ABSTRACT OF DOCTORAL THESIS

„Reactive blending of natural and synthetic degradable polymers”

Author: mgr inż. Elżbieta Getner

Supervisor: prof. dr hab. inż. Ryszard Steller

Investigation results on (reactive) blending of selected natural polymers with biodegradable aliphatic polyesters are presented. The objective of this studies was to evaluate the influence of some elements characterizing the chemical and physical structure of polymers, addition of various modifiers and processing conditions on the ultimate structure and properties of blends with natural polymer as the dominating constituent.

Five series of blends as combinations of three aliphatic polyesters, i.e. polycaprolactone (PCL), polylactide (PLA) and polyhydroxybutyrate (PHB) with two natural polymer – potato starch and wheat gluten, were prepared. The content of the natural polymer in each system varied between 50 and 70 wt%. In order to reduce transition temperatures and to improve processability of brittle PHB its plasticization was carried out. The following plasticizers were used: 10 wt% of tributyrin (in starch based systems), 25 wt% or 30 wt% of poly(ethylene glycol) and 5 wt% of tributyrin (in wheat gluten based systems). The natural polymers were also plasticized. Gluten plasticization was carried out by means of glycerol in amount of 20 wt% or lactic acid in amount of 25, 30 or 35 wt%. Starch was plasticized with glycerol in amount of 20 or 25 wt%. In order to improve compatibility between polyesters and natural polymers, small addition (as a rule 1 wt%) of reactive coupling agents in form of dicarboxylic acids (oxalic or succinic) was applied.

Blends were prepared using a laboratory two-roll-mill and the blending conditions (time and temperature) for each series were chosen to obtain the best homogeneity taking into account the thermal sensitivity of components. Test specimens were formed by compression molding. From PHB-starch and PHB-gluten blends only the compositions with the component ratio of 50/50 were made due to the difficulties connected with the preparation of samples.

All systems were characterized by mechanical, MFR and Vicat temperature measurements. The susceptibility to biodegradation and water action was also studied. For blends with components ratio of 50/50 the structural, rheological and thermal studies (DSC, DMTA, SEM, rotational rheometry, thermogravimetry) have been additionally performed.

The results show that milling is very effective homogenization method of biodegradable polymer blends, although its application for this aim was not described in the literature. The obtained results indicated also that natural polymers after plasticization can exhibit good miscibility mainly with the polyesters amorphous phase. The plasticizing-compatibilizing effect of glycerol in systems with starch is connected with the starch anti-plasticization phenomenon, disappearing at the glycerol content higher than 20 wt%. The enhancement of proadhesive and compatibilizing action of glycerol provides a small addition of oxalic acid, that is probably a consequence of chemical binding of blend components. It has been shown that for gluten systems lactic acid is much more effective compatibilizer in comparison to glycerol. Its use leads to the creation of continuous physical protein network accompanied by the phase inversion. Moreover, the results indicate that the better compatibility of gluten systems was favored by an appropriate polyester plasticization.

Blending of polyesters with natural polymers contributes to substantial changes of mechanical and rheological behavior. In principle, this is connected with the decrease in tensile and impact strengths and deformability and optional stiffness increase. Processability and rheological properties of systems alter depending on the type of polyester and the presence of additives, as well as on the temperature and time of the thermal treatment of blends. The blending of polyesters with starch and gluten affects also the change of thermal resistance, susceptibility to biodegradation and water absorption of blends. The studies validate one of the basic claims of this paper that the presence of natural polymer affect the improvement of polyesters biodegradability, among others, due to the increased water absorption capacity.

The evidence of a better compatibility of blends are, for instance, characteristic changes on tensile curves observed for example in blends with gluten. In these blends the low stiffness range resulting probably from the entropy elasticity of the systems but restricted to small deformations appears. Compatibility of blends is also determined by changes of physical and chemical structure. A significant changes of physical structure (and indirectly the chemical one, especially in systems with dioic acids) were observed in SEM micrographs (size reduction or disappearance of natural polymer granules, blur or disappearance of phase boundaries), thermo-mechanical tests (storage modulus maximum and changes of glass transition temperature) and calorimetric measurements (changes of crystallinity and melting point). Moreover, the chemical structure changes are also indicated by secondary changes in FTIR spectra, signaling the probability of esterification or transesterification reactions between blend components.