

Functional materials based on PA6/PVP blends

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Materials

ABSTRACT

Purpose: The results of investigations of properties of PA6 mixed in state the viscoelasticity from polymer about ability of creating of physical bonds was introduced. The polyvinylpyrrolidone about small molecular weight in this aim was applied ($10 \pm 2,5$ thousand).

Design/methodology/approach: Within the work some results of chosen properties of PA with different percentage composition with the addition of polyvinylpyrrolidone (PVP) have been presented. In chance of mixing PA6 with PVP forms solution PVP in PA6, to which proper are large intermolecular influence, in this case hydrogen bond.

Findings: The functionalactive material was prepared about sharp tuning sorption ability across physical modification polycapamide mixed from bipolar polyvinylpyrrolidone in batch – free state, which be characterizes high ability complex. The properties of the polymer blends depend significantly on the type of the components. That kind of influence manifests especially in the change of the physical properties.

Research limitations/implications: The basis condition for reaching the homogeneity, specific structure and the properties of a polymer material is its mutual miscibility of the polymers. Additional agents that make mixing easier are usually applied; they have reactive effect which results in a chemical modification of output polymer along with the change in its chemical structure and the structure of macrochains. In order to achieve this, the polyvinylpyrrolidone has been used.

Practical implications: It is possible to foresee, that under the influences large tangent stresses and intermolecular interaction colloidal solution PVP in PA forms about sure homogeneity, after cooling which does not the inversion of winding phases. Large intermolecular influence among PVP and PA6 are unquestionable with regard on their chemical building. The probability of influence of intermolecular influences with this reason results, the leaders to creation of new centres of crystallization near cooling the polymer material.

Originality/value: Received however results show thereon that PA with PVP additions create more stable material. Homogeneous material was got about raised elasticity and mechanical durability with perspective of use in textile industry.

Keywords: Engineering polymers; Blends; Polyamide; Polyvinylpyrrolidone

1. Introduction

To obtain polymer plastic with defined properties, polymer mixtures on basis of both polymer with heterotypic and homotypic structure are manufactured, also polymer plastics

waste. The basis to obtain homogeneity as well as defined structure and properties of prepared polymer plastic is mutual miscibility of polymers. Usually additional components are applied to simplify mixing of polymers; they usually work reactively, and, in consequence, chemical modification of the input polymer happens, along with chemical structure change and change in the macrochain structure [1-9].

In the work some investigation results have been presented for PA6 (Tarnamid 27) which is miscible in viscoelastic state with polymer with ability to create physical bounds with substances of inorganic as well as organic origins, also with output polymer. For this purpose, polyvinylpyrrolidone (PVP) has been used, with low molecular weight ($10 \pm 2,5$ thousand). PVP is characterized by high complex-creating ability which, in consequence, has been the reason for its large application for medicine as highly-sorptive component and for textile industry for stabilizing of colouring agents.

2. PA6 modification method

Some mixtures with different concentration of PVP, 1%, 2%, 5%, 10% of weight have been prepared. Mixing has been done with worm injection moulding machine of KM 65 - 160 C1 type with computer control with defined parameters of: temperature – 23 °C, worm rotational speed – 210 rpm, L/D-27, mixing time 90 s.

To grind mixture mass obtained during the process of mixing, UR 160/1A/10 mill has been used.

Out of this mixture, samples for investigation of “dumbbell” type with standard dimensions have been prepared by means of injection method. Injection parameters have been as follows: nozzle temperature – 230 °C; worm area I temperature – 190 °C; worm area II temperature – 210 °C; worm area III temperature – 230-245 °C, mould temperature 40 °C, injection pressure - 60 MPa, clamping time – 5 s, cooling time - 30 s

Following investigation have been conducted:

- properties investigations for obtained mixtures with DSC method,
- strength properties during tension investigations,
- mechanical properties investigations by means of DMTA method,
- softening point investigations by means of Vicat's method,
- water absorbing power test.

Axial tension test has been conducted with the INSTRON tensile machine with tension speed of 90mm/min. Softening point by Vicat's method was determined using testing machine type HAAKE N8. The investigation of DSC method and DMTA method using testing machine type Netzsch was executed.

3. PA6 modification method

It has been proved that mixing, in a plastic state, PA6 with PVP causes creating of hydrogen bonds.. It is possible to foresee,

that under the influence of large mechanical loss angle tangent and intermolecular interaction of colloidal solution of PVP with PA some homogeneity is formed. It is probable that due to intermolecular interactions new crystallization centres appear during cooling of polymer material. Due to intermolecular influences and polarity as well as hydrogen bonds between PA6 and PVP better miscibility of polyamide with water-repellent, non-polar polypropylene. Results of the investigations for DSC method have been presented in table 1 whereas usable properties are represented by table 2.

Table 1.
Technological properties

Composition of sample	Heat of fusion, J/g	Melting point max., °C	Temperature of crystallinity, °C
PA	51,16	223,4	176
PA 98% / PVP 2%	54	226,2	195
PA 90% / PVP 10%	58	224	197

Under the condition of dynamic load one can notice mechanical hysteresis for polymers, which depends on mechanical work loss for one deformation cycle. This loss appear in amorphous phase and depend on molecules movement energy within the substance volume, therefore they are perceivably changing with temperature change.

Maximal loss for polymer material occur for the range of temperature where equality of relaxation time and external load velocity appear – this is the condition which is defined as: $\tau\omega=1$ and it could be attained for vitrification temperature (T_g) [10-15].

Dynamic properties dependence on temperature of polymers in amorphous state is influenced by molecular mass, polarity of polymer, cross-linking degree and crystallinity degree. It is known [5, 6] that along with the increase of amorphous phase, mechanical loss angle tangent increases. Polarity of the polymer decides on intermolecular interactions or on fluctuation net density with increase of which mechanical losses (E'' i $\text{tg}\delta$) increase. Maximal changes for polymers with strong

Table 2.
Usable properties

Composition of sample	Young's modulus, MPa	Hardness, MPa	Yield point, MPa	Elongation at break, %	Softening point by Vicat's method, °C
PA	2983	44,24	54,85	26	167
PA 98% / PVP 2%	2961	43,5	57	172,57	166
PA 90% / PVP 10%	2770	38,2	54,7	127,69	156

intermolecular interactions are seen within the temperature of vitrification. This dependence is inconsistent with dependence of mechanical losses on chemical cross-linking degree, which causes $\text{tg}\delta$ and loss module (E'') decrease due to the reduction of mobility of structural segments.

In this work results of investigations on mixture prepared out of two polymers with strong polarity (PA and PVP) have been presented. Because of this fact in mixtures based on these polymers strong intermolecular interactions appear. These interactions appear in viscoelastic state, which results in decreased value of mass factor of PA/PVP mixtures flow as compared to input polyamid (Fig. 1). The results prove strong influence of PVP on mixture with PA viscosity, even when its concentration is low as compared to mould polymer concentration (2% of mass).

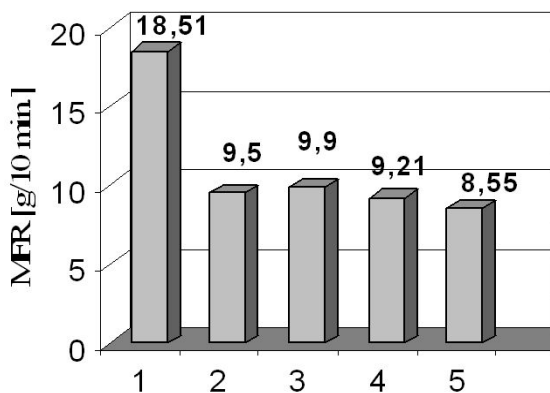


Fig. 1. MFR of polyamid and mixtures of PA with PVP: 1 – PA6, 2 – PA 98%/PVP 2% (dried together), 3 – PA 98%/PVP 2% (dried separately), 4 – PA 90%/PVP 10% (dried together), 5 – PA 90%/PVP 10% (dried separately)

At the same time, increase of mechanical loss angle tangent along with increase of PVP in the mixture (Fig 2) and α temperature change - toward increased values - could be seen. Vitrification temperature of mixture with concentration PVP of 10% increases by 10 °C as compared to PA6. It proves increase in quantity of intermolecular physical bonds in mixture with higher PVP concentration. Due to gelycoidal conformation of macromolecule PVP with pyrrolidone rings outside, hydrogen bonds with macromolecules of PA could be easily created. As a result of this, conservative modulus (E'') of mixtures and PA are little diversified (Fig. 2). Increase of mechanical losses is the factor which causes increase of polymer impact strength [7], which is a desirable effect for crystalline polymers such as PA.

Radical changes of dynamic properties happen when they are saturated with water (Fig. 3). Samples were kept in water for 24 hours.

For positive temperature water acts as plasticizer. For mixtures saturated with water $\text{tg}\delta$ decreases and extends, and, simultaneously, vitrification temperature decreases and conservative modulus increases noticeably.

There second reflex appears for mechanical loss curve with maximal value at the temperature of 3-10°C. This reflex is probably due to activity of solvated with water macromolecules of PVP which freeze at negative temperatures, which results in

increased, as compared to the mixture without saturation with water, value of conservative modulus E' .

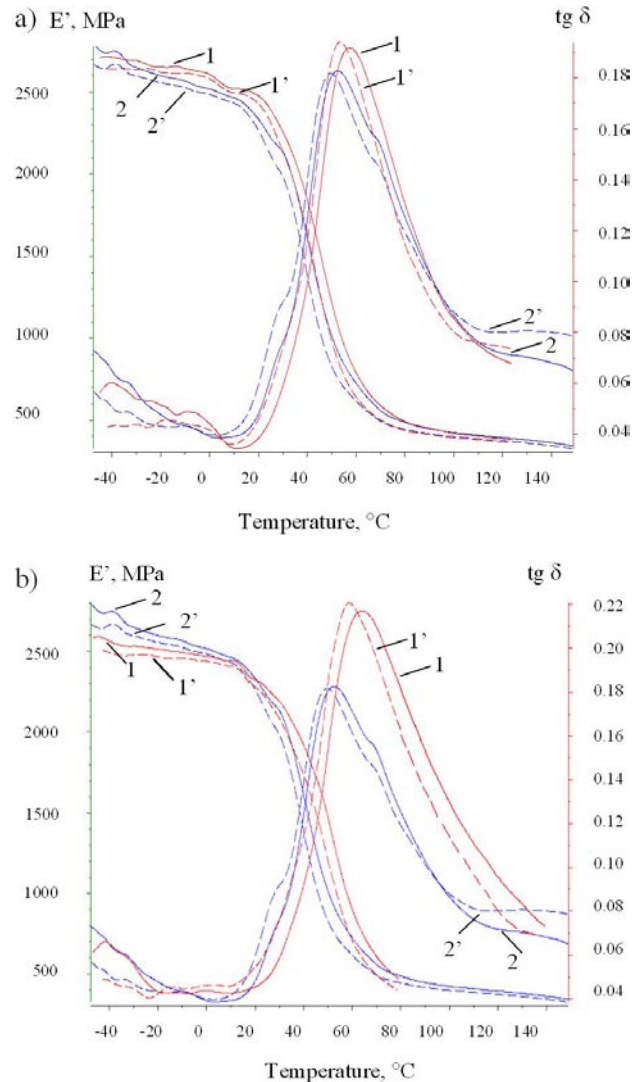


Fig. 2. Conservative modulus E' and $\text{tg}\delta$ curves of dependencies on temperature: a) 1, 1' - mixture of PVP 2%/PA98%, 2, 2' - PA, b) 1, 1' - PVP 10%/PA 90%, 2, 2' - PA; dashed lines - with frequency of 1 Hz, continuous lines - 10 Hz

4. Conclusions

Conducted investigations have proved opportunity of physical modification of PA6 during mixing, in viscoelastic state, with polyvinylpyrrolidone with low molecular weight ($10 \pm 2,5$ thousand). During process of mixing, mixture with visible homogeneity is obtained (due to strong intermolecular interactions) which is characterised by satisfactory mechanical properties which insignificantly differ from PA6 properties, but which shows higher deformability and sorptive power.

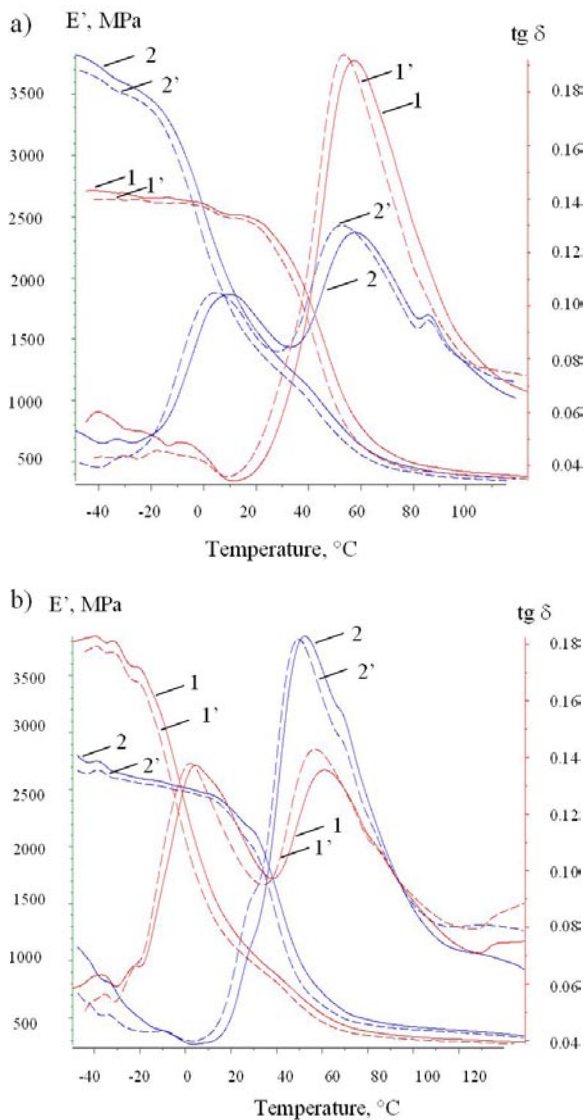


Fig. 3. Conservative modulus E' and $\text{tg } \delta$ curves of dependencies on temperature: a) 1, 1' – mixture of PVP 2%/PA98%, 2, 2' – mixture of PVP 2%/PA98% saturated with water, b) 1, 1' – PVP 10%/PA 90%, 2, 2' – PVP 10%/PA 90% saturated with water; dashed lines – with frequency of 1 Hz, continuous – 10 Hz

References

[1] S.C. Manning, R.B. Moore: Reactive compatibilization of polypropylene and polyamide-6,6 with carboxylated and

maleated polypropylene, *Polymer Engineering and Science* Vol. 39, No 10, 1921 ÷ 1926, 1999.

- [2] J. Campoy, J. M. Arribas, U.M. Zaporta: Crystallization kinetics of polypropylene-polyamide compatibilized blends, *Eur. Polym. J.*, Vol. 31, No 5, 475 ÷ 480, 1995.
- [3] J. Koszkul: Polymeric materials, Publication of Technical University of Czestochowa (in Polish).
- [4] B. Ohlsson, H. Hassander, B. Törnell: Effect of the mixing procedure on the morphology and properties of compatibilized polypropylene/polyamide blends, *Polymer Engineering and Science*, Vol. 39, No 20, 4715 ÷ 4721, 1998.
- [5] K. Cho, B. H. Lee, K. M. Hawang, H. Lee, S. Choe: Rheological and Mechanical properties in polyethylene blends. *Polymer Engineering and Science*, Vol. 38, No. 12, str. 1969 – 1975, 1998
- [6] C. Koning, M. V. Duin, Ch. Paagnoulle, R. Jerome: Strategies for compatibilization of polymer blends. *Prog. Polym. Sci.*, Vol. 23, str. 707 – 757, 1998
- [7] B. Jurkowska, B. Jurkowski, Preparation of polymeric compositions, WNT, Warsaw, 1995 (in Polish).
- [8] Y.X. Pang, D.M. Jia, H.J. Hu, D.J. Hourston, M. Song: Effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene/ poly (ethylene terephthalate) blends. *Polymer*, Vol. 41, No. 1, str. 357 – 365, 2000.
- [9] M.F. Champagne, M.A. Huneault, C. Roux, W. Peyrel: Reactive compatibilization of polypropylene/ polyethylene terephthalate blends. *Polymer Engineering and Science.*, Vol. 39, No. 6, str. 976 – 984, 1999.
- [10] C.R. Chiang, F.C. Chang: Polymer blends of polyamide-6 (PA6) and poly(phenylene oxide) (PPO) compatibilized by styrene-maleic anhydride (SMA) copolymer. *Polymer* 1997, Vol. 38, No. 19, str. 4807 – 4817.
- [11] N. Dharmarajan, S. Datta, G. Ver Strate, L. Ban: Compatibilized polymer blends of isotactic polypropylene and styrene-maleic anhydride copolymer. *Polymer*, Vol. 36, No. 20, str. 3849 – 3861, 1995.
- [12] A. Ibrahim, M. Dahlan: Thermoplastic natural rubber blends. *Prog. Polymer Sci.*, Vol. 23, str. 665 – 706, 1998.
- [13] I. Kelnar, M. Stephan, L. Jakisch, I. Fortelny: Influence of the additive type and modification on the properties of blends of polyamide-6 with poly(styrene-co-maleic anhydride). *Polymer Engineering and Science*, Vol. 39, No. 6, str. 985 – 995, 1999.
- [14] G. Spadaro, D. Acierno, C. Dispenza, A. Valenza: Thermal analysis of blends made with polyamide 6 and γ -irradiated polyethylenes. *Thermochimica Acta* No. 269/270, str. 261 – 272, 1995.
- [15] J.T. Yeh, Ch.F. Jyan, S.S. Yang, S. Chou: Influence of compatibilization and viscosity ratio on the barrier and impact properties of blends of a modified polyamide-6 and polyethylene. *Polymer Engineering and Science*, Vol. 39, No. 10, str. 1952 – 1961, 1999