



Dynamic rheology and dielectric relaxation of poly(vinylidene fluoride)/poly(methyl methacrylate) blends



Yunxiang Zhang^a, Min Zuo^{a,*}, Yihu Song^{a,*}, Xueping Yan^b, Qiang Zheng^a

^a Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^b Department of Material Science and Engineering, Central South University, Changsha 410083, China

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ABSTRACT

The molecular relaxations in melt-extruded poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends with less than 40 wt% PMMA were investigated using dynamic rheological measurement and broadband dielectric spectroscopy. According to dynamic rheology, the total chain entanglement density of the blend melts increased with adding PMMA, and the dissimilar chains were more likely to entangle with each other than similar ones. Furthermore, PMMA facilitated the relaxation process. The dielectric temperature spectra revealed strong structural heterogeneity in the semicrystalline blends whose α_a and α_c relaxations were accelerated by increasing PMMA content. The α_a and α_c relaxations were shown to follow the Vogel–Fulcher–Tamman and Arrhenius equations, which allows assigning their molecular origins clearly to amorphous PVDF interphase and the amorphous portions within the crystalline PVDF phase, respectively. However, there exist structural heterogeneities in amorphous PVDF/PMMA mixture phase associated to intermolecular entanglement between dissimilar chains, giving rise to one or two α_m relaxations in the dielectric temperature spectra depending on the PMMA content.

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1. Introduction

Semicrystalline poly(vinylidene fluoride) (PVDF) has excellent film-forming ability, mechanical property, chemical inertness, and thermal stability, providing a wide range of applications [1,2]. However, the high crystallinity and melting point make it difficult to process, and the low surface tension also limits the application in ultrafiltration membrane and various optoelectronics, especially backing sheet and encapsulating films for Si-based solar cells [3]. For these purpose, several methods for improving PVDF performances have been investigated, such as coating [4], grafting [5], and blending [6]. Among these methods, blending has the advantage of being easy to perform and realize industrially.

PVDF is usually blended with oxygen-containing hydrophilic polymers such as poly(methyl methacrylate) (PMMA) to make blends with desired strength and electric properties [6,7]. PVDF/PMMA blends are completely miscible in the melt state, at all compositions, resulted from dipole–dipole interactions between PMMA and PVDF [8,9]. The blends exhibit a lower critical solution temperature around 330 °C [10]. However, upon cooling from the melt,

the blends show upper critical solution temperature strongly dependent on the blend composition and undergo liquid–liquid and crystallization-induced phase separations in sequence [11]. The solidified blends exhibit either single or multiphase microstructures depending on the conditions of temperature, pressure, and flow to which they are subjected [12,13]. At PVDF content above 40 wt%, the blends are semicrystalline and are consisted of a PVDF crystalline phase, a PVDF amorphous phase, and a PVDF/PMMA mixed amorphous phase [14]. It is reported that PMMA is accommodated between the PVDF lamellae to increase the thickness of the interlamellar amorphous region with increasing PMMA content [15]. However, it is also reported that PMMA is partially excluded from the interlamellar region of PVDF at low crystallization rates [16]. The formation of an interphase in semicrystalline blends has also been proposed for accounting for the gradual transition from the perfect order in the crystal to the isotropy in the amorphous phase [17,18]. The local phase separation which occurs, despite favorable interactions between PMMA and PVDF, is attributed to a PVDF crystal–amorphous interphase (2.5 nm) which rejects PMMA segments [19]. Both the rigid PMMA segments and the PVDF crystals impose confinement effects to the dynamics of the amorphous PVDF segments [20], and the relaxation dynamics in the interphase vary as a function of blend composition [14].

* Corresponding authors. Tel./fax: +86 571 87953075.

E-mail addresses: kezuomin@zju.edu.cn (M. Zuo), s_yh0411@zju.edu.cn (Y. Song).

However, Hahn et al. found that the dielectric relaxation assigned to the glass temperature (T_g) of PVDF remains invariant in the blends with different constituents [21]. There still exist some obvious controversies in the molecular origins about the effect of PMMA on the PVDF relaxation in the semicrystalline blends.

In this paper, the effect of PMMA on the PVDF relaxation in the blends is investigated by using rheological method in the melt state and using dielectric relaxation spectroscopy in the solidified semicrystalline state. The dynamics of various relaxations depending on the blend composition are analyzed to reveal the intermolecular interaction and its influence on the polymer dynamics.

2. Experimental section

2.1. Materials

PVDF resin (FR906) with the melting point of 168 °C was obtained from Shanghai 3F New Mater. Co., China. PMMA resin (IF850) was supplied by LG Co., Korea. Table 1 lists their number- and weight-averaged molecular weights, M_w and M_n , determined from gel permeation chromatography (Millipore Co., USA) using PMMA as the calibration standard.

2.2. Sample preparation

The blends were molten blended by using a twin screw extruder (PRISM TSE 16 TC, Thermo Electron Co., USA) with the temperatures maintained at 180 °C, 185 °C, 190 °C, 190 °C, and 185 °C from the hopper to the die. PVDF, PMMA and their blends were compression-molded at 190 °C and 10 MPa pressure for 10 min to form the test samples and ensure that the macromolecular orientation can relax to an equilibrium isotropic state. Throughout the text, the ratio of PVDF to PMMA in the blend was reported on a weight basis.

2.3. Characterizations

Rheological measurements were carried out using a strain-controlled advance rheometric expanded system (ARES-G2, TA, USA) with a parallel-plate geometry (25 mm in diameter) at temperatures from 160 to 240 °C. Sample disks with the thickness of about 1 mm were placed between the parallel plates and melted before the tests. To ensure that all the oscillatory measurements were performed within the linear viscoelastic regime, a dynamic strain sweep test was first conducted in a strain amplitude (γ) range from 0.01% to 100% with an angular frequency (ω) of 10 rad s⁻¹. Dynamic frequency sweeps from 150 to 0.01 rad s⁻¹ were carried out under $\gamma = 5\%$ in the linear viscoelastic region. Stress relaxation tests were also performed at $\gamma = 5\%$ at 190 °C.

Calorimetric measurements were performed on a differential scanning calorimeter (DSC, Q-100, TA, USA) in a dry nitrogen atmosphere. All the samples were firstly heated up to 200 °C at the heating rate of 10 °C min⁻¹ and held at this temperature for 10 min to eliminate their thermal history, followed by quenching to -80 °C. The glass transition temperature (T_g) was obtained from the second heating scanning at the same heating rate and taken as the midpoint of heat capacity change.

Table 1
Density ρ and molecular weight distributions of PVDF and PMMA.

	ρ (kg cm ⁻³)	M_n	M_w	M_w/M_n
PVDF	1.78	7.9×10^4	20.7×10^4	2.61
PMMA	1.18	4.2×10^4	8.6×10^4	2.04

The microstructure and morphology were observed by a scanning electron microscopy (SEM, S-4800, Hitachi Ltd., Japan). The samples were put in liquid nitrogen for brittle fracture and then the sections were etched for 24 h in a toluene solution. After the solvent evaporated at an ambient environment, the sections were sprayed for the measurements.

Dielectric measurements were conducted on a Novocontrol alpha high resolution dielectric analyzer (Novocontrol GmbH Concept 40, Novocontrol Tech., Germany) equipped with a Novocool cryogenic system for temperature control. The films of about 0.1 mm in thickness were placed between two gold electrodes of 20 mm in diameter. Frequency sweeps were carried out from 10⁻² to 10⁷ Hz at temperatures from -120 to 160 °C. Temperature sweeps were performed at a commonly used frequency of 10 Hz and a heating rate of 3 °C min⁻¹ to examine a variety of relaxations with respect to the composition of the blend.

3. Results and discussion

Time-temperature superposition (TTS) principle can be used to determine the phase separation temperature for polymer blends [22] and its validity can be further checked by the Han plot of storage modulus (G') versus loss modulus (G'') [23]. If the data points of the different isotherms fall on a common line, or at least the data scatter or the line width is not too broad, the TTS principle should be valid and the blends are miscible [9,24].

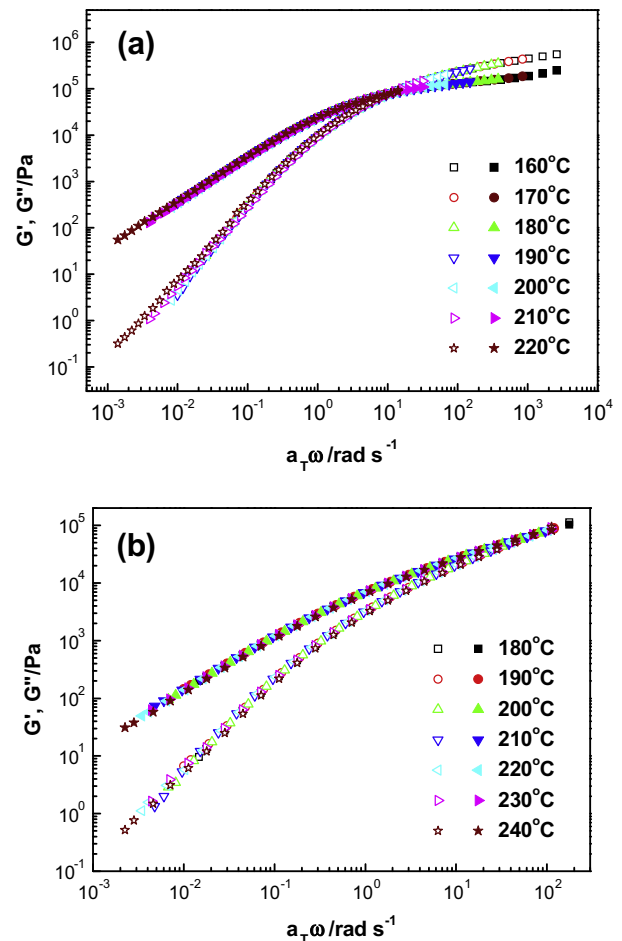


Fig. 1. Master curves of storage and loss moduli (G' and G'') as a function of reduced frequency ($a_T\omega$) for (a) PMMA and (b) PVDF at the reference temperature of 190 °C, respectively. a_T is shift factor for constructing the master curves.

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