

Summary

SUMMARY

Plastic products have gained universal use not only in food, clothing and shelter, but also in the transportation, construction and medical industries.

There is a growing demand for bio-based and biodegradable polymers as a solution to problems concerning the energy resources, the global environment and the solid waste management. Research on bio-based and biodegradable plastics and polymers has been carried out worldwide with the aim of achieving a balance between human activities and the natural environments. Ideal bio-based and biodegradable polymers are defined as materials that are produced from renewable resources and completely degraded to CO₂ & H₂O by the action of microorganisms. From these consideration commercial poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) having a low fraction of 3-hydroxyvalerate appears to nearly meet all these criteria. However, it has some unfavorable properties as a thermoplastic, it is brittle due to high crystallinity and the high melting point leaves only a narrow temperature window for processing and water resistance. The modification of PHBV is a promising method for the preparation of new materials. This enables one to induce special properties and enlarges the field of the potential application of this biopolymer. Among the diverse modifications that are possible to achieve, grafting by synthetic polymer is a convenient method. On the other hand, poly(N-vinylpyrrolidone) (PVP) and (N-isopropylacrylamide) (PIPA) are among the synthetic polymers that have been the subject of many extensive investigations in the field of modern macromolecular bioengineering and biotechnology. In this study, grafting of poly(N-vinylpyrrolidone) and poly(N-isopropylacrylamide) onto PHBV using

2, 2'-Azobisisobutyronitrile (AIBN) and Benzoyl peroxide (PBO) as free radical initiators were investigated. The effect of reaction variables as initiator concentration, monomer concentration and reaction time on the variation of the grafting parameters such as grafting yield and grafting efficiency have been studied systematically. The results indicate that the grafting percentage reached 46 and 82 % for PHBV-g-PVP and PHBV-g-PIPA, respectively. This reveals that the grafting % depends on the reactivity of the investigated monomers.

Evidence of grafting was confirmed by comparing FTIR and NMR spectra of PHBV and the graft copolymers. The results showed that the graft copolymers had the characteristic peaks of PVP and PIPA graft chains and the PHBV base polymer.

The X-ray studies shows PHBV-g-PVP and PHBV-g-PIPA graft copolymers possesses the crystalline diffraction peaks characteristics of PHBV host polymers, indicating that the grafting occurs in the amorphous fraction. The crystallization properties of the graft copolymers properties were also studied using DSC. The results showed, in both two graft systems, that the cold crystallization temperature from the glassy state increased with increasing the extent of grafting, while the T_g and T_m are not affected significantly.

To examine the thermal stability of the prepared graft copolymers, thermogravimetric analysis (TGA) is carried out and compared with the PHBV base polymer. In contrast to bacterial PHBV which degrades in a single step weight loss around 260°C, the decomposition process of the graft copolymers is a more complex, resulting mostly in three and four degradation-steps for the grafted chains of PIPA and PVP respectively. The first one is due to the loss of adsorbed water the second step assigned to the decomposition of PHBV, while the remaining steps are due to the

decomposition of graft chains. The grafting of PHBV did not affect much its onset decomposition temperature.

The swelling capacity of the prepared graft PHBV-g-PVP copolymers was determined in distilled water (pH = 6.5) and the results revealed that the extent of swelling increases with the increase of PVP content. In contrast, PHBV did not swell due to its hydrophobic nature. For PHBV-g-PIPA graft copolymers, the extent of swelling also increases with the increasing extent of grafting. The swelling capacity was also determined in pH = 9 and different temperature ($T = 18, 35, 70^{\circ}\text{C}$) and the results indicated that the swelling increases with increasing pH and temperature, indicating that these copolymers has pH and temperature sensitivity. The antimicrobial (bactericide and fungicide) activity of PHBV-g-PVP copolymers was investigated and found to be improved dramatically with the extent of grafting.

To test the susceptibility of such materials to biodegradation, the graft copolymers as well as PHBV homopolymer were buried in activated soil. The results showed that the biodegradability of graft copolymer is higher than PHBV host polymers and the rate of biodegradation increases with increasing grafting percentage. This indicates that the hydrophilic nature of the PVP and PIPA graft chains plays important role in biodegradation.