Thermal Properties of Copolyetherester/silica Nanocomposites

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Abstract: Thermal properties of copolyetherester/silica nanocomposites were examined by using DSC and TGA. The segmented block copolyetheresters with various hard segment structures and hard segment contents (HSC) were synthesized and their silica nanocomposite films were prepared by solution casting method. The nano-sized fumed silica particles were found to act as a nucleating agent of the copolyetheresters. The nanocomposites always showed reduced degree of supercooling or faster crystallization than the corresponding copolyetheresters. The nanocomposites also showed increased hard segment crystallinity except HSC 35 sample which had short hard segment length. In case of 2GT [poly(ethylene terephthalate)] copolyetheresters, which were not developed commercially because of their low crystallization rate, the hard segment crystallinity increased considerably. The copolyetherester/silica nanocomposites showed better thermal stability than copolyetheresters.

Keywords: Copolyetherester, Silica, Nanocomposites, Crystallization, Thermal degradation

Introduction

Thermoplastic elastomers are composed of hard and soft segment and their elastomeric properties are influenced by physical cross-link and their heterophase microstructures. A segmented block copolyetherester, a thermoplastic polyester elastomer, has crystallizable hard segments which act as physical cross-links and flexible soft segments which are viscous at the service temperature and impart flexibility to the polymer. Since the nature of the physical cross-links of the segmented block copolyetheresters is the crystallites of the hard segment, the crystallization behavior of the hard segment block is very important. The ideal structure of a copolyetherester usually needs a complete separation of hard and soft segment domains and a complete crystallization of hard segment. However, the actual structure of the copoly-etheresters shows two kinds of hard segments, hard segment in a crystalline phase and hard segment in an amorphous phase, which is sometimes mixed with amorphous soft segments. A segmented block copolyetherester having a hard segment content (HSC) less than 50 wt% can be applicable to a spandex-like elastomeric fiber production. However, the lack of crystallinity of a block copolyetherester results in unstable physical cross-links and low elastic recovery of the fiber made from the copolyetherester.

Nowadays, polymer nanocomposites are very important in both academic and industrial points of view. Various nano-sized fillers have been successfully developed as functional modifiers to various polymers. Kim *et al.* [1] found the nano-sized fumed silica had a good nucleation effect on poly(ethylene naphthalate) crystallization, while Jiang *et al.* [2]

found that the introduction of hydrophobic fumed silica into poly(ethylene oxide) (PEO) prevented chain mobility and crystallization of PEO. These results gave us an idea that the nano-sized fumed silica could be used as a nucleation agent which would increase the hard segment crystallinity and reduce the soft segment crystallization.

In the present study, we examined the effect of nano-sized fumed silica on the crystallization in the copolyetherester/silica nanocomposites. We introduced the nano-sized fumed silica into the block copolyetheresters having various structures, and related the thermal properties and crystallization behaviors with the structures of the copolyetheresters

Experimental

Segmented block copolyetheresters with various structures were prepared by the conventional two-step polymerization method [3,4]. The hard segment structures were designed as poly(ethylene terephthalate) (2GT), poly(trimethylene terephthalate) (3GT), and poly(butylene terephthalate) (4GT). The soft segment structure was selected as poly(tetramethylene ether glycol terephthalate) (PTMGT), whose poly(tetramethylene ether glycol) (PTMG) molecular weights were 1000, 2000, and 2900. Sample codes were defined as follows: (hard segment structure)(molecular weight of PTMG)-H(HSC by weight), for example 4GT2000-H35, means 4GT hard segment, PTMG molecular weight 2000, HSC 35 wt%. We varied HSC from 35 to 80 wt%. The hydrophobic fumed silica, Aerogel R202 (Degussa, Inc., primary size is 14 nm) was used. A homogenizer was used for dispersing the fumed silica evenly in the polymer solution in phenol/tetrachloroethane mixed solvent (phenol:1,1,2,2-tetrachloroethane=1:1 by weight). All the nanocomposite films were prepared from

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the 1 wt% silica suspension by the solution casting method. DSC 2910(TA instruments) and TGA-7(Perkin Elmer) were used for thermal analyses under N_2 purging with the scan rate of 20 °C/min.

Results and Discussion

Figure 1 shows the DSC cooling thermograms of the copolyetheresters (4GT2000) (solid line) and their silica nanocomposites (dashed line). There show some differences in the crystallization temperatures (T_c) and the heats of crystallization (ΔH_c) between copolyetheresters and their nanocomposites. Since the degree of supercooling ($T_m - T_c$) represents the driving force for melt crystallization, it could be used as a relative measure of easiness of crystallization from the melt. As can be seen in Figure 1, all the nanocom-
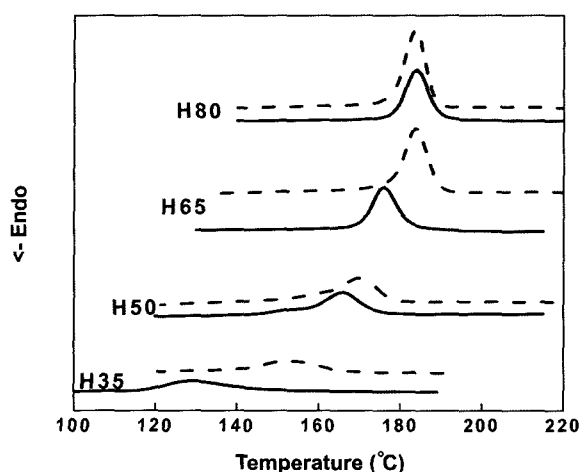

Figure 1. The cooling thermograms of 4GT2000 copolyetheresters (solid lines) and their silica nanocomposites (dashed lines) at various hard segment contents.
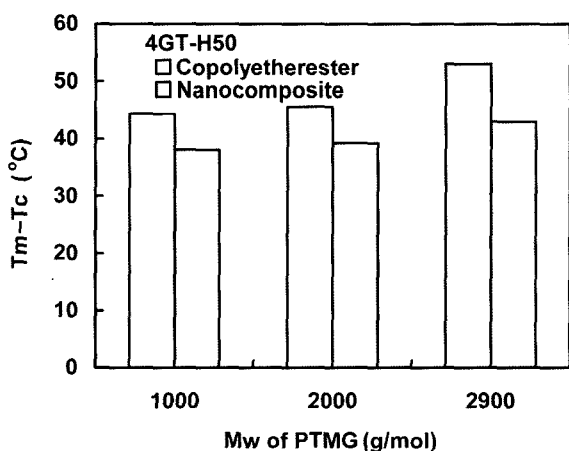
posites show higher melt-crystallization temperatures than the corresponding copolyetheresters, which implies the nanocomposite samples are thought to have experienced easier and faster crystallization from the melts than the corresponding blank copolyetherester samples.

The major parameters which determine crystallization behavior of copolyetheresters are hard segment length, hard segment content as well as hard segment chemical structure. Figures 2-4 showed the effect of these three parameters on the degree of supercooling of copolyetheresters and their silica nanocomposites. As mentioned in the introduction section the HSC of copolyetheresters for elastomeric fiber application is around 50 wt% or less. So, we focused on the HSC 50 wt%. In order to see the effect of hard segment length, we varied hard segment length by applying three different molecular weights of PTMG, i.e., 1000, 2000, and 2900. The resultant hard segment lengths (denoted by the number of hard segment units) of 4GT1000-H50, 4GT2000-H50, 4GT2900-H50 were 6.1, 10.7, 14.8, respectively. As can be seen in Figure 2, 4GT2900-H50 which has the longest hard segment length among three samples shows the maximum depression among them. From this result we tentatively conclude that the effect of silica on the crystallization of the 4GT-H50 copolyetheresters becomes prominent as the hard segment length is increased.

Figure 3 shows the effect of hard segment chemical structure on the degree of supercooling of copolyetheresters and their silica nanocomposites. As can be seen in Figure 3, the silica nanoparticles reduced the degree of supercooling for all the hard segment systems examined. The reduction in the degree of supercooling was most prominent for 2GT system. 2GT copolyetheresters usually have very slow crystallization rate, which limits applications of the copolymer as a thermoplastic polyester elastomer. So, this dramatic depression in the degree of supercooling in 2GT2000-H50 could give a
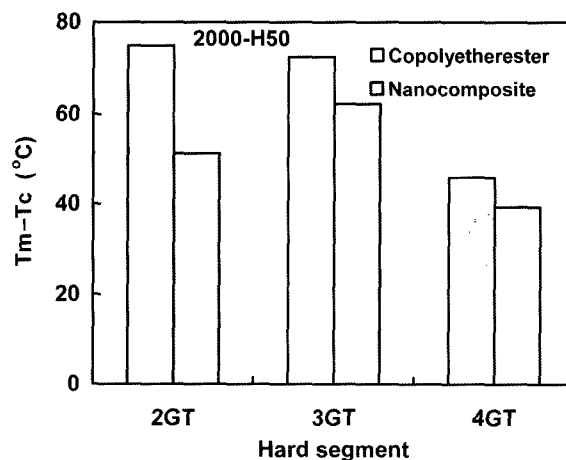

Figure 2. The degree of supercooling ($T_m - T_c$) of 4GT-H50 copolyetheresters and their silica nanocomposites at various PTMG molecular weights.

Figure 3. The degree of supercooling ($T_m - T_c$) of 2000-H50 copolyetheresters and their silica nanocomposites at various hard segment structures.

possibility as a useful thermoplastic elastomer. On the other hand 3GT2000-H50 shows very small depression and the degree of supercooling is the lowest among three. Though we do not know the exact reason, we just think that the effect of silica on the crystallization of 3GT segment is relatively small as compared to 2GT or 4GT.

Figure 4 shows the effect of HSC on the degree of supercooling of 4GT2000 copolyetheresters and their silica nanocomposites. In case of 4GT2000 system there shows considerable depression in $(T_m - T_c)$ for all the HSC examined. Though the depression in H50 was relatively small, we knew that we were able to reduce the degree of supercooling by adding small amount of silica nanoparticles and get faster crystallization of the copolyetheresters.

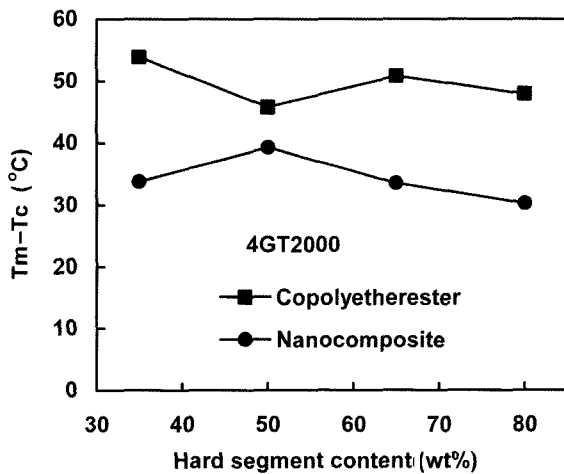Another important point is the hard segment crystallinity

(W_c), which is defined as the crystallinity of the hard segment only. The hard segment crystallinity for the copolyetherester is very important, because the uncrystallized hard segment usually reduces the elastic recovery and enhances the permanent deformation. The W_c can be easily calculated by $(\Delta H_c)/[(\Delta H_c^*)(\text{HSC in fraction})]$, where (ΔH_c^*) denotes the heat of crystallization of pure hard segment, i.e., 33.5 cal/g for 4GT [5]. Figures 5-7 show the W_c of the copolyetheresters and their silica nanocomposites.

The effect of nano-sized silica on the hard segment crystallinity was not simple. As can be seen in Figure 5, the effect of nanoparticle on W_c depends on the hard segment content and the 4GT2000 samples with small HSC shows very small increase or depression in W_c. Figure 6 shows the similar results. From the previous study [6] we found that the hard segment length (HSL) could play the most important role in the crystallization of the copolyetheresters. We calculated

Figure 4. The degree of supercooling $(T_m - T_c)$ of 4GT2000 copolyetheresters and their silica nanocomposites at various hard segment contents.
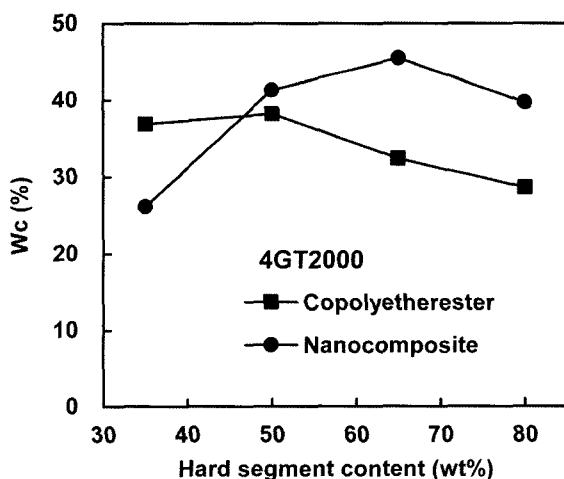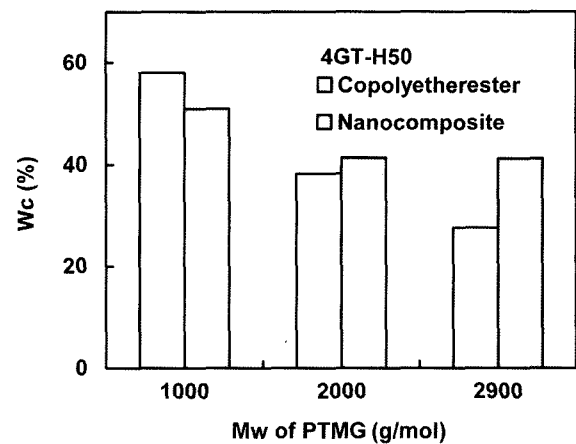

Figure 6. The hard segment crystallinity (W_c) of 4GT-H50 copolyetheresters and their silica nanocomposites at various PTMG molecular weights.

Figure 5. The hard segment crystallinity (W_c) of 4GT2000 copolyetheresters and their silica nanocomposites at various hard segment contents.
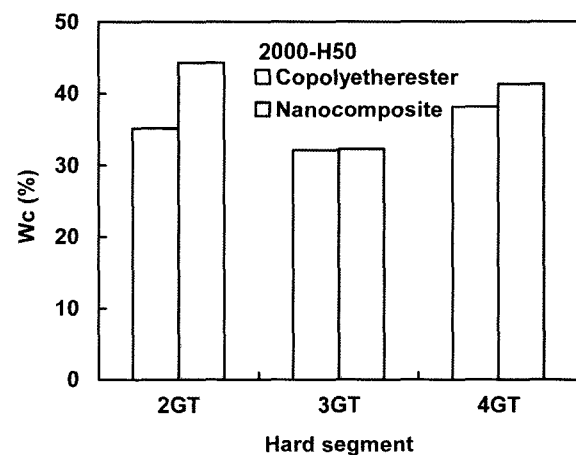

Figure 7. The hard segment crystallinity (W_c) of 2000-H50 copolyetheresters and their silica nanocomposites at the various hard segment structures.

HSL by assuming the equilibrium during synthesis [7]. The HSL's of 4GT2000-H35 and 4GT1000-H50 are 6.2 and 6.1, respectively [8]. These HSL's are relatively short when we compare them with other samples in Figures 5 and 6, for example, 10.7 for 4GT2000-H50. It is thought that the crystallization of short hard segments such as 4GT1000-H50 or 4GT2000-H35 might be hindered by the presence of silica, even though the nano-sized silica enhanced the rate of crystallization of the same polymer. So, we can tentatively say that the hard segment crystallinity of a copolyetherester can be raised by adding nano-sized silica particles when HSL is sufficiently long, for instance, greater than 10. Figure
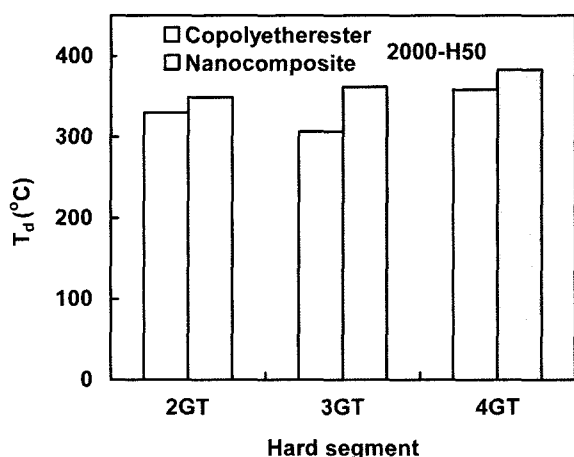

Figure 8. The thermal degradation temperature (T_d) measured at 5 % weight loss in TGA for 2000-H50 copolyetheresters and their silica nanocomposites at the various hard segment structures.
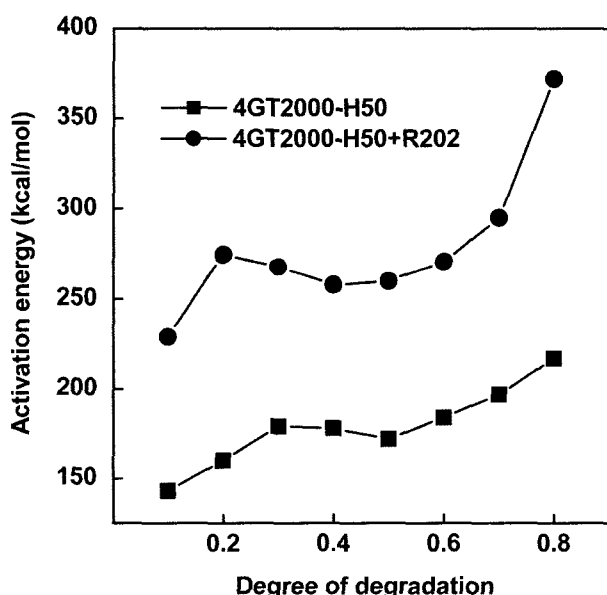

Figure 9. The activation energy of thermal degradation for 4GT2000-H50 and its silica nanocomposite plotted against the degree of degradation.

7 shows the effect of hard segment structure on the W_c of copolyetheresters and their silica nanocomposites at the same HSC (50 wt%). As can be seen in Figure 7, 3GT2000-H50 and 4GT2000-H50 samples show only small increase in W_c, while 2GT2000-H50 shows considerable increase, which is similar to result of Figure 3.

Thermal stabilities of nanocomposites were examined by using TGA. The temperatures at 5 % weight loss, T_d, are shown in Figure 8. All the nanocomposites show better thermal stability than the corresponding copolyetheresters. Especially, copolyetheresters based on 3GT hard segment show the highest increment in the degradation temperature. Figure 9 shows the activation energies of thermal degradation determined by Flynn-Wall method [9]. The activation energies of the silica nanocomposites are in the range of 230-370 kcal/mol showing greater values than those of copolyetheresters by 70-150 kcal/mol. Since the higher activation energy of degradation means higher barrier to degradation reaction, we think that the added silica particles may retard the thermal degradation of polymers. The silica particles are thought to act as walls to the propagation of thermal degradation reaction of copolyetheresters and slow down the total degradation process. Figures 8 and 9 imply that we can improve the thermal stability of copolyetherester by adding very small amount of silica nanoparticles.

Conclusion

We successfully prepared the copolyetherester/silica nanocomposites and investigated the effect of nano-sized silica on the thermal properties and crystallization behavior of the nanocomposites. The nanocomposites always showed reduced degree of supercooling or faster crystallization, which was thought to be due to the nucleating action of silica nanoparticles. The nanocomposites also showed increased hard segment crystallinity except when the hard segment length was short. The depression in the degree of supercooling and the hard segment crystallinity increment were considerable especially for 2GT system, which suggested that copolyetheresters based on 2GT could be used as a thermoplastic polyester elastomer by adding very small amount of silica nanoparticles. The copolyetherster/silica nanocomposites showed better thermal stability than the pure copolyetheresters as identified by TGA 5 % weight loss temperatures and activation energies of thermal degradation.

Acknowledgements

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