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RATTIKARN KHANKRUA : ENHANCEMENT OF THERMAL STABILITY OF BIODEGRADABLE POLYMERS. THESIS ADVISORS : ASST. PROF. SUPAKIJ SUTTIRUENGWONG, Dr.-Ing., ASST. PROF. SOMMAI PIVSA-ART, Ph.D., PROF. HIROYUKI HAMADA, D. Eng. 166 PP.

Biodegradable polymers are currently materials of considerable interest due to their superior advantages such as an environmental benign, originating from renewable feedstock and comparable mechanical properties with conventional plastics. Despite numerous advantages, thermal instability is considered to be the major drawback, which limits their use for some specific applications. Therefore, the objective of the research was to enhance thermal properties of biodegradable polyesters by different three approaches, including the nanocomposite, the grafting reaction and using chain extender method. Biodegradable polyester polymers; poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(butylenes succinate) (PBS) and poly(lactic acid) (PLA) were selected in this work. For nanocomposite approach, silica nanoparticle was used as filler. Polymers were mixed with silica at content varied from 0.1 to 5.0 wt% in a twin screw extruder. The improvement in thermal properties of PHBV, PBS and PLA/silica nanocomposites were achieved which confirmed by TGA and HDT results. The presence of silica nanoparticles increased the onset and inflection temperature of thermal degradation in PLA, PBS as well as PHBV nanocomposites. It showed the great improvement for PHBV nanocomposite. Similar to the HDT results, it was greatly improved for PHBV/silica 5wt% nanocomposites. However, the mechanical performances of nanocomposites depended on the content and the dispersion of silica particles in the polymer matrix. At low silica content of 0.1-0.2 wt%, the mechanical properties were slightly increased, whereas their mechanical properties became deteriorated at the higher silica loading. In the case of the grafting reaction method, maleic anhydride (MA) and benzoyl peroxide (BPO) were used as grafting agent and initiator, respectively. The ratio of MA: BPO was fixed at 2:1. The grafting reaction was carried out by the high speed ball mill with the rotation speed of 325 rpm. The mechanical grafting by ball mill polymers was successfully achieved. MA grafted onto polymers could improve the thermal stability of biodegradable polyester by retarding the formation of cyclic rings (cis-elimination) which is the thermal degradation pathway of polyester. In addition, because the β-C–H bond of PHBV could be activated by the neighboring carbonyl group more readily than in the case of PLA and PBS. Therefore, the thermal stability provided by this method was more prominently observed for PHBV. For the grafting reaction by using supercritical carbon dioxide method, the free radical grafting of PHBV, PBS and PLA film with MA were successfully prepared. The result showed that the average degree of grafting by this method was relatively high achieved. In addition, polymers film grafted with MA showed the improvement of the hydrophilicity, but poor thermal stability. However, the sacrificed molecular weight reduction can be probably caused by the excess or high loading of MA and peroxide, leading to the chain scission reaction, which is the competition reactions occurred during the grafting of MA onto polymer. In the case of improvement, thermal stability of biodegradable polymer by using chain extenders, PLA and 0.5 phr of chain extenders were mixed in the twin screw extruder under the four temperature profiles from the feed zone to die. The processing temperature was varied from 220-250 ^{o}C. The results indicated that the addition of two chain extenders, polycarbodiimide (PCD) and multifunctional epoxide chain extender (ECE) to PLA could prevent the further mechanical deterioration and thermal degradation from the high processing temperature. TGA data of chain extenders added PLA samples showed the improvement of thermal stability by an increase in onset and deflection temperatures when compared to processed PLA alone. In addition, the presence of both chain extenders in PLA also improved elongation at break and impact strength whereas these mechanical properties decreased for processed PLA samples.

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