polymer reviews

Compatibility and transesterification in binary polymer blends

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Polyester blends have been intensively studied both for industrial application and for academic interest. Properties of these blends are related to their miscibility. It has been found that the miscibility reported for certain blends has been influenced by transesterification. For other polyester pairs miscibility is caused directly and only by interaction of components. The miscibility for a variety of polyester blends, including polyester liquid crystals, is discussed and the relationship between the miscibility and transesterification in the individual blend pairs is detailed in this review.

(Keywords: compatibility; transesterification; binary blends; miscibility; polyesters)

INTRODUCTION

Since the early 1970s, many new pairs of polymers have been found to be miscible. Concomitantly, a large research effort has been launched to try to understand the relationship of polymeric architecture to miscibility. One approach has been the measurement of the Flory–Huggins (χ) parameter by crystallizable blend pairs that have been demonstrated to be miscible. However, the Flory–Huggins χ parameter has been found to be an inadequate representation of the thermodynamics of mixing, because the interaction between components is often found to be composition-dependent[1,2]. The parameter χ is still used, as discussed later, as a first-order description of blend miscibility.

Recently, Coleman *et al.* have proposed a χ_{crit} parameter for prediction of the upper limit for miscibility across the entire composition range[3]. They found that the closer the match of the two non-hydrogen-bonded solubility parameters and the greater the relative strength of the potential intermolecular interactions between the polymer blend components, the greater is the probability of miscibility. This conclusion is axiomatic, and the influence of concentration of any inert diluent is not accounted for[3].

A direct approach is to evaluate the specific interaction between chemical moieties of each chain, as generally required to meet the miscibility requirement of an exothermic heat of mixing. If the enthalpy of mixing is negative, i.e. exothermic, specific interactions between polar groups are expected, and consequently ΔG_{mix} will be negative in spite of the small entropy of mixing[4,5]. The interactions may arise from a variety of mechanisms such as dipole–dipole forces, acid–base attraction[6,7], ion–ion interaction[8] or hydrogen bonding[9]. Barlow and Paul with coworkers have reported a serial study on miscibility of bisphenol A polycarbonate (PC) in polyester

blends[10-13]. It is found that, at an optimum density of ester groups in the polyester chain, a maximum interaction between components is achieved, and a miscible blend is formed.
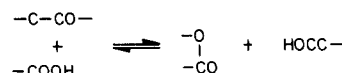
A fascinating feature for blends in the polyester family is the potential for transreaction, also called re-reaction and transesterification. Polyester blends have been studied both for industrial application and for academic interest. Several polyester blends and others with polycarbonate are commercial products: poly(ethylene terephthalate) (PET) with poly(butylene terephthalate) (PBT) is used for moulded automobile parts.

As polyesters readily transesterify, near and above their melting points, interchange reactions commonly occur between constituents[14-25]. This is confirmed from the study of blends of normal (protonated) PET with deuterium-labelled PET by small-angle neutron scattering (SANS). Analysis is based on the difference in coherent scattering length between hydrogen and deuterium chain units. Results show that ester interchange is rapid in the melt and also takes place slowly at 15°C below T_m, resulting initially in the formation of block copolymer consisting of deuterium-labelled and non-labelled segments of PET[24,25].

Kotliar has reviewed interchange reaction involving the condensation polymers, polyesters and polyamides[26]. He discussed the statistics of three different exchange reactions where the chains are terminated by hydroxyl or carboxyl groups. The reactions are intermolecular *alcoholysis*:

$$\begin{array}{c}-O-CO-\\+\\HO-\end{array} \rightleftharpoons \begin{array}{c}-OH+CO\\|\\O\end{array}$$

intermolecular *acidolysis*:

$$\begin{array}{c}-C-CO-\\+\\-COOH\end{array} \rightleftharpoons \begin{array}{c}-O\\|\\-CO\end{array} + HOCC-$$

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and *transesterification*:

$$-O-CO- \atop + \atop -CO-O- \quad \rightleftharpoons \quad {-O \atop |} + {CO \atop |} \atop -CO \quad O$$

In the present paper, transesterification is used as a general term to describe all such interchanges including those with polycarbonate.

Transesterification can be readily facilitated, with the following possibilities: it can open a new route to compatibility and preparation of novel copolymers with degrees of randomness and composition; it can lead to a more uniform polymer by minimizing molecular-weight fluctuations in a melt stream during polymerization and processing[27]; and it can provide for chemical healing of polyester laminates[28-30]. In consequence, there is an increasing interest in understanding the interchange reactions that take place between the different functional groups involved in mixtures of polycondensation polymers, viz. polyesters.

As transesterification proceeds, blends convert first to block copolymers and finally to random copolymers. This is irrespective of reaction origin, whether at chain ends or mid-chain. The complex and competitive processes involved, plus the variety of experimental conditions, can result in a range of reaction rates and resultant molecular chain microstructures. The resultant initial block and eventual random copolymers are expected to exhibit enhanced mutual miscibility over the original unreacted components. Moreover, the transreacted chains probably also facilitate and accelerate the compatibilization and reaction of unreacted chains.

Transreaction in polyester blends depends strongly on their initial compatibility and on the blending conditions. This includes temperature, duration of mixing, preparation method, viscosity match and the presence of catalysts[31] and inhibitor[32-35]. Sometimes different conclusions have appeared in the literature concerning blend properties, just because blends were prepared differently. Previously, we have summarized the thermal and mechanical behaviour of binary polyester blends in their crystalline, liquid-crystalline and amorphous phases[36]. In the present review, those binary blends for which transesterification has been demonstrated will be emphasized, in terms of phase behaviour and properties. The amorphous miscibility known for unreacted binary blends is summarized in *Table 1*.

METHODS FOR ANALYSING TRANSESTERIFICATION IN POLYMER BLENDS

On transesterification, the physical properties and the constituents of the system will change due to the production of new components. Several techniques have been used that can detect these changes.

One of the most commonly used techniques is infra-red spectroscopy (i.r.), which originates from molecular vibrations that cause changes in the dipole moment and polarizability of the molecular chains. These spectra are unique to each molecule and therefore reflect the chain structure, especially the concentration of the constituent groups and the intramolecular forces acting among them. In several of the polyester blend studies, new components produced by reaction have been detected by i.r. studies (*Figure 1*)[37-41].

Nuclear magnetic resonance (n.m.r.) is an even more powerful tool for analysis of polymer microstructure and to provide insight about miscibility and the chemical changes within polyester pairs[31,39-45]. The kinetics of transreaction has been studied by this technique[42].

The sensitivity of spectroscopic techniques is insufficient to detect the single bond per chain necessary to start transreaction. Nevertheless, the thermodynamics of interaction between blend components can be sensitively changed from the onset of transesterification. Therefore methods that detect the thermal or thermomechanical behaviour are widely used in such blend studies. Differential scanning calorimetry (d.s.c.), differential thermal

Table 1 Amorphous miscibility evaluation: binary pairs of polyesters and polycarbonate (references are given in square brackets)

Polymer pair	PC	PBT	PET	Kodar	PCL	PETG	Phenoxy	60% PHB–PET	Vectra
PC	–	No [52–60]	No [38, 61–68]	Yes [69, 77, 78, 113]	Yes [51, 71]		No [85b, c]	No [100–103]	
PBT	–	–	Yes [44, 85a]				Yes [77]	Yes & No [75, 91]	
PET	–	–	–				No [78]	No [92–96]	No [107]
PAr	No [75, 77, 80]	Yes [37, 72, 73]	No [74–80]			Yes [77, 83]	No [77a, 84]	Yes & No [123]	
PHMT								No [106]	
PHP	Yes [122]	Yes [122]	No [122]						

The abbreviations are as follows:

Kodar	Cyclohexanedimethanol–tere/isophthalic acid copolyester
PETG	Cyclohexanedimethanol, ethylene glycol, terephthalic acid (1:2:3) copolyester
PHB–PET	*p*-Hydroxybenzoate (PHB) modified PET copolyester
Phenoxy	Poly(hydroxy ether of bisphenol A)
Vectra	Copolyester of hydroxybenzoic acid and hydroxynaphthoic acid
PAr	Copolyester of bisphenol A tere/isophthaloyl (2:1:1)
PHMT	Poly(hexamethylene terephthalate)
PHP	Poly(hydroxy ether of phenolphthalein)