylene leads to a decrease in strength properties, compared to the original dual blends. Mantioned above can be explained by the formation of an inhomogeneous structure of polyvinyl chloride – ultrahigh molecular weight polyethylene blends, however, as can be seen, the blends are characterized by sufficiently large values of relative elongation at break. Only the three-component blend with polyvinyl chloride additives has significantly less elongation, but retains high strength.

Table 2 shows the physical and mechanical properties of blends based on ultrahigh molecular weight polyethylene while the adding of block (UHMWPE - PP) and CEP copolymer. Block ultrahigh molecular weight polyethylene – polypropylene of 50:50 wt % in initial composition were obtained by rolling at temperatures of 363–398 K for 40 min. The significant changes in properties are not observed, except in the blends containing PP at the reducing yield strength on 60 %, the deformability increases to 200 %.

Adding of CEP into the blend in an amount of 5 % of the total mass caused a decrease in the yield point of polymer blends to 15 %. An increase in the CEP content to 10 % leads to a decrease in the yield point of the blends (to 30 %), but at the same time the deformability significantly improves: the relative elongation at break reached 250 %.

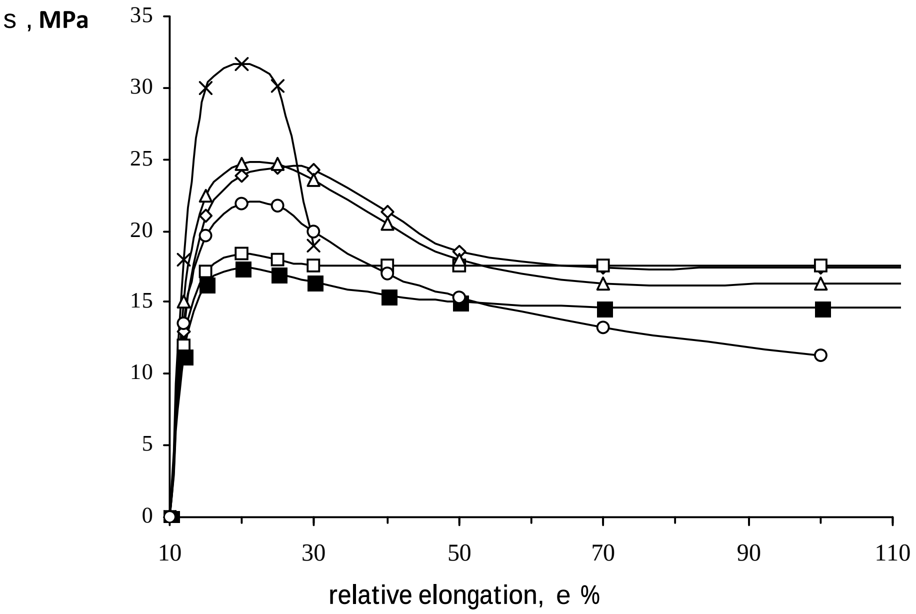

Fig. 1. Tensile curves of polymer blends depending on the polyvinyl chloride content:

- à ¾: HDPE:PVC (50/50/3) e_p – 300 %
- □ ¾ UHMWPE UHMWPE:PP:PVC (50/50/3) e_p – 464 %
- D ¾ UHMWPE: HDPE:PP:PVC (50/50/5/3) e_p – 170 %
- x ¾ UHMWPE: LDPE:PP:PVC (50/50/5/3) e_p – 30 %
- ■ ¾ UHMWPE: LDPE:PVC (50/50/3) e_p – 300 %
- o ¾ UHMWPE:PVC (50/50) e_p – 95 %

Table 2

Physical-mechanical parameters of blends based on ultrahigh molecular weight polyethylene

Blend content, %	Parameters				
	MFI, g/10 min	Plasticity point s_{pl}, MPa	Breaking poin s_p, MPa	Relative elongation at break, e%	Rockwell hardness HB, MPa
UHMWPE:LDPE:PP:CEP = 50:25:25:10	1.58	20.7	16.3	540	9.54
UHMWPE:PP:СЕП = 50:50:10	1.91	25.1	18.2	120	9.57
UHMWPE:HDPE:CEP = 50:25:25:10	1.78	24.7	18.8	135	9.57
UHMWPE:LDPE:CEP = 50:50:20	1.55	17.7	16.5	600	9.54
UHMWPE:LDPE:PP:block =50:25:25:10	1.50	20.1	17.0	600	8.45
UHMWPE:LDPE:HDPE:block = 50:25:25:10	1.40	20.0	17.3	530	8.45
UHMWPE:ПП:block = 50:50:10	1.43	24.6	17.3	130	8.45

Filled blends based on ultrahigh molecular weight polyethylene and polymer additives were obtained by mixing in a viscous state with dispersed $CaCO_3$, which was complicated due to the difference in particle sizes.

Therefore, we tested different methods of adding the filler: 1) by the method of constantly adding powder to the granules in the hopper of the plasticizer; 2) preliminary cold “powdering” of granules covered with a thin layer of neutral (transformer) oil; 3) preliminary hot “powdering” of granules, where the filler was introduced heated to a temperature of 473–523 K. It should be noted that according to our observations, the second and third methods of filler introduction are more technological, which, in addition, give more homogeneous blends of better operational properties.

Continued heating of calcium carbonate at temperatures of 423 K reduces its ability to aggregate and facilitates dispersion in the polymer matrix. Taking into account the fact that the melting of polymers in stationary mode on 70–80 % ensured due to the forces of internal friction of the material, the filler dispersed in the mass should facilitate the heating of the system. The presence of ultrahigh molecular weight polyethylene and calcium carbonate in the system contributes to the increase of shear stresses at a constant shear rate, and therefore will promote dispersion [9, 13].

Physico-mechanical properties of double and triple compositions based on ultra-high molecular weight polyethylene filled with calcium carbonate in comparison with the properties of the original UHMWPE are characterized by satisfactory properties. During the research the UHMWPE:HDPE:$CaCO_3$ double blend with optimal composition 80/20/20 % have been obtained, which with sufficient fluidity (MFI =1.2 g/10 min), (σ_{pl} = 17.5 MPa) posseses high deformability namely, elongation at breaking strength is 210 % and also the triple blend UHMWPE:HDPE:PP:$CaCO_3$=19:76:5:20 %, which is characterized by satisfactory values of plasticity (σ_{pl} = 30.4 MPa) and deformability (ε_p = 160 %) [5, 13].

Comparing the mechanical characteristics of blends of ultrahigh molecular weight polyethylene and high-density polyethylene with the properties of similar materials [11, 12] and the original ultrahigh molecular weight polyethylene we can summarize the following: the polymer composite materials based on ultrahigh molecular weight polyethylene combining sufficient rigidity and elasticity, which are inherent to the structural materials, are not inferior to similar materials made by more complex technology but are characterized by higher fluidity and therefore, higher manufacturability.

Conclusions

Compositions of ultrahigh molecular weight polyethylene containing the polymers of a different structure and low molecular weight mineral additives, such as polyvinyl chloride, copolymer of ethylene with propylene, block (ultrahigh molecular weight polyethylene – polypropylene) and polyethylene terephthalate were studied.

It was determined that supplying of mentioned additives into the composition with ultrahigh molecular weight polyethylene does not significantly change the rheological characteristics of the initial polymer, but stipulates decrease in its physical and mechanical properties.

The creation of composites based on ultrahigh molecular weight polyethylene and dispersed mineral type fillers expands the areas of application of this polymer due to the possibility of processing by common methods, primarily extrusion and injection molding.

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Н. В. Чопик, В. М. Земке. В. В. Красінський, І. Гайдос, Б. В. Левицький
Національний університет “Львівська політехніка”,
кафедра хімічної технології переробки пластмас

ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ПОЛІМЕРНИХ СУМІШЕЙ, ЯКІ МІСТЯТЬ ДОДАНКИ РІЗНОЇ СТРУКТУРИ

Проаналізовано властивості сумішей, наповнених полімерами іншої будови та низькомолекулярними доданками. Обґрунтовано вибір доданків. Встановлено, що трикомпонетні полімерні суміші характеризуються достатнім значенням плинності, що визначає здатність одержаних матеріалів до перероблення. Досліджено вплив складу та природи компонентів на фізико-механічні властивості одержаних композицій. Введення мінерального наповнювача до сумішей полімерів сприяє підвищенню диспергування і розширяє сфери застосування цього полімеру завдяки можливості переробки.

Ключові слова: наповнення; полівінілхлорид; поліолефіни; відносне видовження; полімерні доданки; границя текучості.