



# Toughening brittle polymers with shape memory polymers

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## ABSTRACT

Polystyrene (PS) was blended with shape memory polyurethanes (SMPU). Styrene blocks were grafted onto PU chains during SMPU synthesis to yield a modified SMPU with a higher affinity towards PS. Furthermore, blends containing a compatibilizer, poly(styrene-co-maleic anhydride) (SMA), were also prepared by melt mixing the components. The non-compatible blends display phase separated structures with PS rich and SMPU rich phases, which were less evident in blends prepared with either the modified SMPU or SMA compatibilizer. The elastic storage modulus of PS was less affected when blended with SMPU in samples containing modified SMPU with styrene grafts. The impact strength of the blends with higher contents of SMPU modified with styrene blocks (25 and 50 wt.%), after shape recovery, was higher than the impact strength of neat PS. The incorporation of shape memory polymers into a brittle polymer matrix is a potential strategy to improve the toughness by external stimuli.

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## 1. Introduction

Glassy polymers are normally brittle due to the presence of rigid and highly entangled polymer chains [1]. An elastomeric phase incorporated within a brittle polymer matrix can improve its toughness by dissipating energy during crack propagation [2]. Furthermore, these blends can be manufactured at a lower cost as compared to the synthesis of new polymers with similar properties [3].

Polystyrene (PS), is a typical glassy polymer with high hardness and low ductility. Its low impact strength is due to the presence of benzene rings in the lateral positions, which restricts disentanglements and molecular flow at room temperature (glass transition temperature ( $T_g$ ) between 90 °C and 120 °C) [4]. (polybutadiene, polypropylene, etc.) is largely employed to improve the toughness of PS, such as in the case of production of high impact polystyrene (HIPS) [5–9].

In this work, the hypothesis that the incorporation of shape memory polymers (SMPs) in brittle polymers can improve the toughness of the host material was tested. Moreover, the presence of SMPs in brittle polymers could not only improve the toughness but also could restrict reduction in the elastic modulus and other

properties of the matrix—a phenomenon that is usually observed when elastomeric polymers are used in polymer blends. SMPs belong to a class of active materials that can exist in a temporary shape but can recover their original shape upon the application of a specific stimulus (light, heat, electric field, magnetic field, pH, specific ions, enzymes, etc.) [10–14]. The shape memory behavior of a material is directly associated with its ability to change its modulus under an applied external stimulus in order to freeze in a specific shape or structure [15–18]. The possibility of large reversible changes in shape and the fact that these changes can be triggered through a variety of stimuli allow the application of SMPs in a wide range of medical devices, including vascular grafts, stents, coronary implants, orthopedic braces, and splints [19].

Polyurethanes (PU) have received a great deal of attention due to their segmented structure and the wide range of properties that can be obtained by varying the reagents. Shape memory polyurethanes (SMPUs) are segmented block copolymers comprising of soft and hard segments [20–22]. The hard segments are responsible for the permanent shape of the polymer and have the highest thermal transition temperature. On the other hand, the soft segments are responsible for the thermally stimulated reversal in shape. Vitrification or crystallization of these segments are responsible for fixing the temporary shape [21].

In this work, blends of the brittle polymer, PS, and SMPUs were developed to test the idea that dimensional changes in the dispersed phase, which is composed of a SMP, can enhance the

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toughness of a brittle polymer, such as PS. Moreover, the toughness of polymer blends can be altered by external stimuli, which can trigger shape changes in the dispersed SMP.

## 2. Materials and methods

### 2.1. Materials

Polycaprolactone diol (PCL,  $M_n = 2000$  g/mol), isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), dibutyltin dilaurate stain (DBLT), poly (styrene-co-maleic anhydride) (SMA), maleic anhydride (MA), and tetrahydrofuran (THF) were supplied by Sigma Aldrich (St. Louis, MO, USA). Triethylamine (TEA, 98%) and hydrazine hydrate (HZ, 24%) were provided by Vetec (RJ, Brazil). Polystyrene (PS) was procured from Videolar (RS, Brazil). All reagents were used as received without further treatment.

### 2.2. Synthesis of shape memory polyurethanes

Shape memory polyurethane samples were produced using the prepolymer method [23,24]. Two groups of SMPUs were synthesized. In group 1, the chain extension step was performed with hydrazine and water to yield an aqueous dispersion (named  $PU_{HZ}$ ). In group 2, hydrazine was replaced by SMA dissolved in THF (named  $PU_{SMA}$ ) [25]. The SMA was added in order to improve interfacial interactions with PS.

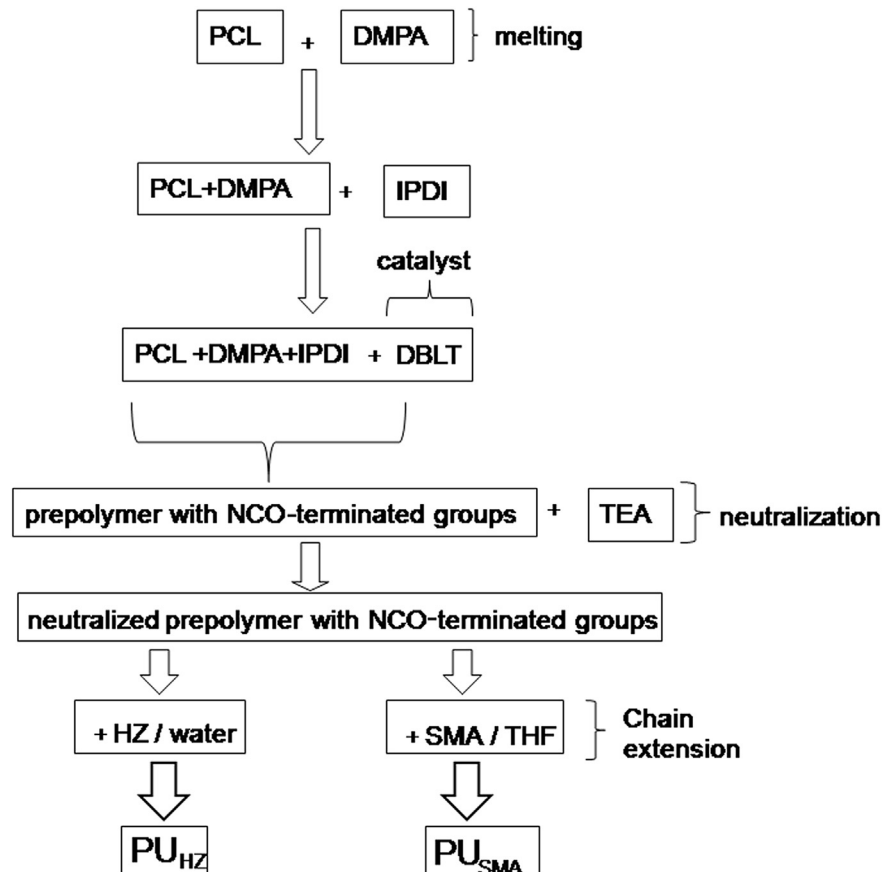
Fig. 1 shows the steps followed during the synthesis of SMPUs. A three-way glass flask (250 mL) equipped with a heating mantle, a mechanical stirrer, and a thermometer was used as the reaction vessel. The reaction was initiated by mixing PCL and DMPA at

80 rpm and 60 °C for 30 min. Subsequently, isophorone diisocyanate was added to the reaction mixture to produce the PU prepolymer. The mixture was allowed to react at 65 °C for 2 h while being stirred at 80 rpm. The catalyst (DBLT) was added in 1 h intervals within 2 h. Free carboxylic groups were neutralized by the addition of triethylamine at 40 °C. The neutralization reaction was carried out over 30 min at 60 rpm. In SMPU group 1, the chain extension and dispersion steps were performed by adding HZ in water and stirring for 30 min at 300 rpm. In group 2, the chain extension step was executed using a THF solution of SMA. The excess NCO groups (NCO/OH ratio) employed in the reaction lead to the formation of NCO end-capped chains. The NCO end groups were then reacted with amine groups (in HZ) and maleic anhydride (in SMA) in the chain extension step. The hydrazine (1.59 g) and SMA (1.10 g) proportions were defined to promote complete consumption of the NCO groups in the prepolymer during the chain extension step through an equimolar reaction (i.e., by assuming that the average concentration of anhydride groups on SMA and amine groups in hydrazine would fully react with the NCO groups).

The solids content obtained from the reactions was approximately 25% for both group 1 and 2. Table 1 shows the reagent masses required in order to obtain the SMPUs.

**Table 1**  
Reagent masses (g) required for SMPU synthesis.

Sample	Water	THF	PCL	DMPA	IPDI	TEA	SMA	HZ	DBLT
$PU_{HZ}$	120.00	–	29.14	1.69	13.10	1.27	–	1.59	0.09
$PU_{SMA}$	–	105.72	29.14	1.69	13.10	1.27	1.10	–	0.09



**Fig. 1.** Synthesis of shape memory polyurethanes (SMPUs).

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