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The Plasticing Effect on Structure Forming and Crystallization Processes in Polymer Blends of Polypropylene-Poly(Vinyl Alcohol)

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There is one established, that glycerol’s injection in (7,0 ÷ 15,0)% of mass. amount into polymer blend of polypropylene/poly(vinyl alcohol) (PP/PVA) of mass equation 30/70% is not changing the structure forming character of PP into PVA matrix: there are parts, films and external shells being formed alongside with PP fibers. When at this, during concentration increase of selective plastifier, there are PP fiber forming process into PP matrix gonna being bad, and those are consisting in average microfiber diameters and mass part of films increase. There are features of structure forming, being linked in plastifying effect of glycerol on the blend melts, and, when simultaneously with, in the those decrease of kinetical stability. There are crystallization temperature of PVA increasing, simultaneously at plasticizer content of 7,0 % of mass., and there is PP crystallization peak absent through polymer amorphization. There is crystallinity’s degree of PP decreases, through high dispersion state of polymer.

Key words: polypropylene, poly(vinyl alcohol), melts of polymer blends, glycerol, microfibers, melting and crystallization.

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Introduction

There are creation of new materials with pre-determined properties of, by development of wasteless and ecologically pure technologies, when using polymer blends, and then, those are leading world trends in the area of chemical fibers. There is simple, available, and also the most effective processing for modification of polymers exists, named as those mixing of. By this, there are properties of the two components combined both and unique effects realized in. There is formation of matrix-fiber morphology in incompatible systems evokes considerable interest, so that one gives a possibility for improving mechanic properties of composite fibers, at the expense of self-reinforcing, and then, in purposes to obtain the thin-fibrous materials of new characteristics, due to micron sizes of filaments and unusual structure of their surface also [1-3]. There is morphology for extrudates of polymer blends determined by macro- and microrheological processes, when during their flow, by crystallization ability of the dispersed phase components and dispersion medium, and by conditions also, when at those there is process of crystallization occuring in.

There is the aim of the work, consisting in determination of the addition's influence (glycerol) as plasticizer, and its concentration on the regularity of structure formation and crystallization processes, in the polypropylene/poly(vinyl alcohol) blend of.

I. Experimental

There are objects studied, as polypropylene/poly(vinyl alcohol) blends (PP/PVA) with their ratio 30/70 mass %. We were used three substantions of , such as isotactic PP (PP 575 P by SABIC), the melting temperature T_{melt} of 172° C; PVA (“Moviol 4-88” ,Kuraray Co,.Ltd., Japan), hydrolysis level of 86.7 ÷ 88.7 %, contents of flying compounds up to 5 mass %, contents of ash in calculation to Na_2O – 0.5 mass %; and glycerol (as chemically pure). There were injection of additions and polymer mixing, carried out with the screw-disk extruder combined (LGP-25). There were glycerol contents (Glyc) in the blends of 7.0; 10.0, and 15.0 mass %. There was viscosity of the melts of PP (η_1), PVA (η_2), and their blends (η_{suml}), determined

Table 1

The influence of glycerol contents on structure forming phenomenon for extrudates of PP/PVA* blends

The glycerol contents, mass. % of	The microfiber characteristics					The contents for other structure types, mass % of		
	long			short		particles	films	ETFS
	d, µm	portion, mass. %	σ^2, μm^2	d, μm^2	portion, mass. %			
7,0	3,0	66,0	2,6	2,4	20,5	3,8	7,0	2,7
10,0	3,5	73,7	2,1	2,2	17,4	3,6	5,2	8,7
15,0	4,4	66,8	2,7	2,6	9,8	1,1	14,7	7,6

*at $\tau = 5.69 \cdot 10^4$ Pa;

Table 2

The influence of glycerol concentration on rheological properties of PVA melt and PP/PVA* blends

The glycerol contents, mass. % of	η_1**	η_1/η_2	η_{sum}	B_1***	B_1/B_2	B_{sum}
7,0	350	1,2	130	1,4	0,9	2,3
10,0	260	0,9	100	1,2	0,7	2,3
15,0	140	0,5	90	1,2	0,7	2,1

* at $\tau = 5.69 \cdot 10^4$ Pa; **η_1 = 300 Pa·s; ***B_1= 1,6

with the capillary viscometry method, with the microviscometer (MV-2), in displacement stress range of $\tau = (0.1 \div 5.7) \cdot 10^4$ Pa, at the temperature of 190° C. There was the elasticity of the melts, and one appreciated from the value of swelling (B) for the blend extrudates, when those were annealed in silicon fluid at 170° C for 5 min. There were processes of structure formation, and those were investigated with optical microscopy technique, carrying out the quantitative analysis of all the structure types in the remains, after PVA extraction from the extrudates studied here. There were results processed by the mathematical statistics technique, when determining the mean diameter (d) of microfibers, those homogeneity distribution (σ^2), and mass part for every of structure types. When at investigating the regularities of phase transitions for the polymers in composites, we were using the differential thermal analysis tecnique. There was thermogram recording technique, and one were carried out with the derivatograph (Q-1500 D, MOM, Hungary). We were used the platinum crucibles and powder of Al_2O_3 r as a standard here. Then, there were samples milled off, and the weight of specimen studied was approximately of 400 mg. There was precision of determination of melting and crystallization temperatures in ± 2° C of. There was sample X-ray phase analysis, carried out by the powder diffractometry technique. There were diffractograms registered with the diffractometer (DRON-4-07) in Cu K_α radiation, when at recording with the Bragg-Brentano geometry in diffraction angle range in $2\theta = (5 \div 70)$ degrees of. There was crystallinity level for the initial polymers, and extrudates thereof, determined with the Matthews method.

II. Results and discussion

There were experimental data obtained showing that, when in the melts of blends to study during their flow, polymer of dispersed phase forms thin streams, which are stretching by flow of the second polymer (matrix). There is structure of extrudate (monofibers), which is originating from of die aperture, and this is the continuous PVA phase, which generally filled with the thin streams of PP, and one lefted as a microfiber shell (MF), after solution of the polymer matrix with water. There were results of quantitative analysis of microstructure of extrudates showed those results meaning in, increase in glycerol concentration does not changing the character of structure forming for PP in PVA matrix: when together with the continuous MF, PP forms other structure types – the particles, films, short MF, and external, thin-fibrous shell – ETFS (Table 1). By this, there is increase in the addition contents causes worsening of fiber formation process (the increase in the mean diameter for long MF and mass part of films). There is selective plastification, when having influence on the rheological properties for one of the blend phase, and thus changes a ratio of viscous-elastic characteristics of the components, those dispersion ability, and deformation along forming streams.

There is process of deformation of polymer drops, when using terms for hydrodynamics, in polymer-polymer systems occurs the most effectively, when there are values of viscosity and elasticity for dispersed phase and dispersion medium close to one another of [1, 4}. There is investigation of the influence of glycerol concentration on the rheological properties of PVA melt shows fact that, its viscosity is regularly reduced (i.e. the plastification effect occurs). There is elasticity for the melts of initial PVA and the blends does not practically change in, considering the equilibrium values of extrudate swelling, when one linked with forming of network hydrogen bonds between the functional groups of PVA macromolecules and glycerol molecules (Table 2).

There are the decrease in dispersion level for dispersed phase component and increase in film forming,

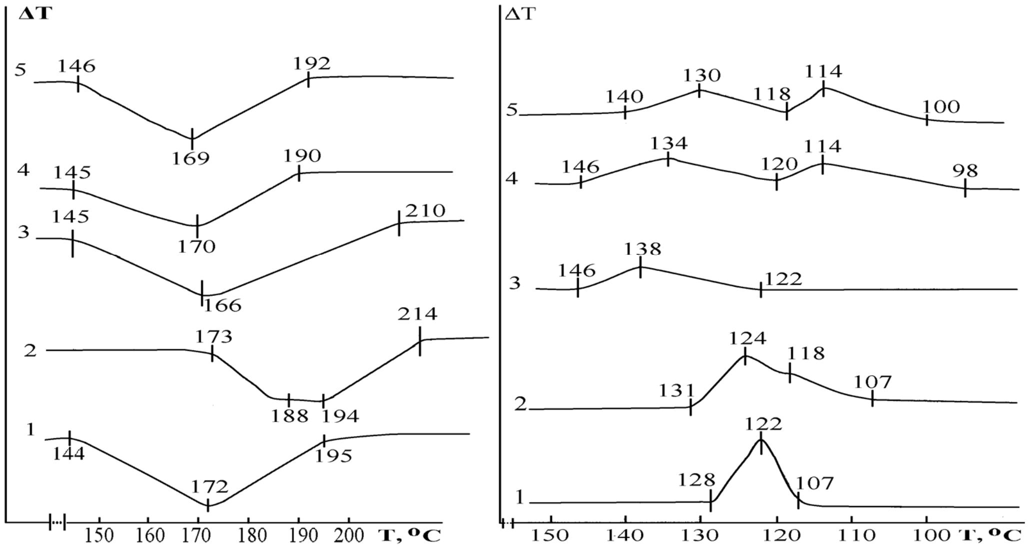

Fig. 1. The thermograms for melting (*a*) and crystallization (*b*) processes of extrudates: 1 – PP; 2 – PVA; 3 – PP/PVA(Glyc) 30/70/(7.0); 4 – PP/PVA(Glyc) 30/70/(10.0); 5 – PP/PVA(Glyc) 30/70/(15.0).

due to deviation of the viscous-elastic properties ratio of the components from a unit and kinetic stability lowering of blends, because of those viscosity reduction in.

It is known, that forming of microstructure of extrudates is essentially caused by the crystallization ability of dispersed phase and dispersion medium polymers of. There is determination of the phase transitions temperatures, and this allows one to appreciate the temperature intervals of processing for polypropylene MF, and wares based on those ones. It should be noted that crystallization process stabilizes the PP streams, which going from the forming aperture. This promotes formation for the thinner MF in. There are PP and PVA polymers both, which having the close melting temperatures of, therefore in thermograms for those blend extrudates, the melting peaks coinciding on. They are weakly intensive ones, so that extrudates were obtained at sharp cooling with water. There is crystallization process going, at low temperature, i.e. one occurs at conditions far from equilibrium of, and so then causes low crystallinity level. There are thermograms of polymer melting and crystallization processes, in extrudates of the plasticized blends, and pure polymers shown on Fig. 1.

There is the most important determined regularity of phase transitions, for the blends to be studied - the presence of one crystallization peak for extrudates PP/PVA(Glyc) with 30/70/(7) ratio. By this, T_{cr} of the first peak does not coincide with T_{cr} of initial PVA and PP, and it is essentially higher, than those crystallization temperatures. There is the glycerol concentration of 7.0 mass % is obviously critical one, because at glycerol contents of 10.0 mass %, and there are peaks of polymers both: at the temperatures of 134° C (PVA) and 114° C, on the thermogram of extrudate crystallization (PP). There are peaks weakly intensive and broad ones, showing the low crystallinity degree, and considerable size distribution for the crystallites in. There are the crystallization peaks for polymers both, when available ones at glycerol contents of 15.0 mass % also. There is such influence of Glyc on the process of crystallization of PP/PVA blend, and one probably consists in that, when at its contents of 7 % in blend melt, when at forming of associates of PVA macromolecules with glycerol molecules being realized as the homogeneous crystallization nuclei and promoting PVA crystallization at the higher temperatures. By this, PP is almost amorphous because one, when exists as highly disperse state of MF, with a mean diameter of 3 μm. That's why, there is no PP's crystallization peak writing on, practically. When at increasing glycerol contents up to 15.0 mass %, its part migrate into separate phase at the boundary layer, and one intensifying the plastification effect, which causes decrease for phase transition temperatures in. This promotes formation for MF of larger diameters, and increase in mass film part of.

In purpose for ascertaining the influence of glycerol contents on structure forming in PP/PVA melt, we were carried out X-ray structure analysis for extrudates. There

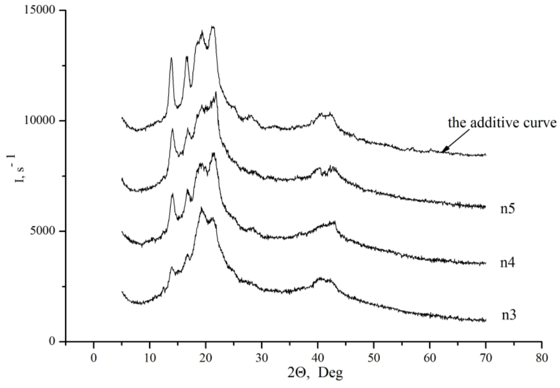

Fig. 2. The diffractograms for the samples of extrudates of PP and PVA blends with glycerol addition in: 7.0 (n3), 10.0 (n4), 15.0 mass % (n5) and the additive diffraction curve for PP/PVA blend.

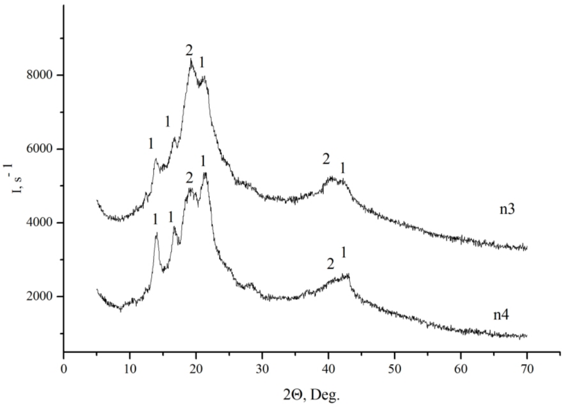

Fig. 3. The illustration for redistribution of crystallinity contribution for PP and PVA in extrudates of blends with glycerol contents of 7.0 (n3) and 10.0 mass % (n4): 1 – the peaks of PP; 2 – the peaks of PVA.

are on the Fig. 2 diffractograms of extrudates for PP/PVA blends with glycerol addition of 7.0, 10.0 and 15.0 mass % showed on.

There are peaks observed in positions of peaks of the initial polymers (Table 2) of the lower intensity, than the same peaks on the additive curve, which shows the partial remaining of crystal structure of PP and PVA in extrudates of the blends with addition of glycerol, and on this confirms on diffractograms of extrudates on the background of the two diffuse maximums, at the angles of 20 and 40 degrees of. There is extrudate containing 7.0 mass % of glycerol has the lowest crystallinity extent amongst the specimens studying therof. This is confirmed with the calculated values for extrudate crystallinity extent of: 22; 30; 30 %, for those containing 7.0; 10.0 and 15.0 mass % of glycerol, accordingly.

In comparison with, there is additive curve shown for PP/PVA blend, calculated on diffraction data of the initial polymers. There is crystallinity extent, for the blend of polymers considered as the additive value, and for the composition given one is 42% of. It should be noted that, when besides the minimal value of crystallinity extent, there is extrudate with glycerol addition of 7.0 mass % has other ratio for the peak intensity of PP and PVA (Fig. 3), in comparison with the extrudates containing of 10.0 and 15.0 mass % of glycerol, just for increase in part of crystal PVA, when relatively to crystal PP *(Fig 3).*

This is showing the fact that, when in crystallinity of the extrudate with glycerol contents of 7.0 mass %, there is contribution of PVA crystallinity prevails, and this explains the absence of thermal effect of crystallization of PP in thermogram of the extrudate given.

Conclusions

There are investigations carried out shows that, when in polypropylene/poly(vinyl alcohol) blends containing glycerol (7.0÷15.0) mass % as a plasticizer, there is phenomenon of specific fiber forming phenomenon is realized clearly in. There is the increase in glycerol concentration, being accompanied with the mean diameter growth of polypropylene microfibers, and the mass film part of. This is explained with fact that, the selective plastification have influence on the rheological properties of one phase, and this causes change in all of the microrheological processes during flow of the blend melt, namely deformation of the polymer drops in phase dispersed, those coalescence into the liquid cylinders, the disintegration of the streams formed, the migration directed and so on.

It has been determined that, when in the extrudates of polypropylene/plasticized poly(vinyl alcohol) blends, there is temperature of PVA crystallization increasing in, which is caused by that in melt associates form for PVA macromolecules with glycerol molecules, that are the homogeneous nuclei of crystallization. When at glycerol content of 7.0 mass %, there is the amorphization of polypropylene taking place, which is caused by its highly dispersed state. When with increasing glycerol concentration up to 15 mass %, there are associates of its molecules forming on, that migrate in the separate phase, and those are the crystallization conditions changing on.

When regarding for the polypropylene/poly(vinyl alcohol) blends studied, there is viscosity of melts decreasing in, which is caused by the plastifier contents growing, and formation of unisotropic structures (microfibers). There are equilibrium values for blend extrudate swelling are lower of, than those analogical ones, and this indicating for the compositions, that the fiber forming is realized in flow of.

There is practical result of investigations in fact of – there is use of water soluble poly(vinyl alcohol) as a matrix polymer giving a possibility to develop the ecologically safe technology for production of polypropylene microfibers, and new materials based on those ones.

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Вплив пластифікатора на процеси структуротворення та кристалізації у сумішах поліпропілен-полівініловий спирт

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Встановлено, що введення (7,0 ÷ 15,0) мас. % гліцерину у суміш поліпропілен/полівініловий спирт (ПП/ПВС) зі співвідношенням компонентів 30/70 мас. % не змінює характеру структуротворення ПП в матриці ПВС: поряд з мікроволокнами, утворюються частинки, плівки та зовнішня оболонка. При цьому зі зростанням концентрації селективного пластифікатора волокнотворення ПП в матриці ПВС погіршується – зростають середній діаметр мікроволокон та масова частка плівок. Особливості структуротворення пов'язані з пластифікувальною дією гліцерину на розплави сумішей та зі зменшенням їх кінетичної стабільності. Методами ДТА та рентгенофазового аналізу виявлено вплив гліцерину на процес кристалізації розплаву. За вмісту пластифікатора 7,0 мас. % температура кристалізації ПВС підвищується, а пік кристалізації ПП відсутній через аморфізацію полімеру. Ступінь кристалічності ПП знижується внаслідок того, що полімер знаходиться у високодисперсному стані.

Ключові слова: поліпропілен, полівініловий спирт, розплави сумішей полімерів, гліцерин, мікроволокна, плавлення, кристалізація.