Application of Model-Free Kinetics to the Thermal Degradation of Poly(L-lactide)/Olive Stone Flour Composites

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Blending of thermoplastics with biomass is a one of the ways to reduce cost and/or to improve mechanical performance of the material, but also to reduce negative environmental impact. The properties of those blends or composites are greatly influenced by addition of the second component. Thus, understanding the thermal stability of poly(L-lactide)/olive stone flour composites (PLLA/OSF) is very important because during processing at high temperatures could be degraded. Many researchers have done much work on the kinetics of the thermal degradation of PLLA but there is no information on PLLA/OSF composites. Due to the fact that polymer degradation includes complex reactions, the model–free kinetics method proposed by Vyazovkin[1] has been applied. PLLA was blended with various amount of OSF (up to 30 phr) using a Brabender plastograph and than pressed in a hydraulic hot press into plates of 35×15×1 mm. The thermal degradation of the composites was investigated by nonisothermal thermogravimetry (TGA, Perkin-Elmer). TG analysis was carried out in the temperature range from 50 to 500℃ under nitrogen atmosphere and heating rates of 2.5, 5, 10 and 20 ℃min $^{-1}$. Thermal decomposition of neat PLLA, OSF and PLLA/OSF composites at the heating rate of 10℃min $^{-1}$ takes place in the range from 250 to 450℃, 100 to 500℃ and 200 to 400℃, respectively. PLLA decomposes in one step while OSF and PLLA/OSF composites decompose in two steps. The activation energy (E) was calculated using a computer program based on the Vyazovkin theory. It predicts isothermal kinetic parameters from nonisothermal data. The prediction was carried out at 200, 240, 280 and 320℃. From the α-T and $d\alpha/dT$-T dependences it is observed that the decomposition of PLLA/OSF composites start at lower temperatures than that of neat PLLA and the temperatures at $(d\alpha/dT)_{max}$ are much lower for the composites. Addition of OSF broadens the decomposition region and it is wider as OSF amount increases. The shape of E-α curves reveals complex reaction mechanism which probably involves a several processes.[2] Upon OSF addition the reaction mechanism of PLLA undergoes a quite change and as the amount of OSF increases the change is more pronounced.

[1] Vyazovkin, S.; Wight, C. A.; *Thermochim. Acta* **1999**, 340-341, 53.
[2] Vyazovkin, S.; Wight, C. A.; *Annu. Rev. Phys. Chem.* **1997**, 125-149, 48.