BLENDS OF BIODEGRADABLE THERMOPLASTICS WITH LIGNIN ESTERS

by

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ABSTRACT

Thermoplastic blends of several biodegradable polymers with lignin (L) and lignin esters were prepared by solvent casting and melt processing. Among the biodegradable thermoplastics were cellulose acetate butyrate (CAB), poly-hydroxybutyrate (PHB), poly-hydroxybutyrate-co-valerate (PHBV), and a starch-caprolactone blend (SCL). Lignin esters included acetate (LA), butyrate (LB), hexanoate (LH), and laurate (LL). Blend characteristics were analyzed in terms of thermal and mechanical properties. The results indicate widely different levels of interaction between two polymer constituents. Melt blended samples of CAB/LA and CAB/LB were compatible on a 15-30 nm scale when probed by dynamic mechanical thermal analysis, and the glass transition temperatures of the blends followed Fox equation, whereas those of CAB/LH and CAB/LL showed distinct broad transitions on the same scale. Melt blending produced well dispersed phases whereas large phase separation evolved out of solvent casting. Crystallinity and melting points of PHB and PHBV were affected by the incorporation of lignin component, revealing some interaction between the blend constituents. Blends of SCL with L and LB revealed significant effect on crystallinity and melting temperatures of poly-caprolactone component, revealing polymer-polymer interaction between SCL and lignin components. An increased degree of crystallinity was observed in the case of higher-T_g L compared to lower T_g LB. Improvement in modulus (and in some cases strength also) was observed in almost all blends types due to the glassy reinforcing behavior of lignin.

Learning is such a process that it is not possible to tell exactly how one acquired a given body of knowledge. This thesis is dedicated to all those who taught me and helped me to acquire that knowledge over the years.

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PREFACE

Recently, there is great interest and awareness in 'environmentally friendly' polymers for various applications ranging from packaging materials to automobile interiors. This research is aimed particularly towards developing materials for biodegradable composites and related applications by modifying existing biodegradable polymers. This study deals with: a) an investigation of the possible factors affecting miscibility/compatibility of polymer blends of biodegradable polymers such as cellulose ester (CAB), polyhydroxy-alkanoates (PHA's), and a starch-caprolactone blend (SCL, tradename "Envar") with lignin esters having varying lengths of side groups; b) the influence of the lignin component in the blend; c) effect of lignin ester component on crystallization of PHA's and SCL.

Concepts of biodegradation and compatibility are introduced along with other relevant theories in *chapter-I*. *Chapter-II* deals with the synthetic and analytical details of lignin esters used as blend components with the biodegradable polymers. *Chapters-III*, *IV* and *V* are concerned with the detailed studies of blends of CAB, PHA's and SCL respectively. Each chapter of the thesis (except *chapter-I*) has its own abstract, experimental sections, discussions and references followed by illustrations. Due to similarity in the topics covered in each chapter, some repetition of material could not be avoided. Apologies are made for these inconveniences and other mistakes that might have avoided my sight.

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GLOSSARY

$\mathbf{DP_n}$	Degree of polymerization
DS	Degree of substitution
$\mathbf{\Delta H_m}$	Enthalpy of fusion (J/gm)
$\mathbf{\Delta H_c}$	Enthalpy of crystallization (J/gm)
$\mathbf{M_n}$	Number average molecular weight (Daltons)
$\mathbf{M_w}$	Weight average molecular weight (Daltons)
$\mathbf{T_g}$	Glass Transition Temperature (^{0}C)
$\mathbf{T_m}$	Melting Temperature (^{0}C)
$\mathbf{T_c}$	Crystallization Temperature (^{0}C)
$\mathbf{X_c}$	Degree of Crystallinity (%)

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