ABSTRACT

Two series of polyurethanes (32~48 wt.% and 46~62 wt.% of hard segment, respectively) containing different starch contents were synthesized in a one-step (all reactants added simultaneously) and two-step reaction (first step: PCL(or PEG)+MDI and second step: addition of starch+1.4 butane diol), respectively by suspending starch granules in polycaprolactone-diol+MDI+1.4 butane diol in a bulk phase at 175°C. The products were characterized by FTIR, SEM, DSC, and swelling behaviour. Their mechanical properties, e.g. tensile strength and elongation, were measured for different starch contents. As a second step, melt rheological properties such as complex viscosity, and loss and storage moduli as a function of shear frequency were studied.

The starch dispersed well as a grafted state in the polyurethane phase. The grafted percentage of polyurethane to starch granules for the samples obtained by one-step reaction increased with the starch content up to a maximum point (about 20 wt.%) and then decreased due to separation between the two phases, probably because of the homo-polymerization tendency of the polyurethane. However, for the samples prepared by two-step reaction, the grafted percentage also showed a maximum point, but at the range of low starch contents(<25% for psb2m3 series and <15% for psb4m5 series) it shows a minimum point or remains constant. The solvent swelling test indicated that the crosslinking of the samples prepared in the one-step reaction was higher than those prepared in the two-step reaction.

The DSC indicated that T_g increased with the starch content due to the decreased average molecular weight of the homo-polyurethane. Three endothermic transitions at 60~70 °C (I), ~150 °C (II), 190~210 °C (III) were observed. Transition I was not changed by the starch content for both series, whereas transition II appeared only for the series of 32~48 wt.% hard segment at the lower range of 26 wt.% of starch content. The temperature of transition III, which is related to the melting point of the hard segments, increased with the starch content despite a decrease in the average molecular weight of the homo-polyurethane. The crystal formation of the hard segments was hindered by the starch addition at the second step inside the polyurethane phase in the two-step reaction.

The TGA indicated that the weight loss proceeded in four steps of temperature range; <290°C(I), 290~380°C(II), 380~450°C(III) and >450°C(IV). The first range (I) was the moisture loss from the sample, which is negligible and the second range(II) was the loss due to dehydroxylation of the starch component. The third range (III) was the decomposition of the polyurethane and the fourth range (IV) was the residual decomposition of the formed char of the blends. The thermal stability of the starch increased whereas that of the polyurethane decreased. For the samples prepared in the two-step reaction, results are similar to those of the samples prepared in the one-step reaction. The samples prepared by different molecular weight of prepolymer(polyethylene glycol) showed one large peak at the temperature of starch decomposition. Here, the polyurethane phase was also decomposed. However, the sample prepared with polyethylene glycol-10000 showed a large peak at higher temperature (430°C), probably due to strong crosslinking because this sample was insoluble in DFM+THF solvent.

The tensile strength and the elongation of the polymers prepared in the one-step reaction as well as two-step reaction slightly increased or were constant up to about 20 wt. % of starch, and then decreased rapidly because of the phase separation (gapping) between the starch granules and the polyurethane phase, and splitting of the starch granules. The elongation and the tensile strength increased first with decreasing crosslinking density, but at very low crosslinking densities the values decreased. Both properties increased generally with the average molecular weight of the separated homo-polymer of the blends. Also, both increased with the molecular weight of polyethylene glycol prepolymer due to the increased crystal formation of the soft segments with the molecular weight of the prepolymer of polyethylene glycol.

The GPC study indicated that the average molecular weight of the homo-polymer of the polyurethane also decreased with the starch content in the one-step reaction as well as in the two-step reaction. Increase of the catalyst concentration did not greatly change the average molecular weight.

Polyethylene glycol as a prepolymer gave much lower molecular weights than the prepolymer polycaprolactone diol. The molecular weights of polyurethane were constant regardless of the molecular weight of the prepolymer.

In the rheological study, the plots of ç* against ù and logG' against logG" indicated that the starch content increased the crosslinking leading to gel point behaviour. This crosslinking increased more for the higher hard segment samples. Increase of the catalyst concentration also increased crosslinking.

The slope of plots of ç* against ù for the samples prepared in the one-step reaction increased with the starch content, whereas that of the samples prepared in the two step reaction increased only slightly or were constant, which indicates a difference in the polymer structure between the two reaction schemes. The plots of logG' against logG" for the samples psb2m3 prepared by two-step reaction indicated that these materials are more viscous than those from one step-reaction. However, for the elastic properties the inverse was observed for the samples psb4m5.

The rheological properties for the samples prepared with different molecular weight of polyethylene glycol were not much changed as a function of the molecular weight of prepolymer, but the storage modulus decreased slightly with the molecular weight of prepolymer, while the viscosity increased with the molecular weight of prepolymer at the range of low frequency.