Study on the Influence of Zinc Oxide (ZnO) Nanolayers on the Permeability of the Bioplastic poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

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Extended Abstract
In the food packaging industry there is a gaining interest in bioplastics to replace conventional plastics, such as PET, PP, etc., as packaging material. Although these new polymers show the advantages of being bio-based and/or biodegradable, it is still a challenge to produce bioplastics with similar properties to the conventional plastics. For food packaging material for example, it is important to maintain food quality. Therefore it is essential to enhance the gas barrier properties of these bioplastics. Recent studies show that gas barrier properties of polymers can be improved through use of polymer nanocomposites, a two-phase system of a polymeric matrix and dispersed inorganic nanoparticles. A limiting factor, however, is the dispersion of the nanoparticles into the polymer. A solution is to deposit the nanoparticles on the polymer surface instead. Here, nanoparticles were deposited at temperatures below 95°C on the surface of the bioplastic PHBV through chemical bath method, which allows low-cost and low deposition temperatures, to study the effect of ZnO nanolayers on the gas barrier properties.

By means of XRD the formation of (002) oriented ZnO was confirmed, while Raman spectroscopy confirmed the chemical structure of the ZnO nanolayer. The influence of the deposition of ZnO layers on the properties of the PHBV bioplastic was investigated by means of differential scanning calorimetry and transmission spectrometry in the wavelength ranging from 200 nm to 800 nm and.

The \( \text{O}_2 \), \( \text{CO}_2 \) and water vapour permeability were measured at a controlled temperature of 10°C, 23°C and 38°C to determine the influence of temperature on the barrier properties. For the \( \text{O}_2 \) permeability these experiments were performed at a relative humidity of 0%, 40% and 80% to also determine the influence of humidity on the oxygen barrier, while for \( \text{CO}_2 \) and water vapour permeability the relative humidity was kept constant at 0% and 100% respectively.

The temperature study showed an increase of the oxygen, carbon dioxide and water vapour permeability with increasing temperature. This is mostly due to an increased free volume in the polymer matrix, improved motion of the polymer segments and a higher energy level of the permeating molecules. It was observed that the deposition of ZnO nanoparticles decreases oxygen, carbon dioxide and water vapour permeability. Temperature dependent measurements show that the activation energy for permeability of pure PHBV is lower than that of PHBV with a ZnO nanolayer on top. The humidity study of the oxygen barrier showed that for pure PHBV the permeability is stable until 40% RH and then increases with 20% at 23°C and even with 45% at 38°C. This is due to the fact that PHBV will absorb moisture from the humid air, which will lead to an increase in free volume and higher permeability values. For the PHBV with ZnO nanolayer an opposite effect is observed. In the region of 0%RH to 40%RH the oxygen permeability increases with 15% at 23°C and 23% at 38°C while afterwards, in the
region from 40% RH to 80% RH, it stays stable. This can be explained by the water absorption properties of ZnO and shows that ZnO not only increases the oxygen barrier but also makes it less susceptible to humid conditions.