

Preparation and Thermomechanical Characterization of Poly(vinyl chloride) Blends Compatible with Terpolymer-Containing Maleic Anhydride

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ABSTRACT: In this study, I aimed to change the thermomechanical characteristics of poly(vinyl chloride) (PVC), which is widely used in commercial areas. Copolymers containing maleic anhydride (MA) units are commonly used to obtain compatible polymer blends. In our study, PVC blends were also prepared with the terpolymers with and without anhydride units. I assumed that the impact of the terpolymer on the thermomechanical characteristics of the PVC material could be more effectively controlled. For this purpose, two sets of six differ-

ent blends of PVC with or without MA were synthesized, among which one was pure PVC, but the other five blends contained 2, 4, 6, 8, and 10% terpolymer. In conclusion, I observed that the terpolymer with the MA unit more regularly changed the thermomechanical characteristics of PVC. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1586–1589, 2004

Key words: poly(vinyl chloride) (PVC); blends; stress; strain

INTRODUCTION

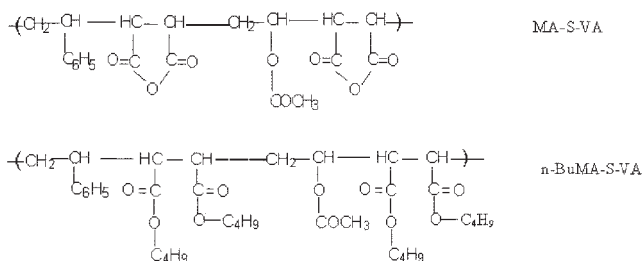
Polymer blends generally exhibit poor mechanical properties because of incompatibility and phase separation.^{1–3} Recently, the commercial importance of polymer blends has become increasingly high because the performance of polymers can be improved by simple blending to fulfill the industry's need for high-performance materials. However, many of these high-molecular-weight polymers are immiscible and incompatible, which leads to poor final properties.⁴ Maleic anhydride (MA) is a reactive monomer, and the copolymers or terpolymers of MA are called *reactive polymers* because of the existence of MA units in their main chains.⁵ The compatibilizer produced by reactive compatibilization exhibits more improved interfacial adhesion in blends than a common physical compatibilizer. Recently, reactive compatibilizers have been extensively investigated as a way to overcome poor properties of blends. The use of MA is one of the most common ways in reactive blending to improve the

interfacial adhesion in immiscible polymer blends.⁶ Copolymers and terpolymers containing MA can be modified because they contain anhydride functional groups in the backbone.^{7–10} In many studies, different copolymers of MA have been used as compatibilizers in the obtained blends of compatible polymers.^{11–17}

It is generally accepted that poly(vinyl chloride) (PVC) is unstable when exposed to high temperatures during its molding and applications. PVC undergoes extensive autocatalytic dehydrochlorination with the formation of conjugated double bonds.¹⁸ PVC plays an important role in the plastic industry and is one of the most versatile thermoplastics, but it must be combined with a number of additives before processing.¹⁹ Many experimental methods have been used to investigate PVC–polymer miscibility.^{18,20–23}

This study was conducted to show the utility of reactive polymers in the preparation of compatible polymer blends. Two sets of six different blends of PVC with or without MA units were prepared that contained various amounts of terpolymers ranging from 0 to 10%. I concluded that the terpolymer with MA units more regularly changed the thermomechanical characteristics of PVC. Thus, the MA terpolymer containing a reactive monomer was observed to constitute a compatible blend with PVC.

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Scheme 1 Molecular structure of MA-St-VA and *n*-BuMA-St-VA terpolymers.

EXPERIMENTAL

Materials

The PVC sample (Breon 113) was obtained from Sussex, United Kingdom. Tetrahydrofuran (THF) was obtained from Prolabo Co. (Nice, France), was analytical grade, and was purified just before use. Vinyl acetate (VA) and styrene (St) (Germont, Merck) were distilled before use. They had the following characteristics; VA had a boiling point of 72°C, and St had a boiling point of 138 °C. MA (Sigma, USA) was purified before use by recrystallization from anhydrous benzene and by sublimation *in vacuo*. Butyl alcohol (Merck) was distilled before use. The terpolymer containing MA was a terpolymer of MA-St-VA, whereas the terpolymer without MA was a terpolymer of butyl maleate (*n*-BuMA) obtained from MA, which was opened by *n*-butyl alcohol. These terpolymers were synthesized and characterized in a previous study.^{5,24} The repeated units of these terpolymers are shown in Scheme 1.

Preparation of the polymer blends and thermomechanical analysis

With 0, 2.0, 4.0, 6.0, 8.0, and 10.0 w/w ratios of MA-St-VA and *n*-BuMA-St-VA, the binary polymer blends were made in THF by the mixture of PVC/MA-St-VA and PVC/*n*-BuMA-St-VA solution in

TABLE I
Amounts of Each of the Polymers Used in the Preparation of the Blends

PVC (g)	MA-S-VA (g)	Blend code	PVC (g)	<i>n</i> -BuMA-S-VA (g)	Blend code
0.50	0.00	1	0.50	0.00	1
0.49	0.01	2	0.49	0.01	7
0.48	0.02	3	0.48	0.02	8
0.47	0.03	4	0.47	0.03	9
0.46	0.04	5	0.46	0.04	10
0.45	0.05	6	0.45	0.05	11

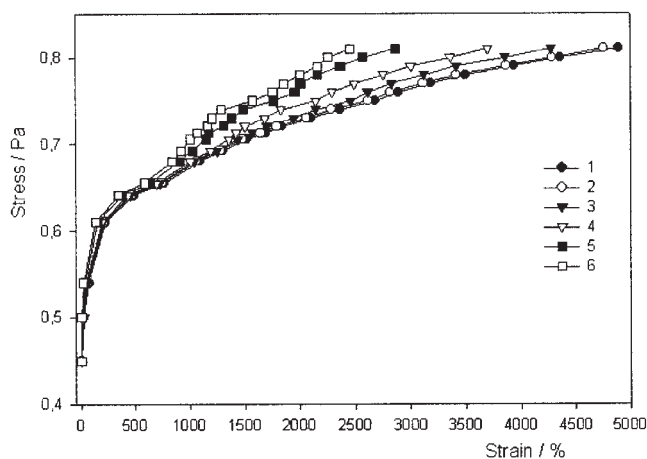


Figure 1 Stress-strain curves of PVC/MA-St-VA blends.

THF. The homogeneous mixed solution was cast into a dry, clean Pyrex Petri dish 5 cm in diameter. The film, which formed on the complete evaporation of the solvent at room temperature, was then dried in a vacuum oven at 50°C to a constant weight. All of the films prepared in this way were 0.1 mm thick. The amounts of PVC and the terpolymers are given in Table I. For determination of the thermomechanical properties, 0.5 g of each polymer sample was put into a film form with THF. A Shimadzu TMA-50 instrument (Japan) was used to record the stress-strain curves of the films. The thermomechanical properties of the polymer blend films were measured at a heating rate of 10°C/min, a loading rate of 5 g/min, and a temperature range from room temperature to 150°C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

This study dealt mainly with the utility of any copolymer containing MA units as a compatibilizer in

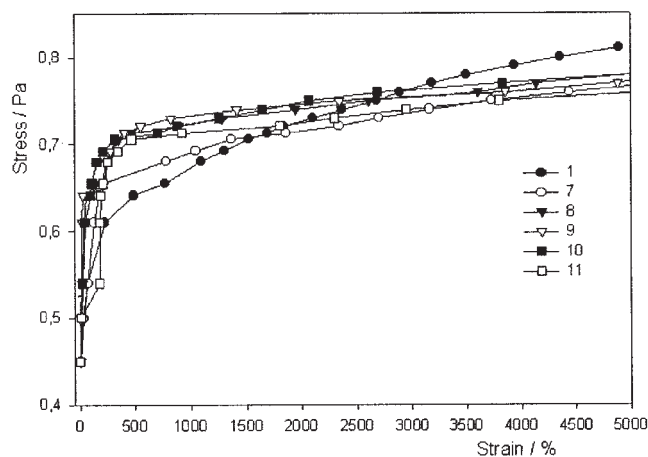


Figure 2 Stress-strain curves of PVC/*n*-BuMA-St-VA blends.

TABLE II
Values of E , T_g , α , and Maximum Stress and Strain of Blends PVC/MA-S-VA and PVC/*n*-BuMA-S-VA

Blend code	E (Pa)	T_g ($^{\circ}\text{C}$)	α ($^{\circ}\text{C}^{-1}$)	Stress (Pa) ^a	Strain (%) ^a	Blend code	E (Pa)	α ($^{\circ}\text{C}^{-1}$)	T_g ($^{\circ}\text{C}$)	Stress (Pa) ^a	Strain (%) ^a
1	1.32	61	1.80	0.641	487	7	0.07	8.86	43	0.655	203
2	1.43	64	1.57	0.641	468	8	0.27	1.93	62	0.713	467
3	1.55	68	1.12	0.641	456	9	0.37	1.23	70	0.721	548
4	1.77	70	0.82	0.641	430	10	0.43	2.36	61	0.706	313
5	2.28	72	0.52	0.641	381	11	1.51	3.08	61	0.706	465
6	3.48	78	0.33	0.641	345						

^a Maximum stress and strain values without deformation.

the preparation of a polymer blend. In this study, a terpolymer, whose repeated units are given in Scheme 1, and a maleate terpolymer that was known to be an ester derivative of the same terpolymer but without any MA was used. For this purpose, two different PVC/terpolymer blends were synthesized and studied to obtain more regular changes in the thermomechanical properties of these different blends. Terpolymers and/or copolymers containing MA, called *functional polymers*, have been used to produce compatible polymer blends in a large numbers of studies. The main aim of this study was also to show the utility of MA units for obtaining compatible polymer blends. After a comparing the results, I concluded that the changes in the thermomechanical characteristics of the terpolymer blends containing MA and PVC were more regular. All of these studies, then, have shown that more manipulated changes can be wrought in the thermomechanical characteristics of PVC with terpolymers containing MA units.

Stress-strain curves for each polymer blend were recorded to determine the thermomechanical char-

acteristics of the PVC/MA-St-VA blends and the PVC/*n*-BuMA-St-VA blends. The stress and strain values for each blend were read from the original curves as plotted on a computer. These are shown in Figures 1 and 2. With these curves, the elasticity modulus (E) values, the maximum stress and strain values without deformation, were obtained. These values are given in Table II. On inspection of the stress-strain curves, the PVC/MA-St-VA blends were shown to have more changes than PVC/*n*-BuMA-St-VA blends. In other words, the PVC/MA-St-VA blends were more compatible than the PVC/*n*-BuMA-St-VA blends.

The E values at certain temperatures were recorded and temperature-log E curves were drawn. These curves are shown in Figures 3 and 4. The mean temperature at which the E value fell suddenly on these curves gave the glass-transition temperature (T_g) value.²⁵ These values are given in Table II.

The stress-strain curves for all of the blends were recorded at increasing load and temperature conditions. From these curves, the temperature-strain

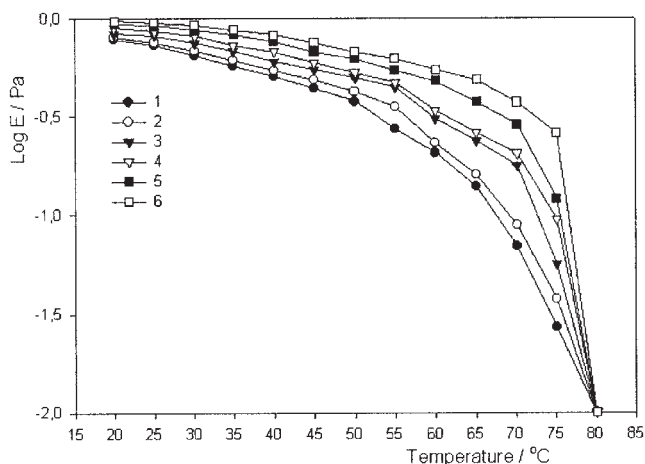


Figure 3 Temperature-log E curves of PVC/MA-St-VA blends.

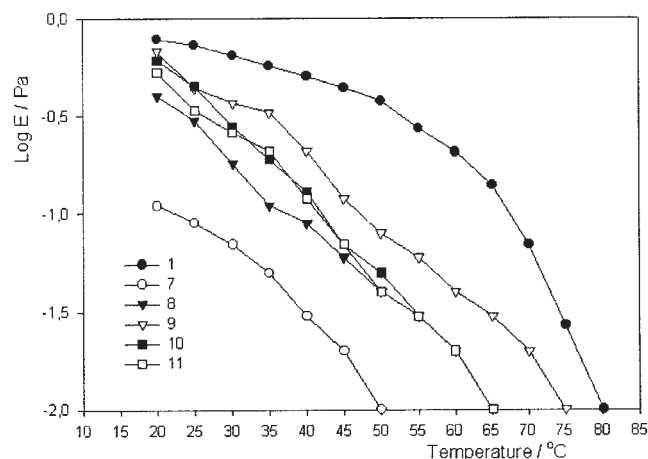


Figure 4 Temperature-log E curves of PVC/*n*-BuMA-St-VA blends.

curves of the PVC/MA–St–VA and PVC/*n*-BuMA–St–VA blends were drawn via computer. These are shown Figures 5 and 6. The coefficient of thermal expansion (α), a value commonly used to compare the thermomechanical properties of polymers, was found from the linear parts of the curves.²⁶ These values are also given in Table II.

Evaluation of the thermomechanical curves of PVC/*n*-BuMA–St–VA blends showed that there was no regularity in these curves. One can easily suggest that the terpolymers obtained by the opening of the MA units could not be used to get a PVC-compatible polymer blend. However, the changes in the thermomechanical parameters of the PVC/MA–St–VA blends were easily determined to be much more regular. The blend got more and more stiff when the ratio of the masses of the MA–St–VA terpolymer increased in blend. Thus, some significant and regular changes in the thermomechanical properties of PVC was achieved by the addition of small amounts, ranging from 2 to 10%, of the MA–St–VA terpolymer, as seen in Table II. As commonly shown in the existing literature, T_g and α are considered to be the most important thermomechanical parameters for the determination of the plastic characteristics of any polymer. Therefore, the manipulated changes in the T_g and α of PVC formed by blend preparation were very important. These types of manipulated changes in the parameters of PVC are expected to increase the widespread utility of PVC in various products.

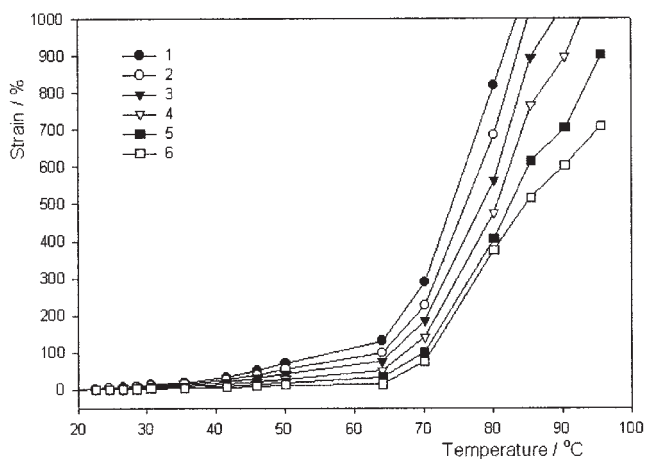


Figure 5 Temperature–strain curves of PVC/MA–St–VA blends.

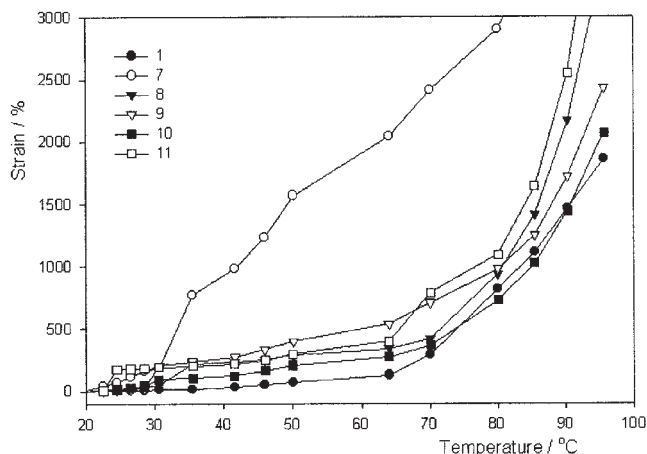


Figure 6 Temperature–strain curves of PVC/*n*-BuMA–St–VA blends.

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