Oleh Suberlyak[1], Nataliya Baran[1], Adam Gnatowski[2], Tomash Jaruga[2] and Yuriy Melnyk[1]

REGULARITIES OF FILMS FORMING ON THE BASIS OF POLYAMIDE-POLYVINYLPYRROLIDONE MIXTURES

[1]Lviv Polytechnic National University, 12, St. Bandera str., 79013 Lviv, Ukraine; natab@polynet.lviv.ua
[2]Czestochowa University of Technology, 19c Al. Armii Krajowej, 42-200 Czestochowa, Poland

Abstract. Modification of polyamide-6 by polyvinyl-pyrrolidone with molecular mass of 12000±2000 has been carried out using their mixing in formic acid solution followed by solvent evaporation. The possibility of films permolecular structure control, physico-mechnical and thermophysical properties by treatment conditions after their formation has been established.

Keywords: polymer, mixture, modification, film, polyamide, polyvinylpyrrolidone.

1. Introduction

Modern industry often uses polymeric mixtures and not individual polymers themselves which ensure the complex of necessary properties at operation under given conditions. The formation of mixture consisting of two or more polymers is one of the simplest and economically profitable production methods of new materials with specific properties [1].

Polymers of constructive polyamide (PA) mixed with polar amphiphilic polymer which is polyvinyl-pyrrolidone (PVP) are among such mixtures. It was established previously [2] that mentioned polymers are thermodynamically compatible owing to the great difference between their molecular masses and similarity of their structures. The similarity occurs due to the presence of PVP polar carbamate groups and polycaproamide peptide groups participating in the intermolecular interaction that favors PVP dispersion in PA melt at the molecular level.

Polyamides have a complex of valuable properties, namely wettability, chemical stability, elasticity and high mechanical strength due to the presence of polar amide groups in their macromolecules which cause strong intermolecular interactions with the assistance of hydrogen bonds [3-5].

PVP fills a special place among a great number of water-soluble polymers owing to its unique properties – surface activity, high hydrophilic ability, wide range of solubility, definite ability to complexation [6, 7].

Among modification methods of polymeric materials the physical methods are of special interest because they give the possibility to create the materials with specific properties without essential financial expenses. Such modification allows to directly change the individual parameters of existing commercial polymers and to extend the area of their application in such a way [8, 9]. The most perspective way of modification is creation of polymer-polymeric compositions. It allows to impart to the material the properties typical for its components and a series of new ones. New properties are conditioned by the specific structure of the mixture and physico-chemical processes proceeding in it. The other way is modification of various materials of both inorganic and organic nature by high-moleecular compounds owing to their adsorption from the solution. These methods are characterized by the influence of several physical and physico-chemical parameters which are connected, first of all, with the variety of polymers chemical and physical structure, system interfacial characteristics, intermolecular interactions, *etc*. [8]. Taking into account all mentioned above, the theoretical bases of polymeric materials physical modification are urgent problems.

The mixtures of thermoplasts based on PA-6 are obtained using the instruments where mixing takes place under the influence of high share stress, when polymers are in a plastic state. Thus, polyamide and polyvinylpyrrolidone are mixed by means of intensive dispersion in an auger masticator under the conditions of polyamide plastic state [10]. The obtained mixture is characterized by the high strength; its degree of crystallinity is higher than that of pure PA; on DSC curve it has one narrow melting peak with maximum at 494 K.

At the same time it should be noted that penetrating films are mostly formed from polymeric solutions [11]. Therefore, when PA-PVP mixtures are used for the formation of penetrating films, it is necessary to study the formation conditions of films based on the solution of individual polymers and the effect of formed films treatment on their physico-mechanical and thermophysical properties. The results will be useful for the ascertainment of rational conditions for films production and areas of their application.

2. Experimental

Polyamide-6 of "Tarnamid-27" brand (Poland) and polyvinylpyrrolidone with a molecular mass of 12000±2000 (MRTU No.3928-71) were used. The formic acid with water was used as a solvent.

PVP and PA-6 were mixed while preparing pouring solutions. For this purpose the dissolving system was prepared by mixing the formic acid with water. Then PA-6 was dissolved and PVP was added. Polymers were dissolved under intensive stirring at room temperature.

The films were formed from the solution by means of "dry formation" – pouring method followed by the solvent evaporation at 353±2 K.

Different treatment conditions were used: (i) hydrothermal treatment (normalization) in water at 368 K for 30 min; (ii) hydration in distilled water at room temperature for 24 h; (iii) additional vacuum-drying in dry-air thermostat at 358±5 K for 2 h.

Physico-mechanical properties of obtained films at rupture were determined using 050/RT-6010 rupture-test machine with a scale factor of 0.01 kg/mm^2. Films samples were as 95×10 mm rectangles, extension velocity was 25 mm/min [12].

Rupture stress (s_r, MPa) is calculated by the following formula:

$$s_r = F_r/A_0$$

where F_r – tensile stress at the rupture moment, N; A_0 – an initial cross section of the sample, m^2.

Elongation at rupture e_r (%) is calculated by the formula:

$$e_r = \frac{\Delta l_r}{l_0} \cdot 100$$

where Δl_r – the change of sample length at the rupture moment, mm; l_0 – an initial length of the sample, mm.

The differential scanning calorimetry (DSC) was used to determine the melting heat and the crystallization heat, as well as parameters of phase transfer. The experiments were carried out using DSC Z20 PC instrument with software produced by NETZSCH. The heating rate was 10 K/min.

The melting heat (J/kg) is calculated by the formula [13]:

$$\Delta H_m = \frac{\Delta H \cdot m_s \cdot A_i}{m_i \cdot A_s}$$

where A_i, A_s – area of heat effect of relatively investigated sample and standard, J/kg; m_i, m_s – mass of relatively investigated sample and standard, kg; ΔH – melting enthalpy of standard, J/kg.

The degree of crystallinity (%) is calculated by the formula [14]:

$$S_c = \frac{\Delta H_m}{\Delta H_c}$$

where ΔH_m – melting heat (enthalpy) of investigated polymer or mixture, J/kg; ΔH_c – melting heat (enthalpy) of fully crystalline PA-6, J/kg (for PA-6 $\Delta H_c = 188$ J/kg) [15].

3. Results and Discussion

For investigations we used films of the following composition (mas %): PA-6–PVP:HCOOH:H$_2$O = 7.2:78:14.8; PA-6:PVP = 98:2. The initial concentration of [HCOOH] was 84 mas %.

We studied the effect of films treatment on their permolecular structure which was characterized by DSC method. For PA-6–PVP mixtures we determined the degree of crystallinity, temperature intervals and heat of phase transfer. The obtained results are represented in Table 1 and Fig. 1.

Fig. 1 represents the experimental results as DSC curves and indicates the dependence of heat absorbed by polymer upon the temperature. The area of DSC thermograms is proportional to the change of heat effect.

Table 1

Operational properties

No.	Melting heat, J/g	Maximum melting temperature (T_m), K	T_m interval, K/ΔT, K	Degree of crystallinity, %
1	57.6	494	490–496 / 6	60
2	5.5	484	480–489 / 9	5.8
	3.3	493	491–497 / 6	3.5
3	56.8	489	483–495 / 13	59.1

Films: 1 – untreated; 2 – hydrothermotreated at 368 K; 3 – hydrated at room temperature for 24 h; before the experiments the films were dried under vacuum at 328±5 K.
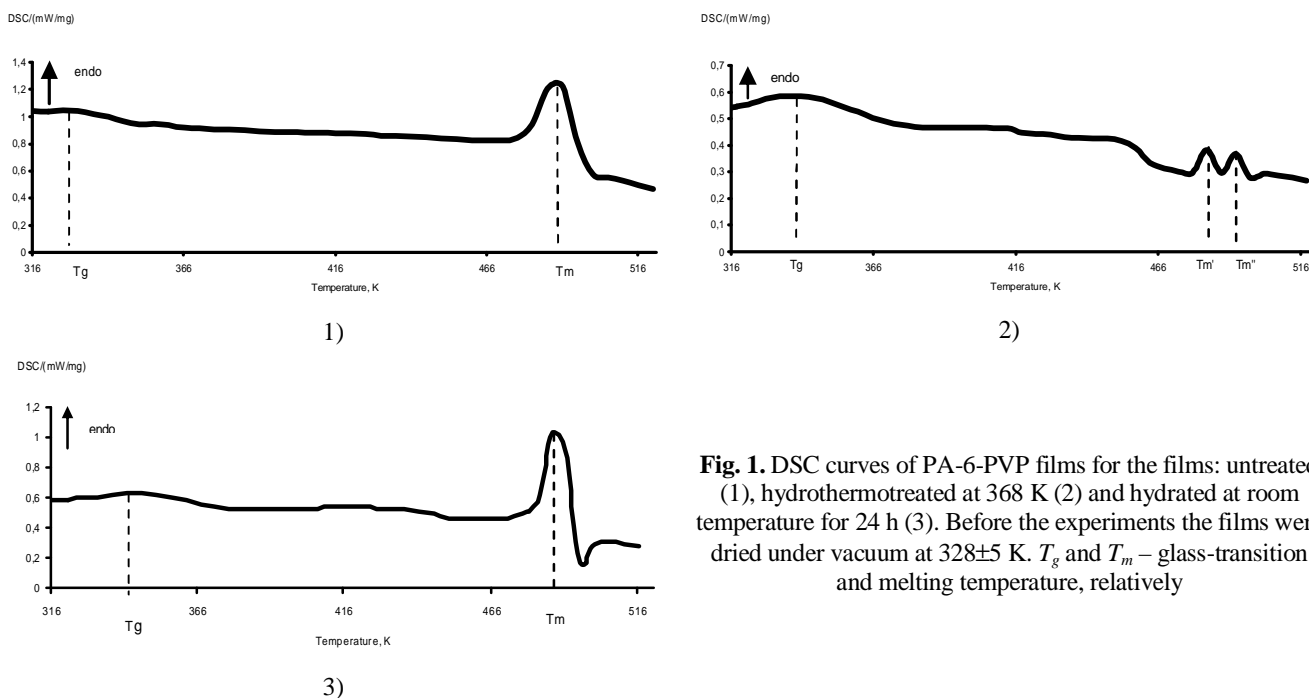
1)

2)

3)

Fig. 1. DSC curves of PA-6-PVP films for the films: untreated (1), hydrothermotreated at 368 K (2) and hydrated at room temperature for 24 h (3). Before the experiments the films were dried under vacuum at 328±5 K. T_g and T_m – glass-transition and melting temperature, relatively

In the range of low temperatures (till 373 K) the endoeffect of β-transfer is observed typical for the beginning of macromolecules segmented movement. These effects are clearer for hydrothermotreated samples. During hydrothermal treatment the free PVP is washed out and thus increases the free volume followed by the increase of segmental mobility.

The method of films' treatment after their formation essentially affects the crystallinity heat, the melting heat and temperature intervals of phase transfer. Thus, the maximum temperature of the melting peak for the films after formation by means of pouring with the following evaporation is 494 K, for the films hydrated after formation – 489 K, and for hydrothermotreated films the doublet melting peak is typical – at 484 and 493 K. The temperature interval (ΔT) considerably depends upon the treatment conditions as well. The widest ΔT is typical for previously hydrated and dried films, and the narrowest – for untreated films (Table 1).

The degree of crystallinity of untreated (1) and hydrated (3) films are higher in 6.5 times than that of hydrothermotreated (2) films. Such a change may be the consequence of the change of segmental mobility of PA-6 macromolecules due to the increase of free volume while washing out the non-bounded PVP. This phenomenon is favorable for destruction of crystallites formed at the beginning.

The experimental results show that the melting heat, maximum temperature of the melting process and total degree of crystallinity are higher for untreated and hydrated films. Obviously, the PVP introduction into PA-6 increases freedom of chain rotation and thus increases the entropy of crystalline state. The presence of PVP macromolecules, a great amount of which is in the dispersed phase and interfacial layers, also affects this factor. PVP macromolecules "crush" the colloidal system with the increase of free volume and favor the increase of freedom of chain rotation, that in its turn, create the greater probability of macromolecules hexagonal packing [16].

Moreover, the increase of the degree of crystallinity of polyamides modified by polyvinylpyrrolidone may be explained by additional heterogeneous crystallization of PA over nuclei which are PVP macromolecules [17].

In a case of hydrothermotreated films (Fig.1, curve 2) endotherms at DSC curves are in the form of doublet melting peaks. It is explained by the fact that the crystalline structure of two types is formed at normalization. PA-PVP is formed as a result of heterogeneous crystallization of PA which is physically bounded with PVP as a heterogeneous nucleus with $T_m = 484$ K; and homogeneous crystalline phase is formed based on PA-6 with $T_m = 493$ K.

Obviously, films hydration with the following drying slightly affects the permolecular structure of the mixture (melting peak is identical with the peak of untreated film) because in such a case a little amount of PVP is washed out from the volume.

The most important mechanical characteristics of polymeric films are their strength and elongation at rupture which determine the operational conditions.

It is expected that the method and conditions of treatment (based on structural analysis) affect the films mechanical properties at extension (Table 2). We found

the rupture stress of untreated films is to be higher than that of the films after hydration. However, elongation at rupture of untreated films is less compared with that of hydrated films. The decrease of strength and the increase of elongation of hydrated films are caused by redistribution of intermolecular interactions and the volume increase of transfer areas. Theses facts favor the change of physical network density in the polymeric mixture.

Table 2

Physico-mechanical properties of the films

No.	Rupture stress, MPa	Elongation at rupture, %
1	39 / 57*	6 /172*
2	28	7
3	22	20

Films: see Table 1. Before the experiments the films 1 and 2 were dried under vacuum at 328±5 K.* – sample was washed out from the mixture obtained at mixing PA in a plastic state [9]

At the hydrothermal treatment of the films at 368 K we also observed the decrease of strength and the increase of deformation (Table 2, No. 1, 2). It is a result of heterogeneous crystalline phase destruction at PVP washing out. Moreover, the relaxation of internal stresses, ordering or recrystallization of polymer and other phenomena connected with the morphology take place during the normalization process. Contraction [3] also belongs to the mentioned phenomena and occurs due to the increase of free volume as a result of PVP washing out.

The decrease of strength and the increase of elongation at rupture of treated films are the results of free volume formation and disorder of permolecular structure. This fact confirms the above-mentioned assumption about the influence of free volume change on the degree of the mixture crystallinity.

The carried out investigations show that at mixing PVP and PA-6 the physical interaction takes place between PA-6 and PVP macromolecules. It affects the permolecular structure of the final polymeric mixture. Equitype change of maximum stress and elongation at rupture after treatment probably is a reason of structure morphology developing in the decrease of γ-phase and appearance of fine α-phase in a polyamide matrix [18]. Although the formation of space network which is not crystallized is not excluded during chemical interaction of PA and PVP at high temperatures.

4. Conclusions

Thus, the experiments established the possibility of formation of modified polyamide films from formic acid solutions of PA-6–PVP mixtures. The efficiency of modification, as well as the possibility of controlled regulation of permolecular structure, physico-mechanical and thermophysical properties of the films depending on the treatment conditions were confirmed.

The modification of polyamides by polyvinyl-pyrrolidone affects the redistribution of intermolecular bonds in the polymeric matrix leading to the change of the structure and character of macromolecule segments packing, characteristics of phase transfer and the increase of the crystallinity degree.

References

[1] Paul D. and Newmen S. (Eds.) Polymernye Smesi. Mir, Moskwa 1981.
[2] Suberlak O., Lewicki W., Tarnawski A. *et al.*: Materialy Polimerowe i ich Przetworstwo, Czestochowa 2004.
[3] Bryk M.: Encyclopediya Membran. Kyivo-Mogylyanska Acad., Kyiv 2005.
[4] Kohan M.: Nylon Plastics. Hanser Publishers, Munich 1995.
[5] Pall D.: Pat. USA 4033881, KMP B01D 39/18. Publ. Jul. 05, 1977.
[6] Valuev L., Vakula L. and Plate N.: Vysokomol. Soed. A, 1984, **26**, 1700.
[7] Sidelkovskaya F.: Khimiya N-Vinylpyrrolidona i ego Polymerov. Nauka, Moskwa 1970.
[8] Gul V. and Kuleznev V.: Structura i Mechanicheskie Svoistva Polymerov. Vyshaya schola, Moskwa 1972.
[9] Levytskyy V., Khromyak U. and Suberlyak O.: Chem. & Chem. Techn., 2010, **4**, 217.
[10] Gnatowski A., Suberlak O. and Postawa P.: J. Achiev. in Mater. & Manufact. Eng., 2006, **18**, 91.
[11] Suberlyak O., Mel'nik Yu. and Baran N.: Rus. Zh. Prikl. Khimii, 2009, **82**, 1898.
[12] GOST 14236-81. Plenki polymernye. Metod ispytaniya na rastyagenie. Izd-vo standartov. Moskwa 1981.
[13] Kong Y. and Hay J.: Polymer, 2002, **43**, 3873.
[14] Chcinski-Arnault L., Gaudefroy V., Gacougnolle J. and Riviere A.: Macromol. Sci. B, 2002, **B41**, 777.
[15] Bershtein V. and Egorov V.: Differentcialnaya Scaniruushaya Calorimetriya v Physicokhimii Polymerov. Khimiya, Leningrad 1990.
[16] Lipatov Yu.: Phyzicheskaya Khimiya Napolnennykh Polymerov. Khimiya, Moskwa 1977.
[17] Sikorski P., Jones N., Atkins E. and Hill M.: 38th Macromol. IUPAC Symp., Warsaw 2000, **3**, 999.
[18] Huvink R. and Stavermann A.: Khimiya i Technologiya Polymerov. V.1. Khimiya, Moskwa 1965.

ЗАКОНОМІРНОСТІ ОДЕРЖАННЯ ПЛІВКОВИХ МАТЕРІАЛІВ НА ОСНОВІ СУМІШЕЙ ПОЛІАМІДУ З ПОЛІВІНІЛПІРОЛІДОНОМ

Анотація. *У роботі проведено модифікацію поліаміду-6 полівінілпіролідоном із молекулярною масою 12000±2000 методом змішування їх у мурашинокислому розчині з наступним упарюванням розчинника. Встановлена можливість регулювання надмолекулярної структури, фізико-механічних і теплофізичних властивостей плівок від умов їх обробки після формування.*

Ключові слова: *полімери, суміші, модифікація, плівки, поліамід, полівінілпіролідон.*