Viscosity, sorption of water and biodegradation of starch/copolyamide blends

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SUMMARY: Compatibility of the components, shear viscosity, sorption properties in liquid and vapor water were determined for the mixture of ternary copolyamides (types 6/66/610 and 6/12/66) and amilose starch. This system was shown to be suitable for creation of biodegradable materials.

Introduction

In recent years an ever increasing interest has been attached to development and production of new materials based on natural polymers and starch. Properties of starch can be improved by blending with synthetic polymers. New materials having good properties can be created on the basis of these blends. Out of 550000 metric tons of polyamides used yearly in Western Europe, 12% is used as functional packaging of foodstuffs [1)]. Similar to other films and plastics, these materials serve for a short time and then are discarded to form municipal waste products. In view of this problem blends of copolyamides with starch are perspective for production of short-lived wares as they contain neither harmful halogens nor toxic heavy metals or toxic organic compounds. Therefore it is necessary to create polyamides/starch blends having a complex of properties providing for their processing and utilization. The environment does not suffer if such polymer wastes are dumped in landfill. This paper is concerned with some structural, rheological and sorption properties of copolyamides (CPA)/starch blends.

Experimental

Polymer blends were prepared from amilose starch (intrinsic viscosity in water being 0.023 m^3/kg) and commercial ternary copolyamides 6/66/610 (I) and 6/12/66 (II). Copolyamides were synthesized from the mixtures of the monomers: ε-caprolactam and hexamethylendiamine salts of adipic and sebacic acid (I) or ε-caprolactam, ω-dodecalactam and hexamethylendiamine salt of adipic acid (II), where the mass proportion of the monomer

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components was 45/10/45 and 40/35/25 respectively. According to the X-ray diffraction examination, CPA I and II had a partially crystalline structure. The blends were press-molded from carefully mixed powders of the copolyamide and starch at the temperature of 175-180 °C and the pressure of 0,5 MPa. The starch concentration of the mixture with CPA I and II was 0-30 mass %. Shear viscosity of the blends was measured using an MV-2 capillary viscometer (with the radius/length ratio of the capillary equal to 1:60) at the temperature of 180 °C and the shear stress of 10^2-10^4 Pa. Dielectric parameters of the blends were determined on the Shering bridge type TR-9701 at the fixed frequency of 7 kHz. Thin films (50 mkm) of the CPA / starch blends were carefully dried in vacuum and then sorption of water vapor was examined on the Mc Bean spring balance at the temperature of 25 °C in an evacuated glass chamber. The amount of water absorbed by the films was determined upon achievement of the equilibrium, for which purpose elongation of the spring was measured using a cathetometer. Diffusion of liquid water in the polymer films and biodegradation of these blends were examined at 30 °C. Biotic degradation of the polymer blends due to microorganisms of the soil were examined in an aerobic condition. Pieces of the starch / copolyamide films were stopped up in the glass bottles with a soil – water suspension. Twenty bottles with probes of the polymer films were used for each composition of the starch blends. The respiration static test was used 2) and mass of the carbon dioxide that was produced by microorganisms from the blend / soil / water environment was determined by the chromatographic analysis.

Results and Discussion

Blends of polyamides with other polymers often represent one-phase systems if the second component is polar and hydrophilic 1). In CPA/starch systems, two components are polar and have affinity for water. One may think that both components are compatible when the content of starch is small. Indeed, the iodine test of all the investigated blends for the free starch phase was negative. Using the dielectric method, it was shown that in the region of the molecular mobility typical of the polyamide chain 3) the maximum of the dielectric loss slightly shifted towards lower temperatures with increasing starch concentration. This result for system CPA II/ starch is exemplified in (Fig. 1).

This is an evidence that the blend components are partially compatible and the weak plasticizing effect is due to partial breaking of the intermolecular H-bonds of the polyamides by the starch component in the amorphous part of the polyamide structure. Analogous data were obtained for the other system studied. There is nothing extraordinary in this result: It is well known that some polyamides can interact with substances containing OH-groups and therefore they are soluble in o-cresol, water/alcohol mixtures and some organic acids.

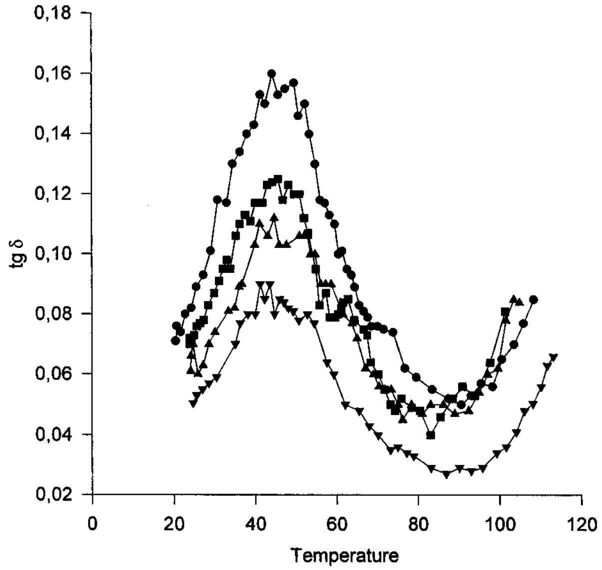

Fig.1: Dielectric loss as a function of temperature in the CPA II/starch system at7 kHz.

Starch concentration: ● = 0, ■ =10, ▲ =20, ▼ =30 mass %.

Rheological curves of the polymer blends were typical of the effective non-Newtonian viscosity of polymer melts [4]. The value of the shear viscosity was found to increase with the starch concentration of the blends. These results are shown in (Fig. 2). Viscosity of the CPA II /starch blend was higher than that of the system I. It is possibly caused by the different of the number of intermolecular H-bond contacts [5] in fragments of the polyamide chains in the mixture with amilose starch.

(Fig. 3) illustrates sorption isotherms of the water vapor absorption by the polymer blends. These curves are similar to the isotherms of polyamides obtained by the authors [5,6]. When $p/p_S \rightarrow 1$, the amount of absorbed water was finite and corresponded to the terminal equilibrium swelling of the samples in water. When the starch concentration was increased, water sorption of all the blends was enhanced.

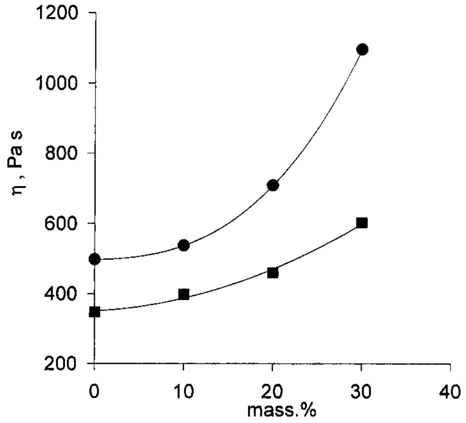

Fig.2 :Concentration dependence of the effective viscosity in CPAI/starch (■) and CPAII/ starch (●) systems. Starch content in the blends is mass.%. Shear rate =2,5 s^{-1}

Similar results were obtained in experiments on swelling of these blends in liquid water. All kinetic curves of this absorption process were typical Fick's curves and therefore we used the equation

$$D = \frac{\pi l^2}{16} \frac{\partial(M_t / M_\infty)}{\partial(t^{1/2})},$$

(where l is the film thickness; t is the swelling time; M_t and M_∞ denote the mass of water absorbed during the time t and after an infinite time respectively) for calculation of the water diffusion coefficient.

(Fig. 4) presents the concentration dependence of the water diffusion coefficient, which is larger in the system I. This is probably due to the fact that the mass ratio of polar (CONH) and aliphatic (CH_2) groups in the polymer chain $^{5)}$ is higher in CPA I than in CPA II, therefore affinity of CPA I to polar molecules of water is larger. The comparison of the data of (Fig.3) and (Fig. 4) shows that sorption of water in the vapor and liquid phase increased with growing concentration of starch in these systems.

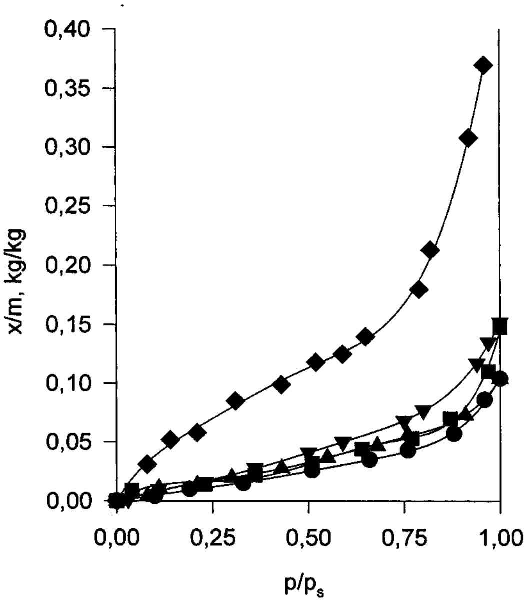

Fig.3: Sorption isotherm of the water vapor in CPA II/starch system. T=25 °C. Starch concentration ● = 0 , ▲ =10, ■ =20, ▼ =30, ◆=100 mass %. x- mass of sorpted water, m - mass of the polymer film.

Systematical determination of the amount of carbon dioxide (CO_2) respired over a long period of time by the soil microorganisms in a soil–water suspension in the presence of the starch-copolyamides films was used to estimate the biodegradability of these materials [2)]. Kinetic curves of the starch-copolyamides biodegradation were examined in the initial stage of this process. The results of such experiments are presented for one of the systems in (Fig. 5). The number of the CO_2 moles are referred to the unit of the initial mass of the polymer film. It is clearly seen the amount of the carbon dioxide respired by microorganisms of the soil in the presence of the starch / copolyamide blends is enhanced with increasing starch content. Analogous data were observed for the second system starch / copolyamide I.

Starch in the polymer blends facilitates biodegradation.

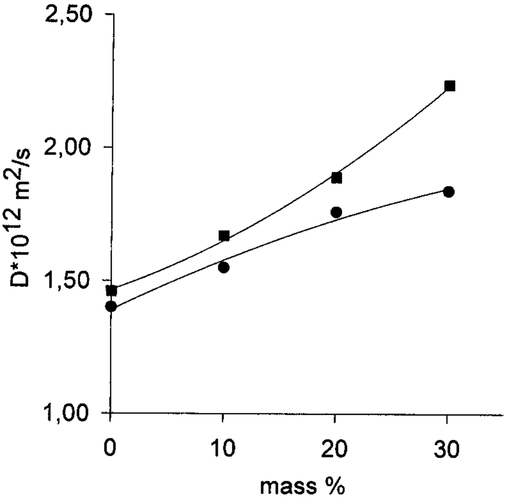

Fig.4 : Concentration dependence of the diffusion coefficient in the CPA I/starch (■) and CPA II/starch (●) systems. T=30 ^{0} C. Starch content in the blend is mass%.

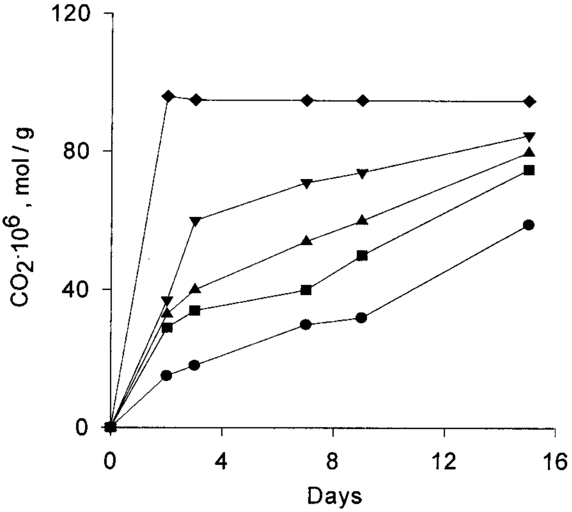

Fig.5: Kinetic curves of biodegradation of the CPAII/starch system in a water-soil suspension.

Starch concentration: ● = 0 , ■ =10 , ▲=20 ,▼ =30 , ● =100 mass %.

Conclusion

Presented data show that blends of ternary copolyamides and 0-30 mass % starch are partially compatible, may be easily adapted to processing and biodegradation under the attack of soil microorganisms in the presence of water. It is possible to create these materials for ecological safe packaging and other wares.

References

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