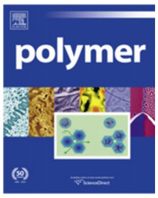
Polymer 51 (2010) 3551–3559

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Radiation crosslinked shape-memory polymers

Walter Voit [a,*], Taylor Ware [a], Ken Gall [b]

[a] Department of Materials Science and Engineering, University of Texas at Dallas, USA
[b] School of Materials Science and Engineering, Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA

ARTICLE INFO

Article history:
Received 26 March 2010
Accepted 22 May 2010
Available online 9 June 2010

Keywords:
Shape memory polymers
Radiation crosslinking
Thermomechanical properties

ABSTRACT

Shape-memory polymers (SMPs) are active smart materials with tunable stiffness changes at specific, tailored temperatures. The use of thermoset SMPs has been limited in commodity applications because a variety of common low-cost plastics processing techniques are not possible with network polymers. In this study of thermoset SMPs, beyond adjusting the glass transition temperature (T_g) between 25 and 75 °C and tuning the recoverable force between 0.5 and 13 MPa, a novel manufacturing process, *Mnemosynation*, is described. The customizable mechanical properties of traditional SMPs are coupled with traditional plastic processing techniques to enable a new generation of mass producible plastic products with thermosetting shape-memory properties: low residual strains, tunable recoverable force and adjustable T_g. The results of this study are intended to enable future advanced applications where mass manufacturing, the ability to accurately and independently position T_g and the ability to tune recoverable force in SMPs are required.

Published by Elsevier Ltd.

1. Introduction

Nearly 2000 years ago in his *Discourses*, Epictetus said that materials themselves affect us little; it is the way we use them which influences our lives [1]. Thermoset shape-memory polymers (SMPs) are self-adjusting smart materials with variable activations [2] and low residual strains [3] but their use and thus influence in mass-market applications has been limited due to manufacturing and scale-up difficulties. Covalent crosslinks preclude thermosets from being melted and reshaped after initial polymerization. Techniques such as injection molding [4,5], blow molding [6] and vacuum-assisted resin transfer molding [7] were developed to enable cheap mass production of thermoplastic polymers, but cannot reshape network polymers. Today, injection molding is widely used for manufacturing a variety of parts, from small custom plastic components to entire car body panels [8]. Reaction injection molding was developed to cure thermoset polymers into complex shapes but necessitates curing polymers directly into a mold [9]. This technique puts constraints on design, limits polymer composition and initiation choices, and suffers from shrinkage problems limiting precision control of final mechanical properties as specific additives are incorporated to manage this shrinkage [10,11].

Vulcanization, named after the Roman god of Fire, utilizes sulfur and heat to crosslink natural rubber (polyisoprene) [12] and has enabled mass manufacture of natural rubber with enhanced network properties. This process overcomes limitations by molding thermoplastic polyisoprene and subsequently crosslinking it with sulfur. Other methods to subsequently crosslink thermoplastics after polymerization and remolding also exist. Targeted irradiation of thermoplastic precursors such as polyethylene can lead to grafting and the creation of a network polymer which resembles chemical crosslinking [13]. Controlled irradiation of myriad polymer systems has provided cost effective methods to bestow enhanced properties upon polymers for industrial applications [14,15]. Much progress in this area has been driven by needs in the oil and automotive industries for tougher, more durable or heat resistant plastics. One such method that has gained widespread acceptance is electron beam (e-beam) irradiation [14,16–21]. That process today is very clean, operates at ambient temperatures, permits greater processing speed and often requires less energy than other methods in which crosslinking occurs post-polymerization [21].

Numerous studies have been undertaken to enhance the effectiveness and minimize the dose required for crosslinking. To minimize the amount of chain scission vs. crosslinking as determined by the modified Charlesby–Pinner equation [22], various polyfunctional monomers can be blended into the thermoplastic networks to enhance crosslinking. Polymer irradiation has been successfully used to impart shape-memory on natural rubber [16,23], polyethylene [24] and poly(ε-caprolactone) [25,26]. The crosslinking effects of ionizing radiation on synthetic polymers

---

* Corresponding author. Tel.: +1 972 883 5788; fax: +1 972 883 5725.
E-mail address: walter.voit@utdallas.edu (W. Voit).

0032-3861/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.polymer.2010.05.049

is defined by the classical Charlesby–Pinner equation shown in Eq. (1) [27].

$$s+s^{1/2} = \frac{p_0}{q_0}+\frac{1}{q_0\mu_2 d} \tag{1}$$

In the classical Charlesby–Pinner equation, s is sol fraction, p_0 is degradation density, q_0 is crosslinking density, μ_1 is initial weight, average degree of polymerization and d is radiation dose. A linear data set is generated when $s + s^{1/2}$ is plotted vs. $1/d$. A linear fit yields intercepts at $1/d$ equals zero and $s + s^{1/2}$ equals two. The $1/d$ equals zero intercept represents the ratio of scission to crosslinking (p_0/q_0). The $s + s^{1/2}$ equals two intercept represents the minimum dose of gelation (d_0).

The use of multifunctional monomers, such as trimethylolpropane triacrylate (TMPTA) to crosslink acrylic polymer chains can be achieved at reduced dose levels and yield optimum properties without deterioration of the base polymer [28,29]. Thus far, the effect of e-beam radiation has been investigated on synthetic acrylic elastomers [16] and acrylic rubbers [21] but no systematic modification and curing of an acrylate system demonstrating useful and tunable shape-memory properties has been investigated. In particular, the authors are not aware of any published work that has demonstrated a controllable shape-memory effect in radiation crosslinked acrylic polymers by simultaneously optimizing recoverable force, glass transition temperature and polymer toughness.

The shape-memory effect is observed in both thermoplastic and thermosetting polymers with various chemistries. The fundamental distinction is that the memory in thermoplastics can be erased over multiple cycles, especially over large applied strains. One class of thermoplastic shape-memory polymers relies on block copolymers with alternating hard (crystallized) and soft (amorphous) segments [30,31]. The hard segments act as net points while the soft segments can unwind, uncoil and provide strain capacity. However, even at ambient temperatures, physical crosslinks can often break down with applied strain, hold time, or exposure to humidity, rendering the material incapable of remembering its fixed shape resulting in an effective loss of memory. Thermosets have seen a rise in importance through their benefit to custom biomedical devices [32]. Several recent studies have proposed novel devices fabricated from SMPs [33–40], some of which have been shown to potentially impact minimally invasive surgery and implants. Compared to other shape-memory materials such as nickel titanium shape-memory alloys, which recover strains on the order of 10 percent, SMPs can recover strains on the order of 50–800 percent, enabling them to experience relatively large on-demand shape changes in severely restricted environments [34,41–43].

Fig. 1 schematically demonstrates the shape-memory cycle in a polymer. A polymeric device is first synthesized into a permanent shape by standard polymer processing techniques (previously, custom machining was used to sculpt complex geometries). Subsequently, the polymer is heated above a critical temperature, such as the glass transition temperature (T_g), and thermomechanically deformed into a temporary shape, a process known as shape storage (Fig. 1). The polymer remains in the stored shape until it is heated in the vicinity of its T_g, upon which it will experience controlled shape recovery. Control of T_g enables the underlying polymer to be targeted for a specific application where shape change can be programmed at a specific temperature. Control of rubbery modulus, through varying crosslinker density, enables the underlying copolymer to be targeted for a specific application where specific recoverable force is necessary. Conversely, if recoverable strain if more important than recoverable force, the copolymer can be similarly optimized to demonstrate a large difference between the maximum achievable strain, $e_{\max}$, during deformation and permanent plastic strain after recovery, e_p [44].

Although materials may possess a useful shape-memory effect, they may not be important in engineering applications due to manufacturing limitations. The goal of this work is to demonstrate a cost-effective manufacturing technique to enable shape-memory polymers with useful properties for a wide variety of applications. In this work, we propose such a manufacturing technique, *Mnemosynation*, and examine the resultant shape-memory polymers and their relevant thermomechanical properties.

2. Results

Mnemosynation is a five-step polymer manufacturing process developed to enable mass production of acrylic thermoset SMP devices, which would otherwise be cost-prohibitive using traditional thermoset polymerization techniques. Named for the Greek goddess of memory, Mnemosyne [45], this manufacturing process is the controlled imparting of memory on an amorphous thermoplastic material utilizing radiation-induced covalent crosslinking, much like *Vulcanization* of rubber is the controlled imparting of recoverable elastomeric behavior on a rubber using sulfur crosslinks. *Mnemosynation* combines advances in radiation grafting and advances in simultaneously tuning the mechanical properties of acrylic SMPs to enable traditional plastics processing (blow molding, injection molding, etc.) and allows thermoset shape-memory properties in complex geometries. An overview of *Mnemosynation* in acrylate systems are as follows:

1. Combine selected linear acrylic monomers and (photo)initiator in optimum ratios to tailor T_g, and M_w (thus melt viscosity) of the thermoplastic precursor
2. Polymerize, with for example ultraviolet (UV) light based on the photoinitiator used (e.g. long wave UV at 365 nm for 2,2 dimethoxy-2-phenylacetophenone) for a specified time and intensity (both polymer system dependent), to achieve desired degree of polymerization.
3. Blend, mechanically or otherwise, the thermoplastic precursor with an optimized amount of crosslinking agent (e.g. TMPTA) at an optimized temperature (polymer system dependent).

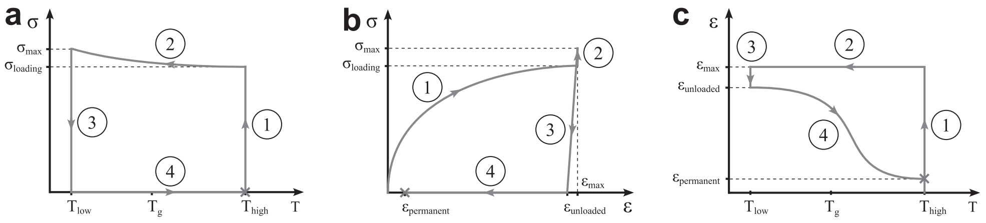


Fig. 1. Demonstration of the shape-memory cycle in a) stress–temperature, b) stress–strain and c) strain–temperature regimes. Step 1 is isothermal loading. Step 2 is cooling at constant load. Step 3 is isothermal unloading. Step 4 is shape recovery upon heating.