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Blending Effect of Maleic Anhydride-Styrene-Methyl Methacrylate Terpolymer on Polyvinylchloride (Pvc)/Polystyrene (Ps) Mixtures

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ABSTRACT

The blending effect of poly maleic anhydride-styrene-methyl methacrylate (MA-St-MMA) terpolymer on non-miscible PVC and Polystyrene was studied depending on their thermomechanical properties. Depending on the amount of the synthesized and used compatibilizer the tensile strength, modulus, and thermomechanical properties of the blends are enhanced. The unmodified and blends with small amounts of compatibilizer exhibit two-step degradation whereas those containing 6, 8 and 10 percent compatibilizer showed a single glass transition (Tg). All the results reveal that PS/PVC mixtures modified with MA-St-MMA have superior mechanical properties and phase adhesions than mixtures without terpolymer.

Keywords: Polymer blend, Compatilization, Maleic anhydride, Poly vinylchloride, Polystyrene, Terpolymer

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Introduction

From an economic point of view, polymer blending is an important scientific activity because this technique sometimes allows the creation of technical plastics with superior properties. However, for thermodynamic reasons, many polymers do not mix homogeneously at molecular-scale without a suitable compatibilizer. Factors preventing homogeneous mixing are phase separations and interfacial tensions between the two polymers. One of the ways to refine the phase separation morphology of blends composed of two polymers is by adding a compatibilizer [1]. There are many successful studies in which polymer pairs are blended by adding a maleic anhydride based co- or terpolymers as compatibilizers [2-6]. In immiscible binary polymer systems, co- or terpolymers containing maleic anhydride and styrene often act as excellent compatibilizers. In immiscible resins, if such a compatibilizer is used, polar maleic anhydride adds stiffness, thermal stability, and chemical activity to the system, while non-polar styrene contributes to the ease of processing [7, 8]. Polymer mixtures are usually prepared by extruders, banbury mixers, and solution casting.

Due to the synthesizable amount of compatibilizer used in this study, solution casting method was preferred in order to produce test specimens in sufficient quantity. By using the common solvent determined in the study, it was possible to obtain the desired polymer mixtures via solution casting.

Materials and Methods

Apparatus

In the study, DSC measurements were recorded by Shimadzu DSC instrument at a heating rate of 10°C/min under nitrogen atmosphere. Thermomechanical analysis (TMA) was conducted on Perkin Elmer Pyris Diamond DMTA instrument at penetration mode . The storage (E’) and loss (tan δ) moduli were measured at a heating rate of 5ºC/min under nitrogen. All experiments were done on solution cast films.

Chemicals

A commercially available PS compounding grade, and PVC powder with 57 % chlorine content were purchased from PETKIM (Turkey) and used as provided. Maleic anhydride (MA), Styrene (St), and Methyl methacrylate (MMA) and benzoyl peroxide used in the synthesis of MA-St-MMA terpolymer were at analytical grade and Sigma-Aldrich brand. All of the organic solvents used are analytical grade and are Sigma-Aldrich brand.

Synthesis of MA-St-MMA Terpolymer

The terpolymer agent was synthesized according to protocols previously used in our laboratory [9]. The three monomers in molar ratios of 2:1:1 were allowed to react in a glass flask. The volume of the triple mixture prepared as 14.7 g MA 1.5 mol. (dm^3)$^{-1}$, 8,59 mL St 0.75 mol. (dm^3)$^{-1}$ and 7,51 g MMA 0.75 mol. (dm^3)$^{-1}$ was completed to 100 mL with 2-butanone solvent and complete dissolution was achieved. 0.15% by mole Benzoyl peroxide was added and the mixture was reacted at 70 °C for 3 hours. The resulting viscous solution was transferred to a glass beaker and treated with excess ethanol. The precipitated resin was washed 5 times with ethanol. Then placed in a vacuum oven and left to dry at 35 °C.

Co-solvent Determination

Solubility tests of immiscible polymer pairs PS and PVC and the terpolymer were performed to determine the co-solvent. For this test, 0.1 grams of each polymer sample was added separately to 10 mL of selected solvents. Thus, solutions with a concentration of 1g/dL were obtained. Each separate solution was left overnight to complete dissolution by diffusing the solvent. Clear solutions were recorded as soluble, turbid solutions as partially soluble, and solutions with residue at the bottom were recorded as unsoluble.

Preparation of PVC/PS Blends

Powdered polymers containing equal parts PS and PVC by mass were dissolved in 25 mL THF solvent. 0, 2, 4, 6, 8, and 10 % compatibilizer terpolymer was added to these solutions. These solutions were poured into a petri dish. The solvent was evaporated. Solid mixtures obtained at the bottom of the Petri dish were used as specimens. The samples obtained are given in Table 1.

Table 1. Prepared PS/PVC and compatibilizer blends

PS/PVC C/g.dL^{-1}	MA-St-MMA % (w/w)					
	0	2	4	6	8	10
1.0	x	x	x	x	x	x

Thermal Studies

The glass transition temperature (Tg) of pure polymers and their blends were recorded at Shimadzu DSC instrument. The calibration were done with an Indium standard and the measurements carried out under continuous nitrogen flow. The weight of the mixtures used in DSC pan was kept as 10 miligram and the heating rate was set at 10 °C/min.

Mechanical Studies

The mechanical studies were conducted using Universal Tensile Machine (UTM). The measurements of the mechanical properties of the stretched specimens were done at 25 °C.

Results and Discussion

Selection of the Common Solvent

The dissolution experiments showed that the co-solvent of the polymers is THF, The findings are given in Table 2.

Table 2. Dissolution data of PVC, PS and MA-St-MMA polymers.

Polymer	THF	Toluene	MEK	DMSO	DMF
PVC	+	±	+	-	+
PS	+	+	±	-	+
MA-St-MMA	+	-	+	±	±

(+) Soluble (–) Insoluble (±) partially Soluble

Characterization of the Synthesized Compatibilizer

When the infrared peaks are read from Figure 1; The peak at 1780 cm^{-1} and weak peak at 1825 cm^{-1} are belong to stretching of anhydride carbonyl (C=O) groups. The peak at 1760 cm-1 belongs to vibrations of the methyl methacrylate (C = O) groups. The two peaks appeared between 2900 cm^{-1} and 2800 cm^{-1} in the spectrum are belong to stretching vibration of –CH sp^{3} of the MMA. Again the vibrations of these methyl groups are observed at 1445 cm^{-1}. The both peaks at 705 cm^{-1} and 870 cm^{-1} are C-H stretchings of the styrene part.[6] It can be said that the terpolymer used as compatibilizer was successfully synthesized.

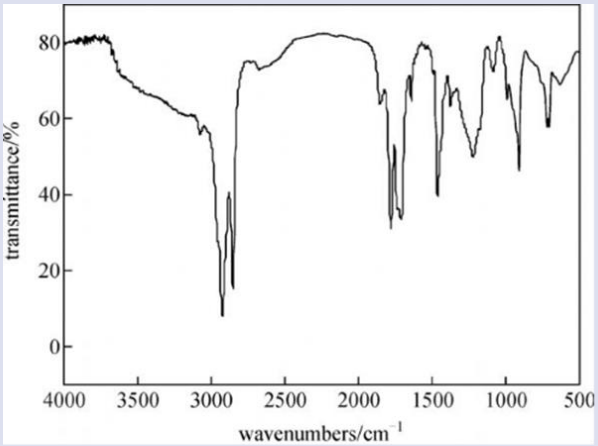

Figure 1. FTIR spectrum of the synthesized MA-St-MMA terpolymer

Thermal Studies

Tg's, obtained from DSC were given at Figure 2. As shown in Fig. 2, two glass transition temperatures were obtained for the blends contained 0, 2 and 4 % MA-St-MMA compatibilizer. The glass transition temperature (Tg) of a polymer blend is often taken as a criterion for determining the miscibility of its components. [10-13] The two Tg's obtained corresponding to their homopolymer glass transitions are due to each component gaining segmental mobility independent of the other as a result of their incompatibility. As can be clearly seen in Figure 2, mixtures with little or no compatibilizer added have two step Tg transitions. However, when the amount of compatibilizer increased and showed its blending effect, specimens showed a single Tg transition. Single Tgs' was read for the mixtures with compositions 6, 8 and 10 % MA-St-MMA which refer to compatibility of these blends for these compositions. Tg temperatures read from the DSC thermogram seen in Figure 2; for mixtures where compatibilizer is effective, single and determined as between 88-89 °C.

At Figure 3, it is interesting that in the temperature range of 25-50 °C all the mixture samples expanded and pushed the probe up. It is possible to accept this as an experimental error. However, at later temperatures association of the blending effect of the used compatibilizer particles probably accounts for the decreased penetration. At these temperatures the probe penetrates the samples at a rate invertedly proportional to their Young modulus' (Fig.4). Again, from Figure 4, as the compatibilizer ratio increases, the Young's modulus, which is a measure of stifness [14-15], increases.

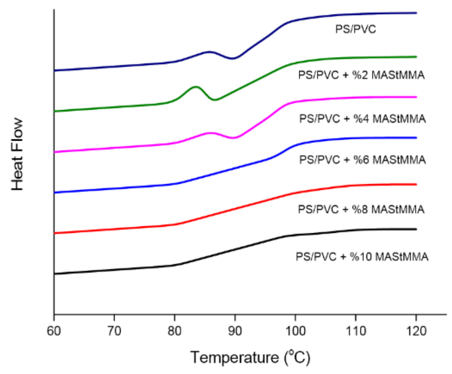

Figure 2. DSC curves of the blends

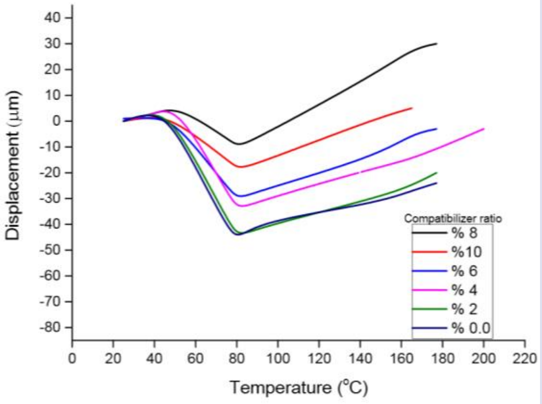

Figure 3. TMA curves of the blends

Mechanical Tests

The addition of MA-St-MMA as compatibilizer for PS/PVC blends increased the tensile strength (Fig. 5), and modulus but reduced the britlleness (Fig. 6). Figure 6 shows typical stress-strain curves of the blends at various combatibilizer compositions.

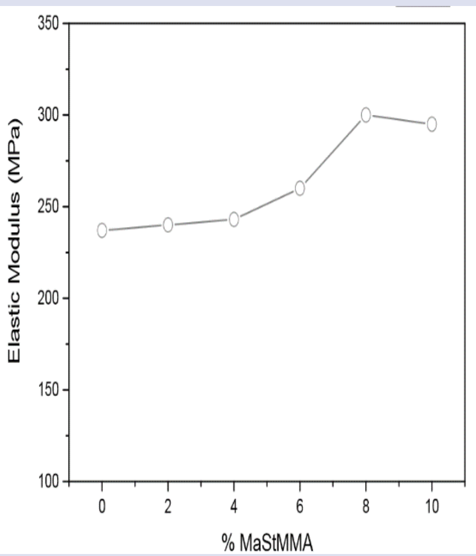

Figure 4. Variation of elastic modulus with compatibilizer rate

With lower MA-St-MMA content, the test specimens of the blends break before reaching the yield point. This clearly demonstrates the high brittleness of unmodified blends. In contrast, 4, 6, 8 and 10 % modified PS/PVC mixtures exhibit ductile behavior; and these samples were not broken before the yield point was reached.

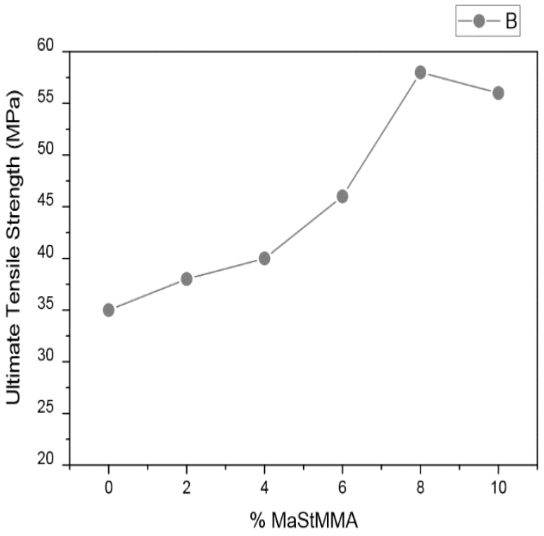

Figure 5. Variation of ultimate tensile strength with compatibilizer rate

When all mechanical findings are evaluated together it can be said that; the terpolymer compatibilizer used, preventing phase separation by acting as a bridge between polymer strands and thus made them miscible, as a result of this increased stiffness, tensile strength and ductile behavior of the blends.

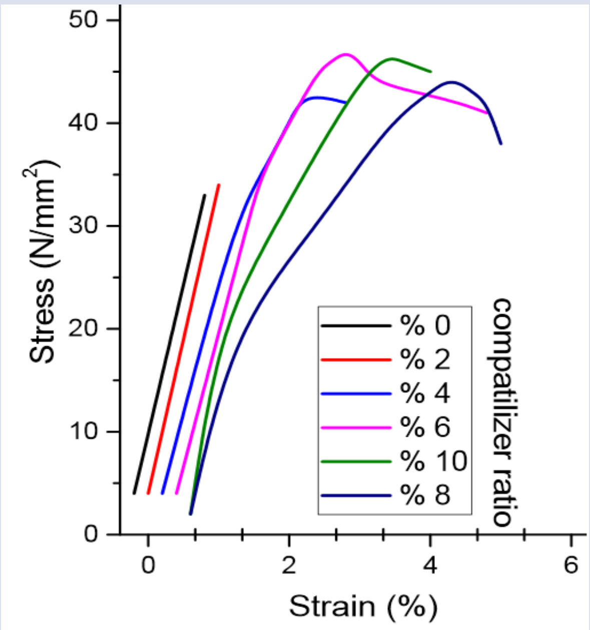

Figure 6. Typical stress-strain behaviour of PS/PVC blends with different compatibilizer ratios

The monomers that the terpolymer is synthesized are shown in Figure 7 below.

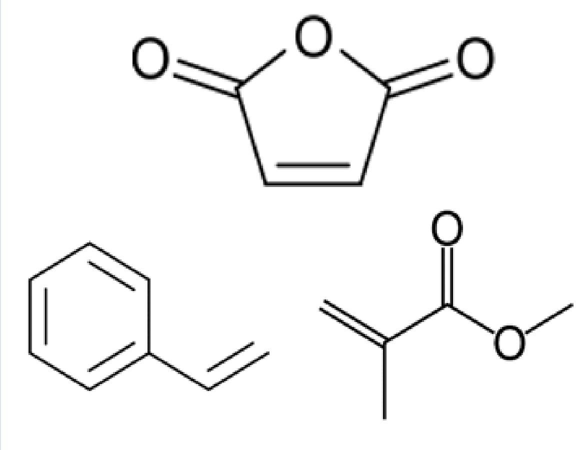

Figure 7. Chemical structures of the terpolymer's monomers (From left to right: MA, St, MMA)

Conclusion

At the end of this study, we showed that the MA-St-MMA terpolymer acts as an effective compatibilizer between polyvinyl chloride and polystyrene. In addition, with this study MA-St-MMA terpolymer not only provided PS/PVC pair mixing, but also improved its thermal and mechanical properties. With the findings it was seen that the thermomechanical properties of the immiscible polystyrene and polyvinyl chloride couple were improved with the compatibilizer used. By this study, it was seen that the terpolymer containing maleic anhydride was a good compatibilizer. Also, using co- or ter-polymers containing reactive polymers such as maleic anhydride to mix immiscible polymers seems to be a viable route.

Finally, it can be stated that, solution casting, and thermomechanical studies, are simple, low-cost and rapid methods which can be used as a useful tests to research the miscibility of polymer blends.

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Conflicts of interest

The author state that did not have conflict of interests

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