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Material Properties

Rheology, morphology and mechanical properties of compatibilized poly(vinylidene fluoride) (PVDF)/thermoplastic polyurethane (TPU) blends

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Abstract

Compatibilized blends of poly(vinylidene fluoride) (PVDF) and thermoplastic polyurethane (TPU) were developed using maleated PVDF (PVDF-g-MA). Excellent compatibilization between PVDF and TPU was demonstrated by rheological, morphological, and mechanical measurements. The introduction of PVDF-g-MA into the PVDF/TPU blends caused an increase in viscosity and storage modulus. Much finer morphologiy was clearly observed by SEM. The tensile tests showed that the tensile strength and ultimate elongation achieved a significant improvement with addition of PVDF-g-MA.

Keywords: Compatibilization; Maleated poly(vinylidene fluoride) (PVDF-g-MA); Thermoplastic polyurethane (TPU)

1. Introduction

Poly(vinylidene fluoride) (PVDF) has excellent mechanical properties, excellent chemical resistance, and remarkable weathering resistance [1–3]. Thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics with elastomeric properties. Due to TPUs excellent physical properties, chemical resistance, abrasion resistance, good adhesion and ease of processing, its application can be found in almost all industrial branches, such as engineering materials, coatings, adhesives as well as films [4–7]. A high-performance engineering polymer might be produced by blending these two polymers. Unfortunately, both TPU and PVDF polymers are incompatible at all compositions. Yue and Chian [8] reported that the TPU/PVDF blends showed layered-type structures, due to their immiscibility, which resulted in low mechanical properties.

Recently, modification of PVDF by grafting has received much attention. Chen and Hong [9] synthesized a series of copolymers P(MMA-SSA) with different monomer unit ratios via free radical solution polymerization. By blending the resultant P(MMA-SSA) with PVDF in an organic solvent, followed by casting, a uniform distribution of nano-scale domains of SSA segments was found throughout the membrane matrix. Hester et al. [10] reported the direct preparation of amphiphilic graft

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copolymers having PVDF backbones by ATRP of hydrophilic side chains initiated at the secondary halogenated sites of PVDF. ATRP of a polyoxyethylene methacrylate (POEM) macromonomer incorporating roughly nine ethylene oxide (EO) units was used to prepare an amphiphilic graft copolymer, PVDF-g-POEM. Zhai et al. [11] synthesized a PVDF-g-PBIEA copolymer via graft copolymerization of an inimer, 2-(2-bromoisobutyryloxy)ethyl acrylate (BIEA), with ozone-pretreated PVDF. The BIEA polymer (PBIEA) side chains allowed the initiation by ATRP of functional monomers on the copolymer and the membrane surface. Hence, PVDF-g-PBIEA-ar-NaPSS copolymer was prepared via ATRP of sodium 4-styrenesulfonate (NaSS) initiated from the PVDF-g-PBIEA copolymer side chains. Ying et al. [12] synthesized AAc-g-PVDF copolymer via thermally induced graft copolymerization with acrylic acid (AAc) in NMP, with ozone-pretreated PVDF. Clochard et al. [3] reported the investigation of grafting of acrylic acid in/onto pre-irradiated PVDF films, and the examination of reaction parameters, monomer concentration and inhibitor concentration. Among various techniques for grafting in semicrystalline polymers, ionizing radiation has the advantage of inducing the formation of stable radicals able to initiate the monomer grafting in a second step. This elegant and easy technique is known as post-radiation grafting.

TPU is a linear segmented block copolymer composed of alternating hard (adduct of diisocyanate and small glycols) and soft (e.g. polyester, polyether, hydrocarbon, silicone, etc.) segments. The hard segments are held together by interchain hydrogen bonds to form physical crosslinks. At melt temperatures, the hydrogen bonds break and linear primary chains are released. Meanwhile, urethane linkages (–NHCOO–) in the hard segments become unstable and reversibly decompose into free isocyanate and alcohol [13]. Lu et al. [14] investigated reactions between a series of model urethane and various types of functionalities including hydroxyl, epoxy, acid, anhydride, secondary amine and primary amine. It was found that amine (both primary and secondary) is the most reactive functional groups toward urethane linkage among all used functionalities. Anhydride, acid, and hydroxyl groups may also be used depending on specific situations. Lu et al. [14–16] also investigated compatibility of the amine functionalized PPs (PP-g-NH_2 and PP-g-NHR) with TPU, and found that the PP-g-NHR shows slightly higher compatibility with TPU than the PP-g-NH_2. Although amine is the highly reactive functional group toward urethane linkage, it can react with PVDF by the dehydrofluorination process. Anhydride, acid and hydroxyl groups are well-suited functionalities for reactively compatibilizing PVDF/TPU blends.

In this work, we synthesized PVDF-g-MA by the mixing of pre-irradiated PVDF and maleic anhydride. Their compatibilization effects on the PVDF/TPU blends were investigated by rheological, morphological, thermal and mechanical measurements.

2. Experimental

2.1. Materials

The PVDF was SOLEF 11010 from Solvay. The TPU (TPU, Desmopan W DP 85085A, Shore hardness: 85A) was provided by Bayer. Maleic anhydride (MA) was from Beijing Chemical Plant. Dimethyl sulfoxide (DMSO) and ethanol were from Beijing Chemical Plant.

2.2. Radiation grafting of PVDF with MA: PVDF-g-MA

About 60 g of PVDF were placed in polyethylene lined paper envelopes and irradiated with a ^{60}Co to a total dose of 15 kGy. After irradiation, PVDF and MA were blended in a Haake torque rheometer (Rheomix-600P) equipped with two counter-rotating roller blades at 185 °C and 30 rpm for 5 min. The polymer was dried at 100 °C in a vacuum oven for 24 h before processing to eliminate the residual MA. After drying, the polymer was purified by dissolving in DMSO and precipitating in ethanol. Finally, the polymer was dried under vacuum overnight at 100 °C; the grafted MA concentration of 1.06 wt% was determined by chemical titration.

2.3. Melt blending

Melt blending of PVDF, TPU and PVDF-g-MA was performed in a Haake torque rheometer (Rheomix-600P) equipped with two counter-rotating roller blades at 185 °C and 40 rpm for 5 min.

2.4. Rheology

Oscillatory rheological characterization of the blends was carried out at 180 °C on a Modular

Compact Rheometer (MCR300, Paar Physica) with a 25 mm parallel plate arrangement. The rheometer oven was purged with dry nitrogen during measurement to avoid degradation, and measurements were made over a frequency range of 0.1–100 s^{-1}. Samples were compression-molded at 185 °C under a pressure of 5 MPa for 5 min.

2.5. Scanning electron microscopy

The blends were cryo-fractured in liquid nitrogen. The fracture surface was coated with gold for examination of morphology by scanning electron microscope (XL30ESEM-FEG) at 20.0 kV accelerating voltage.

2.6. Tensile test

Mechanical properties of the samples were determined on an Instron 1121 testing machine according to GB/T 1040-1992 (China).

3. Results and discussion

3.1. Rheology

Plots of complex viscosity versus angular frequency for the PVDF/TPU blends at 70/30 with various content of PVDF-g-MA are given in Fig. 1. It can be noted that the PVDF/TPU blend without PVDF-g-MA has significantly lower viscosity than the others. This abrupt viscosity drop is probably due to interfacial slip between the uncompatibilized phases, since there is very weak interaction between the PVDF and TPU. After the introduction of the anhydride-functional group, the PVDF/TPU/PVDF-g-MA blends exhibited higher viscosities. However, viscosities of those PVDF/TPU/PVDF-g-MA blends do not differ much in the range from 0.1 to 100 1/s.

Storage modulus versus angular frequency for the PVDF/TPU blends at 70/30 with various PVDF-g-MA contents is reported in Fig. 2. As for the case of complex viscosity, the PVDF/TPU/PVDF-g-MA blends show an increase in storage modulus, as compared with the PVDF/TPU blends, over the whole range of frequency investigated.

3.2. Morphology

The existence and effect of compatibilizers can usually be seen from the blend morphology. Scanning electron microscopy (SEM) is a powerful tool to examine morphology in polymer blends. In secondary electron images (SEI), PVDF and TPU cannot be distinguished clearly, so backscattered electron images (BEI) was chosen in this study to examine blend morphology. Fig. 3 shows the SEM micrographs of the PVDF/TPU blends at 70/30 with various PVDF-g-MA contents. It is observed that these blends could be characterized by particle-dispersed type of morphology, in which the minor component is dispersed in the matrix of the other. Compared with the PVDF/TPU blend,

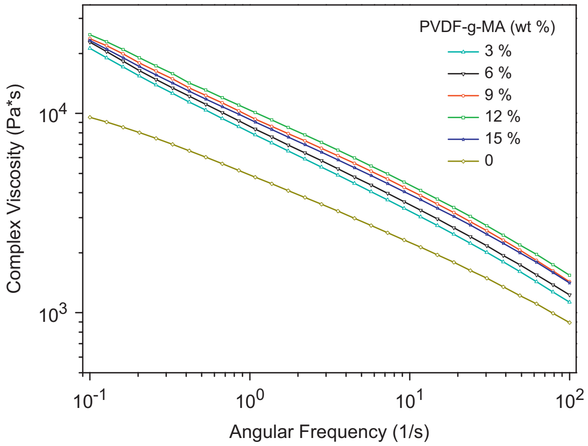

Fig. 1. Complex viscosity as a function of angular frequency for the PVDF/TPU blends (weight ratio: 70/30) with various content of PVDF-g-MA.

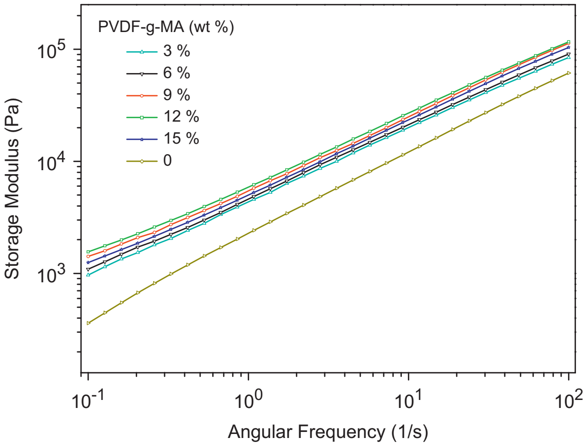

Fig. 2. Storage modulus as a function of angular frequency for the PVDF/TPU blends (weight ratio: 70/30) with various content of PVDF-g-MA.

the PVDF/TPU/PVDF-g-MA blends display significantly finer morphology, i.e. much reduced particle size of the dispersed phase. In addition, particle size distributions are much narrower. Nonetheless, morphology differences are relatively small among those PVDF/TPU blends with various PVDF-g-MA contents.

3.3. Mechanical properties

Fig. 4 illustrates the stress-stain curves of the PVDF/TPU blends at 70/30 with various PVDF-g-MA contents. The values of tensile strength, elastic modulus, and ultimate elongation are listed in Table 1. Pure TPU is ductile elastomer, which can contribute to ultimate elongation in PVDF/TPU blends. If the blends are well compatibilized, both ultimate elongation and tensile strength will be improved. It can be noted that both tensile strength and ultimate elongation are significantly higher after adding PVDF-g-MA in the PVDF/TPU blends. These significant improvements in the mechanical properties are due to finer morphology and stronger interfacial adhesion between PVDF

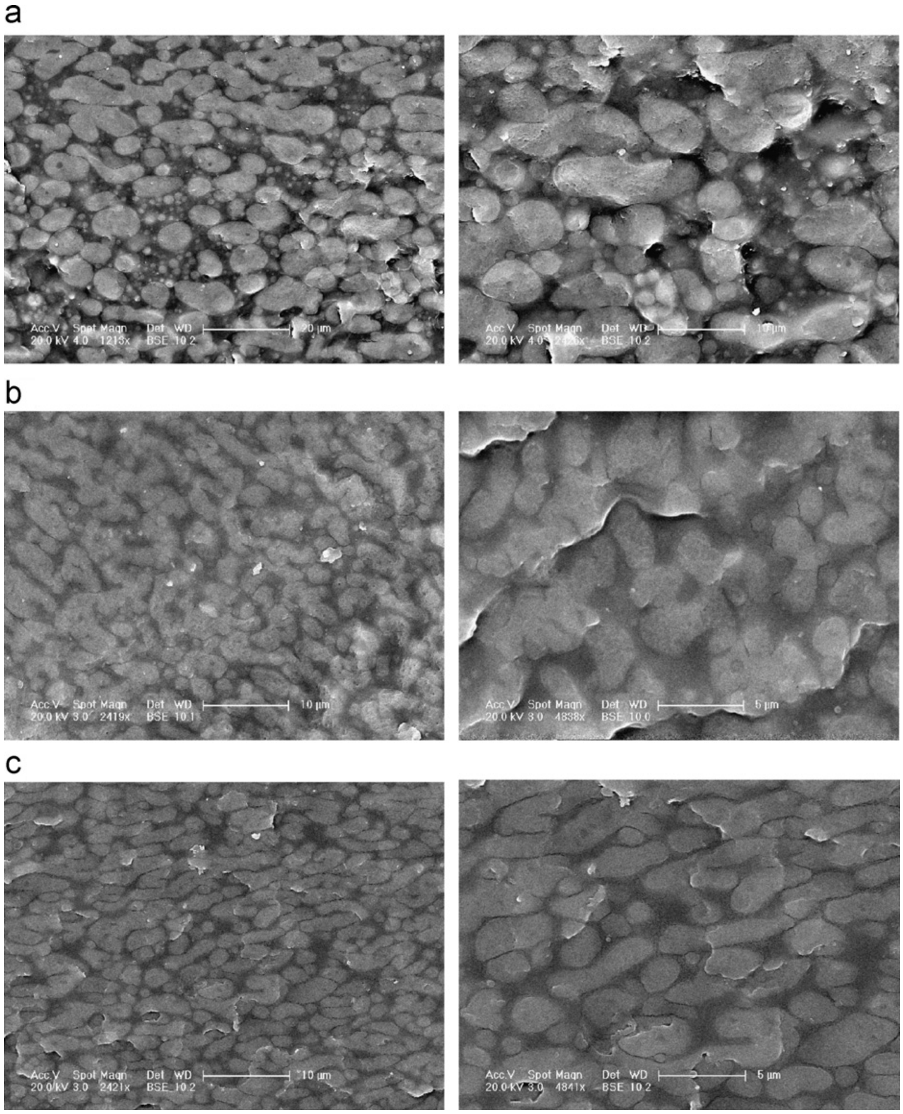

Fig. 3. Scanning electron micrographs of the PVDF/TPU blends (weight ratio: 70/30) with PVDF-g-MA content of: (a) 0 wt%, (b) 3 wt%, (c) 6 wt%, (d) 9 wt%, (e) 12 wt%, (f) 15 wt%.

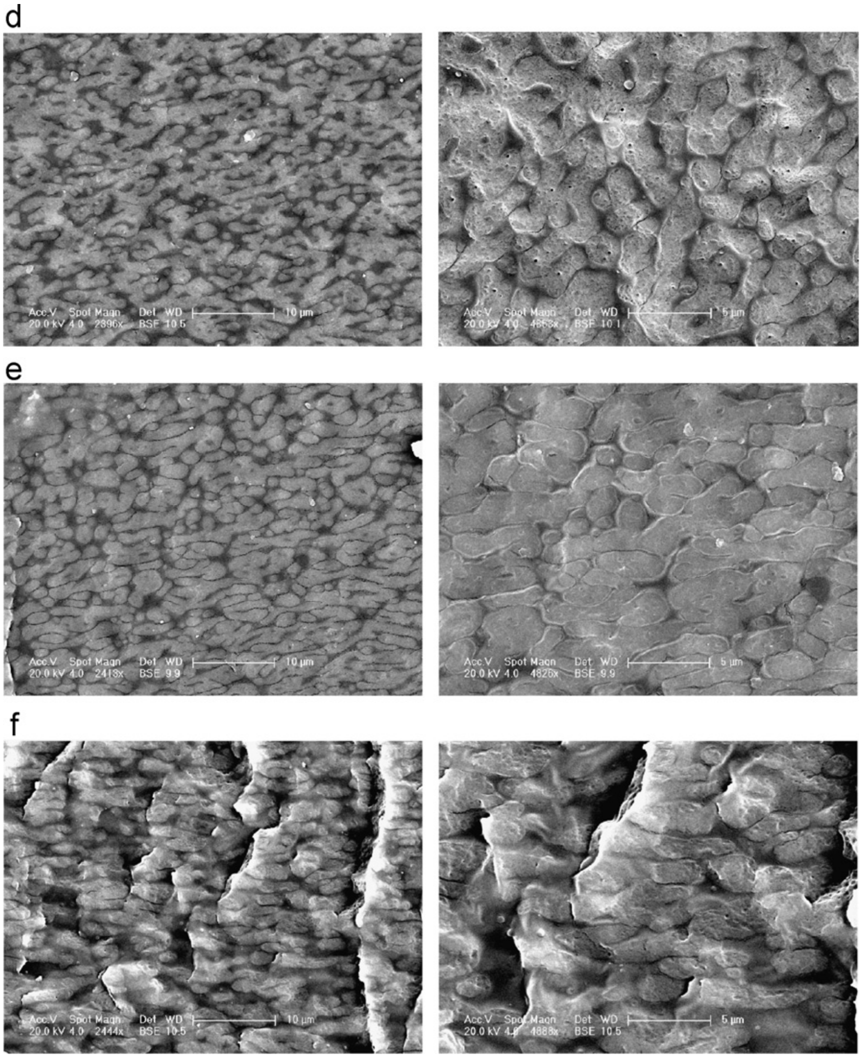

Fig. 3. (*Continued*)

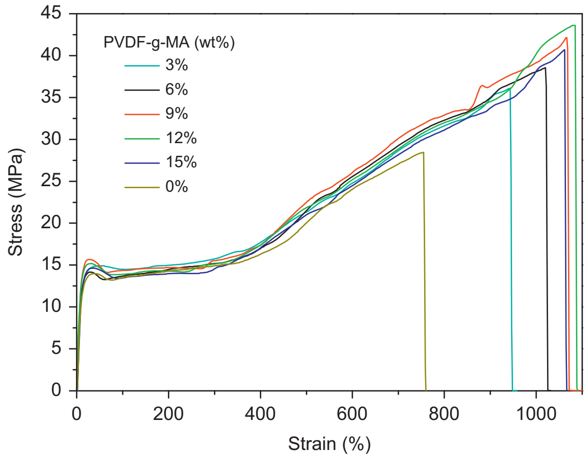

Fig. 4. Stress–strain curves of the PVDF/TPU blends (weight ratio: 70/30) with various content of PVDF-g-MA.

Table 1
Mechanical properties of the PVDF/TPU blends (weight ratio: 70/30) with various content of PVDF-g-MA

PVDF-g-MA content in PVDF/TPU blends (wt%)	Tensile strength (MPa)	Elastic modulus (MPa)	Ultimate elongation (%)
0	28.448	173.55	755.08
3	36.119	178.25	943.59
6	38.559	176.51	1022
9	42.147	209.63	1066.1
12	43.613	195.74	1083.8
15	40.707	158.78	1061.8

and TPU phase. All the compatibilized blends with different PVDF-g-MA contents showed quite similar stress–strain behavior.

4. Conclusions

Compatilized PVDF/TPU blends can be produced by adding PVDF-g-MA. Excellent compatibilization between PVDF and TPU was confirmed by rheological, morphological and mechanical properties. The introduction of PVDF-g-MA into the PVDF/TPU blends caused an increase in viscosity and storage modulus. SEM observations revealed that PVDF-g-MA addition could lead to much finer morphology. The tensile strength and ultimate elongation achieved a significant improvement with addition of PVDF-g-MA.

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