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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Immiscible Polymer Blends Containing Dibutyrylchitin as Environmentally Friendly Materials

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Version of record first published: 24 Sep 2006

To cite this article: Joanna Marszałek, Lidia Szosland & Maria Mucha (2000): Immiscible Polymer Blends Containing Dibutyrylchitin as Environmentally Friendly Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 354:1, 427-433

To link to this article: http://dx.doi.org/10.1080/10587250008023635

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 354, pp. 427-433
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Immiscible Polymer Blends Containing Dibutyrylchitin as Environmentally Friendly Materials

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The morphological and physical properties of polymer blends containing dibutyrylchitin (DBCh) are presented in this paper. Two different synthetic polymers, polystyrene (PS) and poly(vinyl acetate) (PVAc) were blended with dibutyrylchitin in common solvent (dimethylformamide or methanol) in various weight fractions of DBCh. The films of the blends were prepared by casting method. A polarizing microscope with computer image analyser and differential scanning calorimeter (DSC) were used to evaluate the phase morphology. Microscopic studies indicate heterogeneous structures of both blends. DSC studies show that a characteristic endothermic peak observed for DBCh influenced by water moisturizing effect is shifting toward lower temperatures with an increasing content of the synthetic polymers. The values of glass transition temperatures Tg of both synthetic polymers were found weakly affected by the presence of DBCh.

Keywords: polymer blends; dibutyrylchitin; morphological studies; physical properties

INTRODUCTION

Blends of biopolymers with common polymers are of great significance with expanding application to biomedical, biochemical and biodegradable materials.

Chitin is a biopolymer being second to cellulose produced by biosynthesis. It occurs in some animals, where it is an important constituent of the exoskeleton. The major factor limiting the original chitin utilisation is

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its insolubility in popular solvents. Chemical modification of chitin may destruct the hydrogen bonds in chitin and make functional groups interacting with other polymer.

Chitosan and dibutyrylchitin are products obtained by chemical modification of the chitin. Chitosan is soluble in weak acidic solvents and it forms a compatible one-phase blends with water soluble polymers. Miscibility, morphological structures and physical properties of the blends of chitosane acetate salt with poly(ethylene oxide) and poly(vinyl alcohol) in solution and solid state were studied[1-5] recently.

Dibutyrylchitin (diester of chitin)[6] is a less known derivative of chitin than chitosan. Because of its excellent solubility in organic solvents it attracted some attention and new achievements are predicted in the use of DBCh as a biodegradable component of polymer blends for special purposes.

In the present work miscibility of blends of dibutyrylchitin with polystyrene or poly(vinyl acetate) prepared by casting technique from solution in common solvent (dimethylformamide or methanol) is studied.

EXPERIMENTAL

Materials and blends preparation

Dibutyrylchitin (DBCh) is synthesised in the Department of Physical Chemistry of Polymers. Polystyrene (PS) is a commercial product and poly(vinyl acetate) (PVAc) with molecular weight of $83*10^3$ obtained from Aldrich–Chemie.

Dibutyrylchitin blends containing PS in a film form were prepared by mixing PS/dimethylformamide solutions of 5% concentration by weight with DBCh/dimethylformamide solutions of 2% concentration by weight in

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appropriate amount. The films of ~ 30 μm thick were made by casting techniques at temperature 80°C and dried for 1 hour.

Dibutyrylchitin blends containing PVAc were prepared by mixing PVAc/methanol solutions of 5% concentration by weight with a DBCh/methanol solutions of 2% concentration by weight in appropriate amount. The films ~ 30 μm thick were produced by casting techniques at room temperature and dried at temperature of 60°C for 1 hour.

The blends were obtained and characterized in the whole changing composition range. All components of the blends are amorphous. A pure DBCh has shown a very low crystallinity degree[5].

Methods

Morphological studies of these films were performed by means of polarizing microscope with a computer image analyser MultiScan.

Differential scanning calorimetry enabled a study of some physical properties of the prepared films. The measurements were made by unit Mettler FP 85 in temperature range 25÷160°C at a heating rate of 10°C/min.

RESULTS AND DISCUSION

Optical microphotographs have shown a heterogeneous structure of the amorphous blends of DBCh/PS and DBCh/PVAc (Fig. 1). Both blends containing DBCh prepared from a homogeneous solution in common solvents appear heterogeneous in a solid state. The observations in the optical microscope lead to the conclusion that a separation of the components occurs during solvent evaporation both slow (dimethylformamide) or fast rates (methanol). It is perhaps due to various solubilities of both components in the used solvents. Further studies to

obtain more homogeneous blends as solid films and fibers will focus on using first a different solvent and an effective compatibilizer.

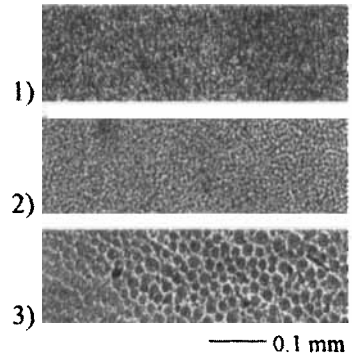

FIGURE 1 Micrographs of heterogeneous blends DBCh/PS of various PS content: 1) 0.4, 2) 0.5, 3) 0.6

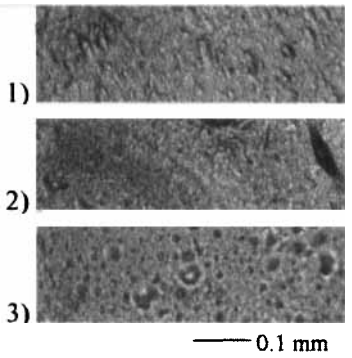

FIGURE 2 Micrographs of heterogeneous blends DBCh/PVAc of various PVAc content: 1) 0.3, 2) 0.4, 3) 0.7

An important aspect dealing with thermal behaviour of the blends is variation of Tg as a function of the blend composition.

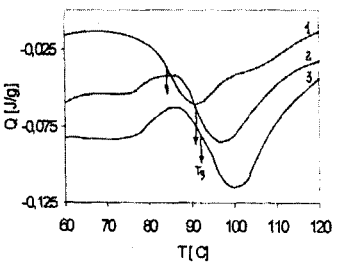

FIGURE 3 DSC curves in the vicinity of Tg of PS (I run) of DBCh/PS blends of various weight fractions of PS content: 1) 1.0 (pure PS), 2) 0.9, 3) 0.8

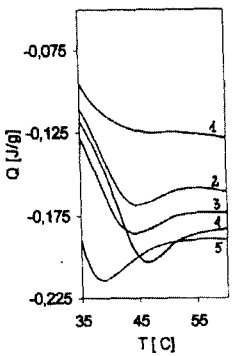

FIGURE 4 DSC curves in the vicinity of Tg of PVAc (I run) of DBCh/PVAc blends of various weight fractions of PVAc content: 1) 0.1, 2) 0.5, 3) 0.6, 4) 0.8, 5) 1.0 (pure PVAc)

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Figures 3 and 4 show the DSC curves of the blends containing various weight fractions of PS and PVAc. The glass transition temperatures (Tg) of the synthetic polymers (PS and PVAc) in the blends are here clearly seen if their fractions are higher than 0.4. The Tg values are not clearly affected by the presence of DBCh (Figs. 5 and 6) due to immiscibility of the components. A difference between I and II studies (lower Tg in I run) results probably from the presence of the residual solvent .

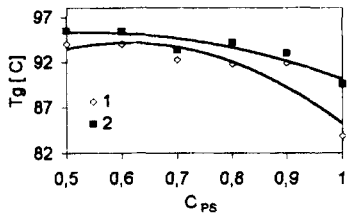

FIGURE 5 Tg of PS in the blends with DBCh versus weight fraction of PS (I and II runs)

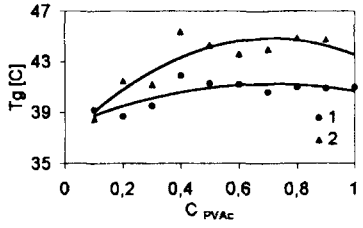

FIGURE 6 Tg of PVAc in the blends with DBCh versus weight fraction of PVAc (I and II runs)

In the vicinity of weight fraction of DBCh equal to 0.5, a phase conversion of the blend components is observed (Fig. 1). The effect is also reflected in DSC analysis in the vicinity of water loss temperature equal to 100°C. Figures 7 and 8 show a behaviour of the characteristic endothermic peak with an increasing content of synthetic polymer in the DBCh blends the peak is shifting toward lower temperatures (Figs. 9 and 10) and completely disappears if DBCh content is lower than 0.4 where water loss is very much limited. DBCh forms inclusions in PS matrix which are almost completely separated from the surface. In the case of DBCh/PVAc the effect is not so clear (Figs. 11 and 12). The presence of water loss peak on DSC thermograms results from hygroscopicity of DBCh and it is suppressed in the following DSC runs.

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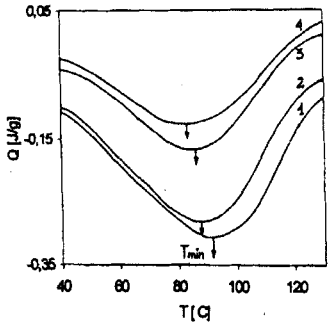

FIGURE 7 DSC curves (I run) of DBCh/PS blends of various weight fractions of DBCh content: 1) 1.0 (pure DBCh), 2) 0.8, 3) 0.6, 4) 0.5 in the vinicity of endothermal peak characteristic for DBCh

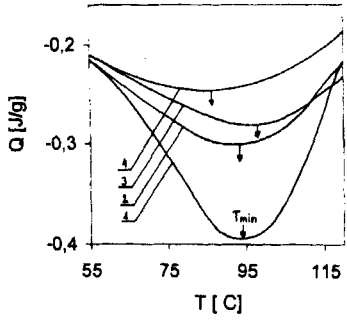

FIGURE 8 DSC curves (I run) of DBCh/PVAc blends of various weight fractions of DBCh content: 1) 1.0 (pure DBCh), 2) 0.6, 3) 0.4, 4) 0.2 in the vinicity of endothermal peak characteristic for DBCh

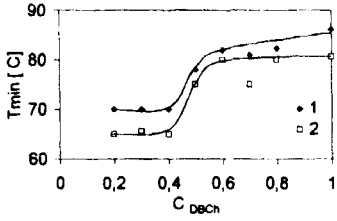

FIGURE 9 Tmin (taken from Fig. 7) versus weight fraction of DBCh (I and II runs) for DBCh/PS blends

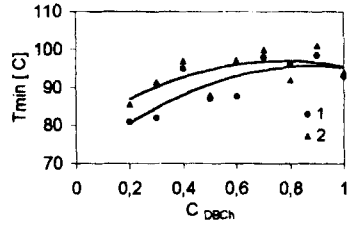

FIGURE 10 Tmin (taken from Fig. 8) versus weight fraction of DBCh (I and II runs) for DBCh/PVAc blends

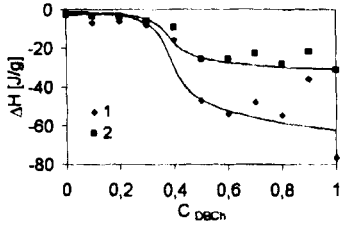

FIGURE 11 Change of water loss enthalpy (ΔH) with increasing weight fraction of DBCh in the DBCh/PS blends

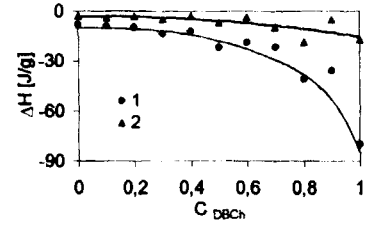

FIGURE 12 Change of water loss enthalpy (ΔH) with increasing weight fraction of DBCh in the DBCh/PVAc blends

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CONCLUSIONS

The mixed solutions of PS or PVAc with DBCh in common solvents are clear and homogeneous. The polymer separation occurs during a solvent evaporation in the process of the film preparation by the casting method thus the solid blends containing various weight fraction of DBCh are found heterogeneous.

Only small shift of Tg's of the synthetic polymers in blends is observed. It indicates on the immiscibility of the polymer components due to probable lack of polar interactions between their chains in the absence of solvent. The glass transition temperature of DBCh is probably covered by the water loss peak and it is not clear distinguish.

The solid blends containing DBCh in the amount higher than 50% save the useful hydrophilic properties of DBCh. The purpose of the presented studies was to take into account the possibility of the application of chitin derivative (here DBCh) for mixing with synthetic polymers to prepare biodegradable blends with hydrophilic properties. The biodegradation process of the blends is now under study.

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