

# Preparation of Compatible Blends of Poly(methyl methacrylate) Used in Dentistry with a Reactive Terpolymer Containing Maleic Anhydride and Their Thermomechanical Characterization

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**ABSTRACT:** This study focuses on the preparation of compatible blends with the poly(methyl methacrylate) (PMMA) using a reactive terpolymer maleic anhydride–styrene–vinyl acetate (MA–St–VA). In the first series of experiments, binary blends of the PMMA and the MA–St–VA terpolymer have been prepared in tetrahydrofuran. The PMMA and the MA–St–VA terpolymer formed the compatible blends. The effects on thermomechanical properties of MA–St–VA terpolymer ratio in the blends were studied. The glass transition temperatures ( $T_g$ ), thermal expansion coefficient ( $\alpha$ ), and other thermomechanical parameters for the

blends have been established by TMA method and the compatibility of two polymers has been evaluated by these TMA parameters. The addition of MA–St–VA terpolymer to PMMA made a plasticizing effect on PMMA. This effect regularly changed with the increasing of the terpolymer in the blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 363–367, 2006

**Key words:** compatibility; blends; poly(methyl methacrylate) (PMMA); terpolymer; maleic anhydride

## INTRODUCTION

Commercial importance of polymer blends have highly increased because of the fact that the performance of polymers could be improved simply by blending to fulfill industry's need for high performance materials.<sup>1–4</sup> Many of the commercial polymers are immiscible and incompatible, which lead to poor final properties.<sup>5,6</sup> To develop durable industrial products, it is necessary to explore the thermomechanical properties of these blends. Thermomechanical analysis (TMA) method can be used as a way to measure the thermomechanical properties of polymer.<sup>7–11</sup>

Maleic anhydride (MA) is a reactive monomer. Copolymers or terpolymers are called reactive polymers because of the existence of MA units in the main chain. There is a large amount of literature on different copolymers of MA used as a compatibilizer in the obtained blends of compatible polymer.<sup>12–17</sup> In our laboratory, copolymers of MA are currently used as reactive polymers in the preparation of the compatible polymer blends via the MA moiety.<sup>18</sup>

Poly(methyl methacrylate) (PMMA) is one of the most important of widely used polymers. This study looks into the PMMA used in dentistry. It is thought that

elastic properties of PMMA would increase by adding a small amount of maleic anhydride–styrene–vinyl acetate (MA–St–VA) reactive terpolymer into PMMA. In this case, the aim is to prove that PMMA, which is used in dentistry, could be used in this field for different purposes as well. Upon examination of TMA results, it is seen that glass transition temperature value decreases fairly when MA–St–VA reactive terpolymer with a ratio of 8–10% (w/w) is added into PMMA.

## EXPERIMENTAL

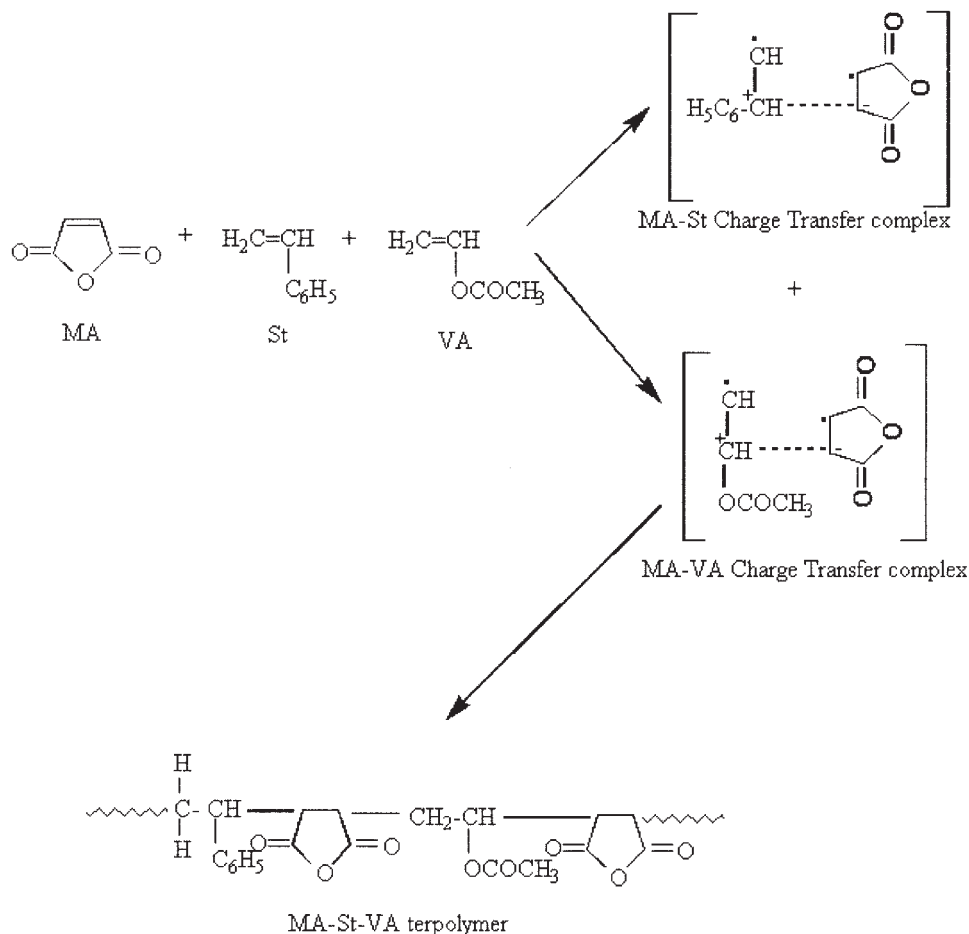
### Materials

PMMA used in dentistry was obtained from Vertex Company, (Bedford, MA, USA). MA was obtained from Aldrich Chemical Company (Haverhill, UK). VA and St were obtained from Merck Company (Darmstadt, Germany) and were distilled before use. They had the following characteristics: VA, bp 72°C; St, bp 138°C. Methyl ethyl ketone and ethyl alcohol were obtained from Merck Company. AIBN was purified by re-crystallizing twice from Chloroform solution. Analytical grade tetrahydrofuran (THF) was obtained from Prolabo Company, Nice, France.

### The experimental technique of the terpolymerization

The terpolymer was produced using MA, St, and VA, taking the mole proportions of 2 : 1 : 1 in methyl ethyl

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**Scheme 1** The terpolymerization of MA–St–VA with the formation of CTCs.

ketone in the presence of AIBN as initiator at 70°C. Required amounts of monomers: MA (7.35 g, 0.075 mol), St (3.8 cm<sup>3</sup>, 0.0375 mol) and VA (4.4 cm<sup>3</sup>, 0.0375 mol) with initiator (AIBN 0.08 g). The terpolymer was precipitated in ethyl alcohol and then dried at 35°C in a vacuum. MA with monomers St and VA forms the terpolymer by charge transfer complex (CTC) formation reaction, according to Scheme 1. A Perkin-Elmer 1600 FTIR was used for the spectroscopic characterization of terpolymer.

#### The thermomechanical characterization and the preparation of the polymer blends

Binary polymer blends were made in THF by mixing 1 g of PMMA/MA–St–VA solution in THF as 0, 2.0, 4.0, 6.0, 8.0, 10.0% (wt/wt) ratio of MA–St–VA in polymer blends. The amounts of the terpolymer and PMMA have been given in Table I. The homogeneous mixed solution was cast into a dry, clean Pyrex Petri dish of 50 mm diameter. The film formed on complete evaporation of the solvent at room temperature was then dried in a vacuum oven at 50°C to constant

weight. All of the films prepared in this way were 0.1 mm thick.

Thermomechanical properties of the polymer blends in the state film were measured on a Shimadzu TMA-50 at a heating rate of 10°C min<sup>-1</sup>, the loading rate of 5 g min<sup>-1</sup>, and a heating range from room temperature to 150°C in nitrogen atmosphere.

## RESULTS AND DISCUSSION

Ternary monomer systems containing MA as electron-acceptor monomers and vinyl monomers as electron-

**TABLE I**  
The Amounts of the Terpolymer in the PMMA Blends

Polymer blends	Amount of the MA–St–VA terpolymer (g)
Pure PMMA	0.00
PMMA + 2% MA–St–VA	0.02
PMMA + 4% MA–St–VA	0.04
PMMA + 6% MA–St–VA	0.06
PMMA + 8% MA–St–VA	0.08
PMMA + 10% MA–St–VA	0.10

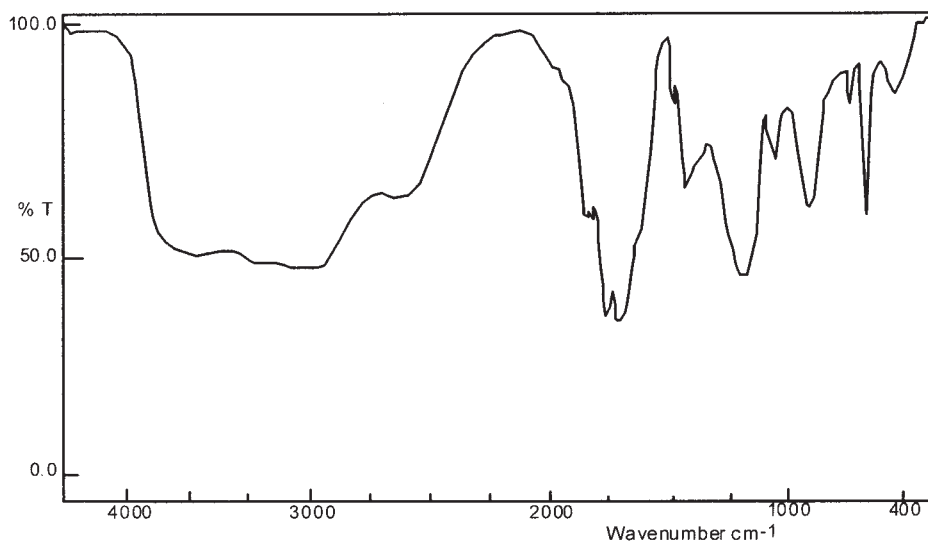


Figure 1 FTIR spectrum of the MA-St-VA terpolymer.

donor (or acceptor) monomers differ from other multi-component monomer systems in that radical terpolymerization occurs via CTCs; the mechanism of terpolymerization and of occurring CT complexes is given in the Scheme 1. There is an abundance of literature on this subject matter.<sup>19-22</sup> The FTIR spectrum of MA-St-VA (Fig. 1) terpolymer showed significant signals at  $2860\text{--}2980\text{ cm}^{-1}$  (C—H);  $1860, 1804, 900\text{ cm}^{-1}$  (C=O and C—O—C of MA).

FTIR analysis of the PMMA/MA-St-VA blends showed a shift of the carbonyl band of PMMA to lower wavenumbers. The reason of this shift is due to a specific interaction of hydrogen bonding type between carbonyl groups (C=O) of PMMA and hydrogen from (HCCH) group of MA in the terpolymer. The carbonyl band in the pure PMMA is  $1733\text{ cm}^{-1}$ , whereas the carbonyl band in the blends is  $1723\text{ cm}^{-1}$ . FTIR spectra of pure PMMA and the blend are given in Figure 2.

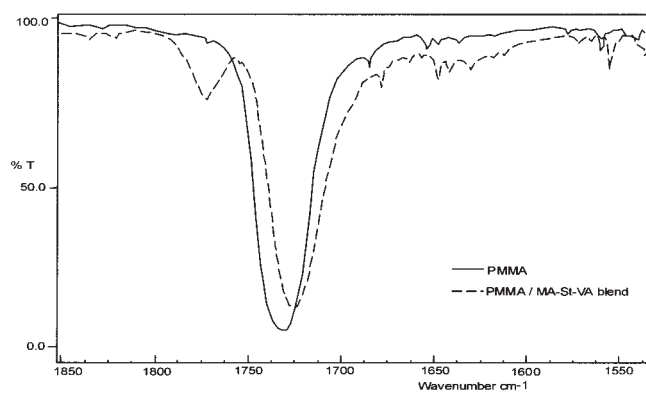


Figure 2 FTIR spectra of PMMA and PMMA/MA-St-VA blend.

Thermomechanical curves (TMA) of the PMMA and PMMA/MA-St-VA blends are given in the Figures 3–5. Different thermomechanical parameters are obtained from each curve. These thermomechanical parameters are playing a big role on the use area of a polymer, and determination of their usage. In Figure 3 stress-strain curves, permanent deformation point can be designated. In this way, some parameters such as maximum extension, maximum loading, and maximum applicable heat can be found in polymers without deformations.<sup>23</sup> Utilizing Scheme 1 stress-strain curves, aforementioned thermomechanical parameters are found and presented in Table II. As it is seen from these parameters, addition of terpolymer to the PMMA has produced a plasticization effect and increased the elasticity feature of PMMA.

Temperature-strain curves in Figure 4 had been obtained from polymer blend stress-strain curves car-

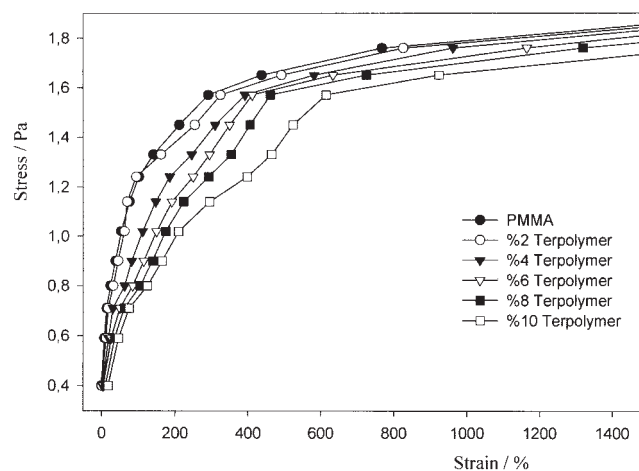


Figure 3 Stress-strain curves.

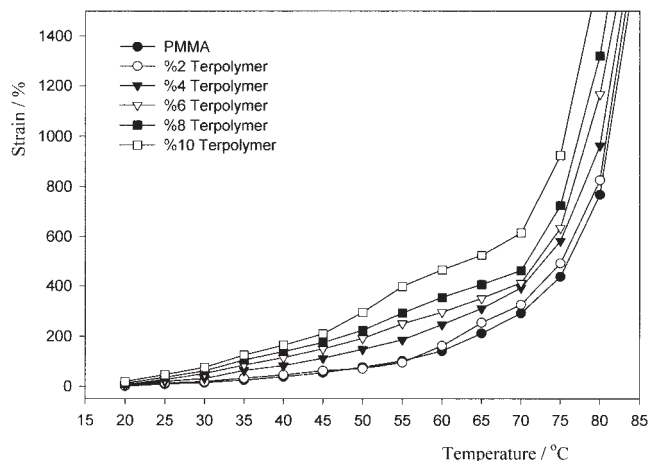


Figure 4 Temperature-strain curves.

rying the values read at specific heat strain values and transferred to the opposite graphic. The thermal coefficient of expansion ( $\alpha$ ), a value commonly used for comparing thermomechanical properties of polymers, was found from the linear parts of the curves and are given in Table II. These values are proofs that appropriate polymer mixtures have been obtained, that the increase on CTE values was regular, and also that MA-St-VA terpolymers have plasticizing effects on PMMA.

Stress-strain curves have been obtained by rising heat and loading on polymer samples, in particular heat  $E$  values have been read and temperature-log  $E$  curves are shown in Figure 5. Average heat of these sudden drop on  $E$  values on the curves gives us glass transition temperature ( $T_g$ ) value.  $T_g$  values of PMMA and its blends have been found using this method and are given in the Table II. Changing a polymer's  $T_g$  value means that polymer's usage is increasing. In this study, a reactive polymer MA-St-VA terpolymer has

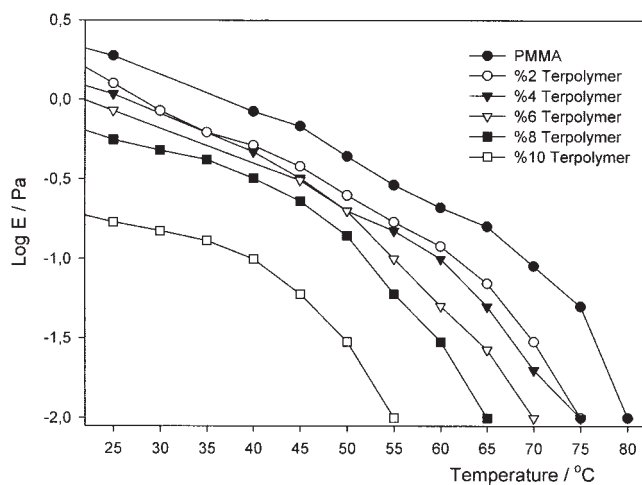


Figure 5 Temperature-log  $E$  curves.

TABLE II  
The Values of  $\alpha$ ,  $T_g$ , and  $E$  of PMMA and PMMA/MA-St-VA Blends

Polymer blends	$\alpha$ ( $^{\circ}\text{C}^{-1}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$E$ ( $\text{kg cm}^{-2}$ )
Pure PMMA	1.85	70	880
PMMA + 2% MA-St-VA	2.15	61	777
PMMA + 4% MA-St-VA	4.03	54	435
PMMA + 6% MA-St-VA	5.55	48	351
PMMA + 8% MA-St-VA	6.50	44	285
PMMA + 10% MA-St-VA	7.45	42	247

been used and  $T_g$  value of PMMA has been reduced from  $70^{\circ}\text{C}$  to  $42^{\circ}\text{C}$ . When the percentage of terpolymers in the blend is increased,  $T_g$  values decrease regularly, and it is important from the control of  $T_g$  value of PMMA point of view.

Stress-strain curves linear parts slope gives modulus ( $E$ ) values of elastic polymers.  $E$  values of PMMA and its blends have been found and shown in the Table II. Decrease of  $E$  values is an indication that the elasticity features of polymer blends are increasing. As in other thermomechanical parameters, there is a steady decrease in the  $E$  values. Elasticity properties of PMMA have increased regularly as the proportion of MA-St-VA polymers in the blend decreased. Therefore, it can be easily said that PMMA and MA-St-VA terpolymers are compatible blends.

Silicon-based soft retaining materials have quite a few disadvantages and many studies were conducted to eliminate these disadvantages. In this study, we have observed that PMMA gains plastic characteristics as a result of reactions with the MA, which is a functional polymer.

## CONCLUSIONS

The MA-St-VA terpolymer synthesized in our previous work<sup>24</sup> has been studied as plasticizer for PMMA used in the dentistry field. TMA curves and regular change in the thermomechanical parameters showed miscibility of PMMA with the MA-St-VA terpolymer. This miscibility is due to a specific interaction of hydrogen bonding type between carbonyl groups (C=O) of PMMA and hydrogen from (HCCH) group of MA in the terpolymer. In conclusion, we have reported that it would be advantageous to improve the elastic properties of PMMA used in the dentistry field by the addition of the terpolymer in different ratios.

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