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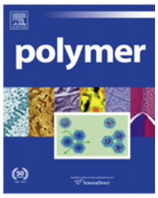

Radiation crosslinked shape-memory polymers

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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.

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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

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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).

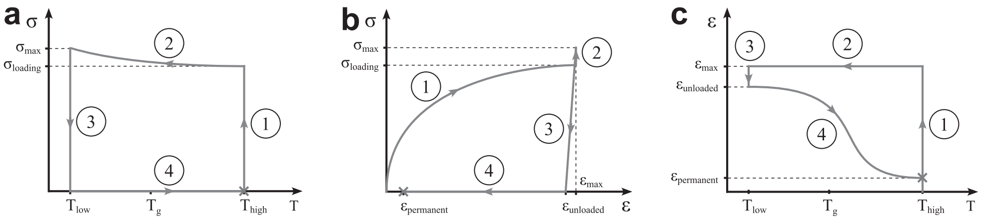

Fig. 1. Demonstration of the shape-memory cycle in a) stress–temperature, b) stress–strain and c) strain–temperature regimes. Step 1 is isothermal loading. Step 2 is cooling at constant load. Step 3 is isothermal unloading. Step 4 is shape recovery upon heating.

4. Injection mold (or otherwise shape) a device using the polymer blend resulting from step 3.
5. Cure shaped part from step 4 with ionizing (e.g. e-beam) radiation at a specified dose (polymer system dependent) to covalently crosslink and obtain desired thermomechanical properties

The novelty in this process lies in the ability to finely tune the thermomechanical properties through modifications at each step in the process. The process enables mass-manufacture of thermoset acrylates and allows independent control of T_g and the rubbery modulus, E_R. The correct ratio and type of linear monomers must be combined with the proper concentration of (photo)initiator to tailor the thermoplastic precursor. The correct ratio of crosslinking agent blend must be mixed in at the correct temperature to facilitate homogeneity in the mixing process and ensure proper dispersion of the agent throughout the polymer. The blended system must be exposed to the proper dose of high-energy radiation to target specific crosslink densities and ensure control of the end thermomechanical properties. Preliminary results presented in this work describe the optimizations made within the *Mnemosynation* process to enable materials with tuned thermomechanical and shape-memory properties.

2.1. Altering dose

Thermoplastic PMA polymerized with 0.10 wt% of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was pelletized and blended with 0.00, 1.00, 3.00, and 5.00 wt% of radiation sensitizers TAIC and TMPTA. Samples were pressed or molded into flat sheets and subsequently exposed to increasing doses of e-beam radiation of 5, 10, 25, 33, 66, 100, 200 and 300 kGy. After radiation crosslinking, samples were soaked for one week in acetone. Fig. 2a and b show the effects of network formation (gel fraction) as a function of radiation dose across the four composition ranges of each radiation sensitizer. Unblended PMA (0% TAIC or TMPTA) does not begin to crosslink until exposed to at least 25 kGy. Samples with increasing TAIC show a gradual increase in crosslinking which mimics the shape of the pure PMA curve while samples radiation-sensitized with TMPTA at 3.00 and 5.00 wt% begin to crosslink below 5 kGy. Charlesby–Pinner analyses confirm these trends. Fig. 3a and b show a decrease in slope with increasing radiation sensitizer and predict a decrease in the minimum dose for gelation as shown in Table 1. This minimum dose for gelation can be found by extrapolating the linear fit to assess the value of radiation dose (d) when the graphed function of sol fraction ($s + s^{1/2}$) is equal to 2. Additionally, Table 1 shows R^2 values for all blended TAIC samples and for the 1.00 wt% TMPTA sample to be above 0.9, but a breakdown in fit to Charlesby–Pinner analyses is observed in the 3.00 and 5.00 wt% TMPTA samples.

The MA-co-IBoA polymer systems blended with TMPTA or TAIC® were characterized by running dynamic mechanical analysis (DMA) on a broad range of compositions varying both the amount of crosslinking agent and the exposure to high-energy e-beam radiation. Fig. 4 shows the increase in rubbery modulus of PMA sensitized with 5.00 wt% TMPTA with increasing radiation dose. Only the rubbery regime is displayed to accentuate differences in the range of rubbery moduli between 0.5 and 1.8 MPa. T_g for these samples did not vary by more than 3 °C from 28 °C.

2.2. Altering crosslinker concentration

Fig. 5a and b highlight the differences between materials crosslinked during polymerization and materials crosslinked through irradiation at 50 kGy. At similar concentrations of TMPTA first as a crosslinker during polymerization and then as a radiation sensitizer, the rubbery modulus drops from 3.25 MPa to below 1 MPa for the radiation-sensitized samples. This difference is also coupled with a 10 °C increase in T_g for radiation crosslinked samples for the 5.00 wt% TMPTA blends as compared to samples crosslinked during polymerization. Fig. 5b additionally includes PMA blended with 9.00 wt% TMPTA to demonstrate the fact that rubbery modulus can additionally be increased with increasing sensitizer concentration.

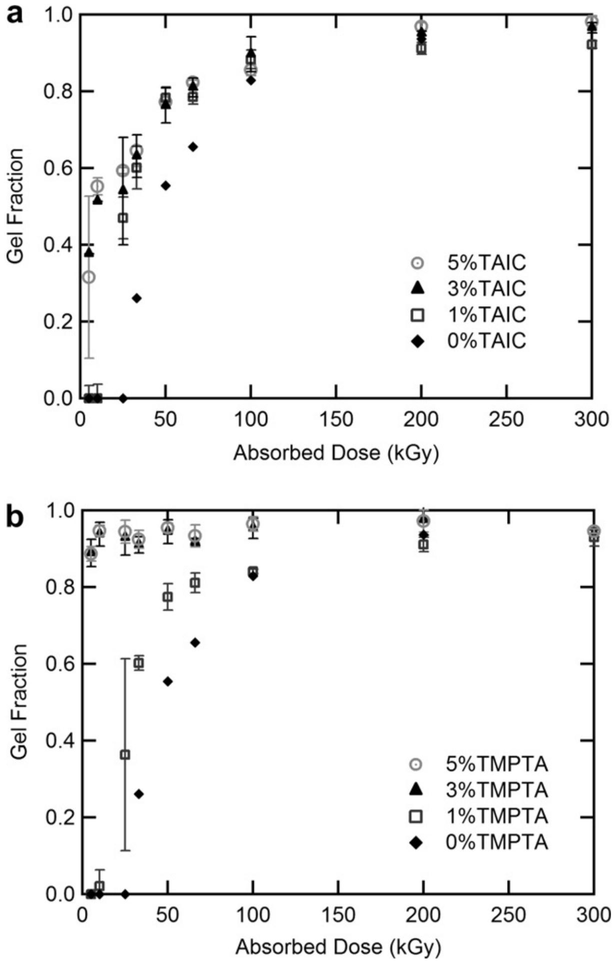

Fig. 2. Gel fraction ($n = 3$) as a function of radiation dose for PMA blended with increasing concentrations of a) TAIC® and b) TMPTA.

2.3. Manipulating glass transition

T_g can be manipulated independently by altering the ratio of linear builders in radiation crosslinked SMP systems. Table 2 shows the T_g and rubbery modulus (E_R) of PMA copolymers polymerized with 30.0 wt% of other listed monomers and subsequently blended with 9.00 wt% TMPTA and radiation crosslinked at 5, 50 and 300 kGy. Each sample showed the highest T_g at 50 kGy while the peak in E_R varied among samples. Across samples, the T_g is shifted by more than 30 °C without significantly affecting E_R. Fig. 6 assesses the gel fraction of three particular copolymers blended with 9.00 wt% TMPTA. CXEA oligomers blended with 9.00 wt% TMPTA demonstrate a higher gel fraction at all radiation doses than sensitized PMA while copolymers of PMA and 4-*tert*-butylcyclohexyl acrylate (*t*BCHA) show significantly less formed network structures. Fig. 7 compares the storage modulus of 94:6 MA:IBoA

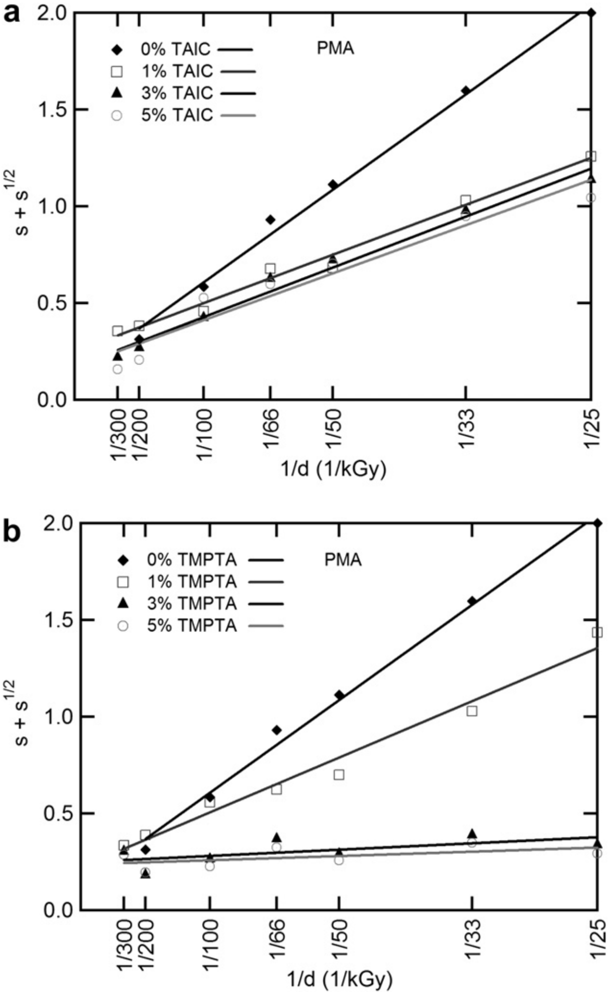

Fig. 3. Relationship of $s + s^{1/2}$ and $1/d$ for PMA blended with a) TAIC® and b) TMPTA and subsequently irradiated.

copolymers and 70:30 MA:IBoA copolymers each sensitized with 9.00 wt% TMPTA and subsequently irradiated at 50 kGy. The T_g is shifted by nearly 20 °C while the rubbery modulus does not move by more than 0.5 MPa. It should be noted that a single glass transition is observed in all irradiated samples.

2.4. *Tuning mechanical properties*

Large scale tunability of rubbery modulus is demonstrated in Fig. 8. 94:6 MA:IBoA copolymers are blended with increasing concentrations of radiation sensitizer from 6.25 wt% TMPTA and 25.0 wt% TMPTA. A greater than order of magnitude increase in rubbery modulus from 1.09 to 13.13 MPa is observed in samples irradiated at 50 kGy. Fig. 9 shows the difference in thermomechanical behavior of the 94:6 MA:IBoA copolymer system sensitized with 25.0 wt% TMPTA and subsequently irradiated at 50 kGy. This copolymer exhibits the highest toughness at the onset of T_g, the highest total strain-to-failure at T_g and the lowest stresses when elongated in the rubbery regime. Table 3

Table 1
Radiation crosslinking parameters of PMA-crosslinker blends.

Crosslinker	p_0/q_0	d_0 (kGy)	R^2
0%	0.129	25.57	.993
1% TAIC	0.248	14.30	.985
3% TAIC	0.173	14.00	.982
5% TAIC	0.170	13.21	.934
1% TMPTA	0.223	15.94	.976
3% TMPTA	0.248	1.836	.383
5% TMPTA	0.237	1.240	.300

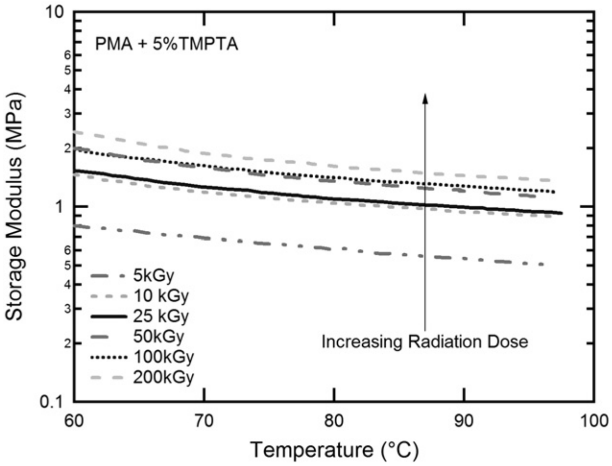

Fig. 4. The dynamic mechanical response in the rubbery regime of PMA blended with 5 wt% TMPTA at increasing radiation doses.

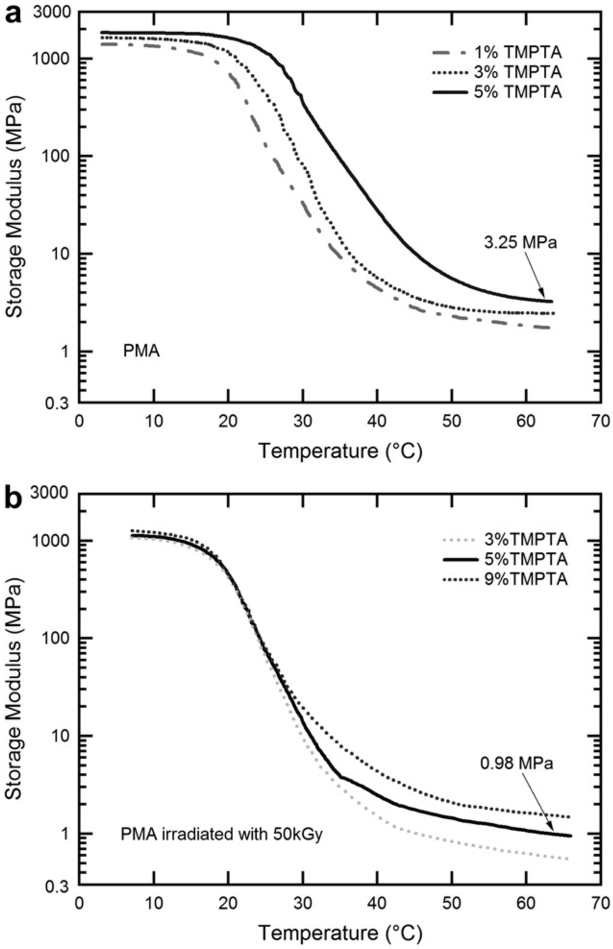

Fig. 5. The dynamic mechanical response of PMA with increasing TMPTA a) crosslinked during UV polymerization and b) crosslinked during electron beam radiation at 50 kGy.

Table 2
The thermomechanical effects of irradiation on a 70:30 wt% MA:linear builder copolymer system blended with an additional 9 wt% TMPTA.

Linear Builder	T_g (°C) 5 kGy	T_g (°C) 50 kGy	T_g (°C) 300 kGy	E_R (MPa) 5 kGy	E_R (MPa) 50 kGy	E_R (MPa) 300 kGy
IboA	52.2	55.6	52.2	0.79	0.82	1.1
TbCHA	47.0	59.8	51.4	0.46	0.98	0.47
NiPAAM	61.3	69.2	67.2	0.57	0.68	0.97
AMO	61.6	68.6	61.2	1.0	3.2	1.2
CXEA	32.1	34.7	30.1	0.92	2.1	2.1

presents maximum stress and strain data for poly(MA-co-IBoA) sensitized with either 3.00 wt% TMPTA or 25.0 wt% TMPTA. At 3.00 wt% TMPTA maximum strains were measured by crosshead displacement to be above 700% for samples strained in the rubbery regime and above 1000% for samples strained at T_g and at onset. Testing limitations prevented accurate large strain measurements of the deformation of these samples, but the given metrics present comparative order of magnitude bounds on maximum strains. The stresses obtained at the given strains present lower bounds of the maximum stress each material can withstand. This metric is highest at onset of T_g. In comparison, samples blended with 25.0 wt % TMPTA strain an order of magnitude less than the samples sensitized with 3.00 wt% TMPTA but demonstrate stresses roughly four times larger.

Fig. 10 demonstrates the shape-memory cycle on both MA–-IBoA copolymers blended with 3.00 wt% and 12.5 wt% TMPTA. When strained to 50%, the 3.00 wt% TMPTA samples shows residual strains of 3.00% while the 12.5 wt% sample fully recovers.

3. Discussion

Mnemosynation enables exploration into shape-memory polymer systems and emergent properties that have not traditionally been studied because the resultant devices would have been cost prohibitive. These new devices can now be manufactured through traditional plastics processing techniques and still possess end thermomechanical properties of thermoset shape-memory polymers. We believe that this manufacturing technique opens the door to a swath of new commercial products that could benefit from tunable thermoset shape-memory properties and are, for the first time, able to be produced in a low cost manner and able target these specific thermomechanical properties: T_g and E_R.

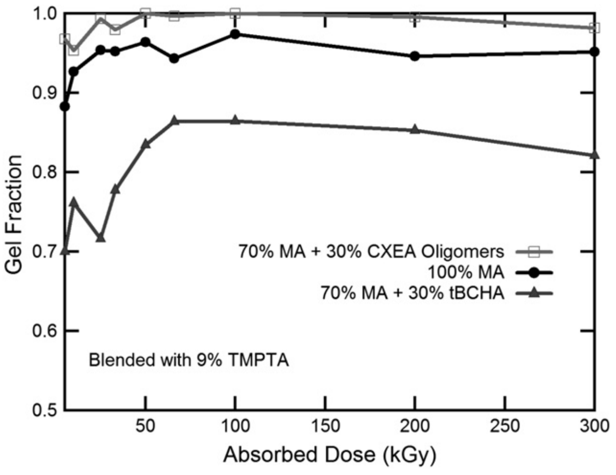

Fig. 6. Gel fraction as a function of radiation dose for selected copolymers from Table 2 compared with a control of PMA, each blended with 9 wt% TMPTA.

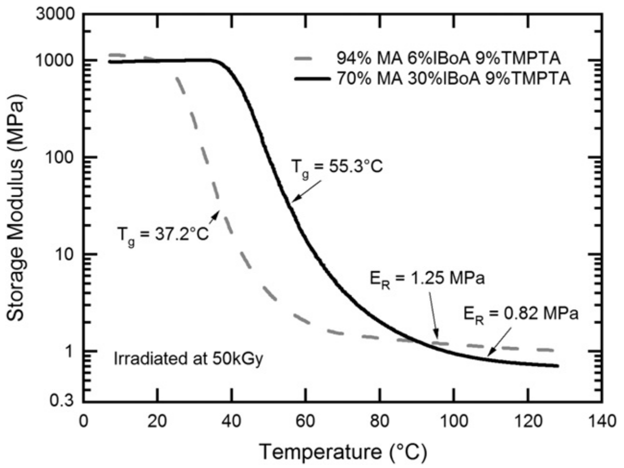

Fig. 7. The effect on rubbery modulus and T_g of changing the composition of linear builders from 94:6 to 70:30 wt% MA:IBoA when blended with 9 wt% TMPTA and irradiated at 50 kGy.

3.1. Altering dose

TAIC and TMPTA have both been proposed as radiation sensitizers, but in the acrylate systems assessed, the performance of TMPTA as a radiation sensitizer was far superior to that of TAIC. The efficacy of each is shown in Figs. 2 and 3 and Table 1. The behavior of the TAIC-sensitized systems at doses from 0.00 to 5.00 wt% follows the Charlesby–Pinner model well, which describes random crosslinking. This indicates the relative ineffectiveness of TAIC in promoting additional crosslinking. Deviation from the line of fit of the 5.00 wt% TAIC blend as seen in one minus the R^2 value is 0.066. This means the TAIC blends when irradiated do not dramatically alter the crosslinking of the underlying polymers. This is further evidenced by a decrease in minimum dose for gelation from 25.57 kGy to only 13.21 kGy.

The TMPTA, however, is very effective a sensitizing radiation crosslinking. R^2 values below 0.400 indicate that the Charlesby–Pinner equation does not predict the experimental sol–gel values well and that TMPTA is effective in inducing additional crosslinks when irradiated. This trend is also noticeable in 3.00 and 5.00 wt% TMPTA blends in Fig. 2b, which show gel fractions above 90% across all doses from 5 kGy onward. As further evidence, the minimum dose for gelation is below 2 kGy for both the 3.00 wt%

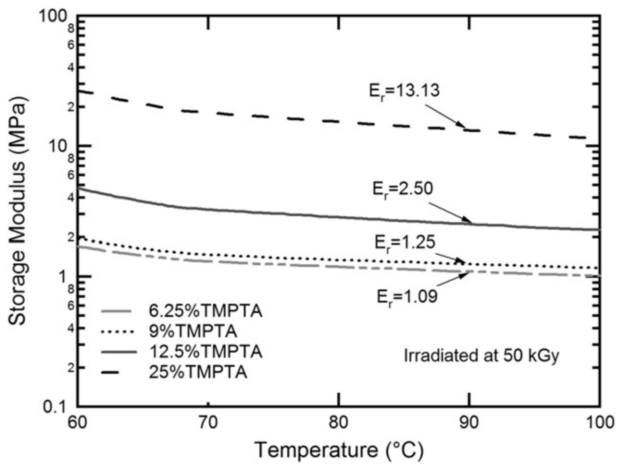

Fig. 8. The effect on rubbery modulus of changing the blend concentration of TMPTA in 94:6 MA:IBoA copolymers, irradiated at 50 kGy.

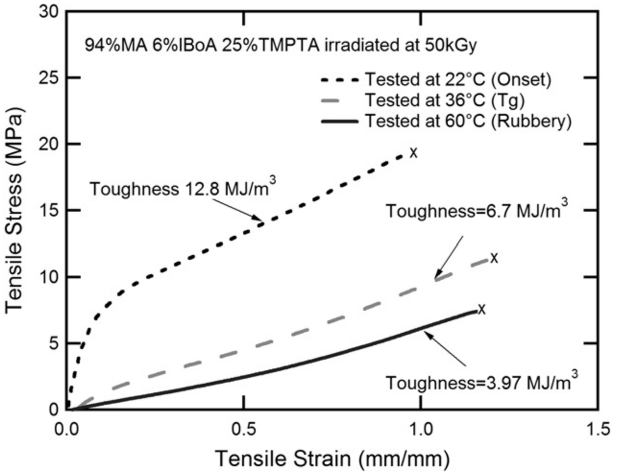

Fig. 9. The stress–strain responses and toughnesses of 94:6 MA:IBoA copolymers blended with 25 wt% TMPTA and irradiated at 50 kGy. Test was performed at onset (22 °C), T_g (36 °C) and in the rubbery regime (60 °C).

and 5.00 wt% TMPTA blends, indicating the relative ease with which crosslinks can be induced even at low radiation doses. Thus TMPTA blended into PMA systems sensitizes crosslinking much more effectively than does TAIC.

Several factors combine to dictate the value of the scission to crosslinking ratio, p_0/q_0, which is determined by extrapolating the linear fit of $1/d$ vs. $s + s^{1/2}$ onto the y axis, where $1/d$ would be equal to zero. The ratio is lowest with no blended sensitizer. As reactive as the sensitizers are, some amount of sensitizer will not incorporate into the network and wash out during the gel analysis, which in turn will appear as if there is less crosslinking relative to scission. Thus increasing the amount of sensitizer in general increases the apparent ratio. This seems counter-intuitive, but although there are more crosslinking events at higher sensitizer concentrations, the ratio does in fact increase to a point. Once enough sensitizer is incorporated, such as at 5.00 wt%, the ratio begins to taper off again, representing that the amount of unincorporated material is heavily outweighed by the increases in crosslinking and the relatively higher number of total events.

The ability to move E_R is primarily shown in Fig. 8 through an increase in the concentration of the TMPTA blend. However, Fig. 4 presents an alternative way to increase E_R by changing the radiation dose to which the polymer is exposed. Fig. 4 demonstrates the ability to move rubbery modulus with altering the dose alone, but the magnitude of this change is dwarfed by the control of E_R seen in Fig. 8 by altering the amount of blended sensitizer TMPTA. It is important to note in Fig. 4 however, the positive effect that increasing dose has on increasing E_R.

3.2. Altering crosslinker concentration

Fig. 5 compares materials crosslinked during polymerization to materials in which crosslinking was induced by radiation sensitization through the *Mnemosynation* process. Increasing the amount of tri-functional crosslinker in systems crosslinked during polymerization from 1.00 to 5.00 wt% has a large effect on the E_R, nearly doubling it from 1.72 to 3.25 MPa. In *Mnenmosynated* systems such as those pictured in Fig. 5b, the incremental effect of increasing blend composition has a much smaller effect on both T_g and E_R. Increasing the blend concentration from 3.00 wt% TMPTA to 9.00 wt% TMPTA, E_R increases from 0.55 MPa to 1.55 MPa while the T_g remains constant.

3.3. Manipulating glass transition

The most challenging aspect of this work was to devise a system that showed true independent control of the T_g and E_R. In traditional systems this can be accomplished by copolymerizing various linear monomers with different side groups that dictate the end chain mobility and thus T_g of the polymer on the macro scale. Often this is accomplished by copolymerizing acrylates with methacrylates. The additional methyl group opposite the ester group off the main polymer chain after polymerization, creates a backbone ternary carbon, leading to increased steric hinderance, that impedes molecular motion and thus raises the T_g. So although methacrylates are often used to raise the T_g in SMP systems, their effect in radiation crosslinked systems is undesirable. The ternary carbon is a target for chain scission, which drives the scission to crosslinking ratio over 1 and leads to poor mechanical properties. Thus a fundamental challenge exists to raise the T_g while avoiding chemical structures that typically move T_g upward such as backbone ternary carbons. A search of a variety of copolymer candidates was condensed into five candidates in Table 2: isobornyl acrylate (IBoA), 4-*tert*-Butylcyclohexyl acrylate (TbCHA), *n*-isopropyl acrylamide (NiPAAm), 4-Acryloylmorpholine (AMO) and 2-carboxyethyl acrylate oligomers (CXEA). Isobornyl acrylate was selected due to the large increase in T_g exhibited by MA–IBoA copolymers.

There is uncertainty concerning the specific targets of radiation crosslinking of acrylates as to which bonds from the thermoplastic polymer chains act as active sites when exposed to radiation. One theory has proposed that hydrogen atoms connected to main chain carbons are potential sites for crosslinking [21]. Another theory predicts that α-hydrogen atoms, bound to the carbon atom which is in turn bound to the ester in the acrylate side chain, are the most likely targets, in turn generating a free radical which becomes a site for crosslinking [46,47]. Data from Fig. 6 support the latter hypothesis. *t*BCHA only contains two α-hydrogen atoms while MA contains three α-hydrogen atoms and the CXEA oligomers contain four α-hydrogen atoms. Increased gel fraction is observed in copolymer systems irradiated at the same dose with additional α-hydrogen atoms. While other variables may be at play, the authors believe that the number of α-hydrogen atoms is directly related to crosslinking efficacy in systems crosslinked by electron beams.

Although IBoA only has two α-hydrogens (compared to more in alternative lower T_g choices), it was chosen as a candidate to copolymerize with MA that would raise the T_g in place of a methacrylate. The bulky nature of the large side group increases steric hindrances and moves the T_g considerably as seen in Table 2. Fig. 7

Table 3
The max strains and stress at max strain of 94:6 MA:IBoA blended with 3 and 25 wt% TMPTA at onset, T_g and in the rubbery regime.

Crosslinker	Max strains (mm/mm)			Stress at max strain (MPa)		
	T_g−12 °C	T_g	$T_g + 24$ °C	$T_g - 12$ °C	T_g	$T_g + 24$ °C
3% TMPTA	>10[a]	>10[a]	>7[a]	>4.8[a]	>2.9[a]	>1.7[a]
25% TMPTA	0.835 ± 0.13	1.14 ± 0.06	1.09 ± 0.10	19.9 ± 3.5	13.8 ± 3.6	6.67 ± 2.0

[a] Minimum bounds on strain-to-failure, max stress.

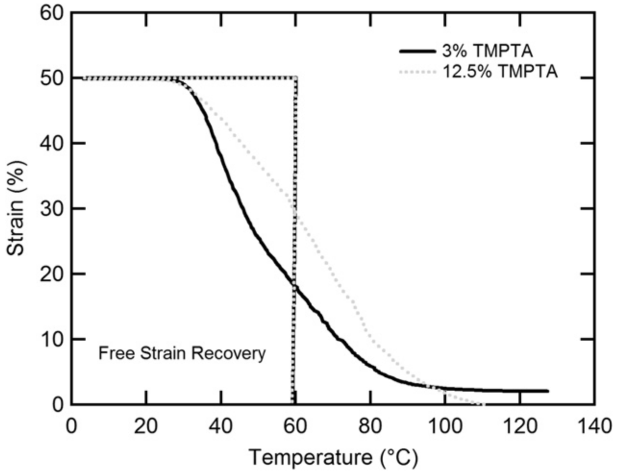

Fig. 10. Free strain recovery of 94:6 MA:IBoA blened with 3 and 12.5% TMPTA strained 60 °C to 50%, cooled to 0 °C, unloaded and heated to 120 °C at 5 °C per minute.

additionally demonstrates the ability to shift T_g using MA–IBoA copolymers. By increasing the concentration of IBoA relative to MA from 6.00 wt% to 30.0 wt%, T_g is moved upward by nearly 20 °C without adversely affecting the rubbery modulus by more than 0.5 MPa. This miscibility of each blended and irradiated system is demonstrated through the presence of a single glass transition.

3.4. *Tuning mechanical properties*

Fig. 8 demonstrates the ability to alter E_R by more than an order of magnitude by increasing the amount of radiation sensitizer blended into the given copolymers. The extent of crosslinking is primarily governed by the amount of sensitizer blended into the copolymer while the T_g is primarily driven by the main chain interactions of the specific concentration of linear copolymers selected. Thus independent control of E_R and T_g has been established, and this allows specific polymer systems to be designed for specific applications with specific thermomechanical needs. *Mnemosynation* yields the added benefit of enabling mass-market scale up of devices though the ability to perform traditional plastics processing steps on the material to shape it into complex geometries before it is radiation crosslinked at very low costs.

Fig. 9 is noteworthy in that it demonstrates predicted shape-memory stress–strain properties of blended copolymers when tested at the onset of T_g, at T_g and in the rubbery regime. As in traditional lightly crosslinked shape-memory polymer systems, the strain-to-failure is highest at T_g while the toughness is the greatest at the onset of T_g. Table 3 tabulates the stress–strain response for samples crosslinked with 3.00 wt% TMPTA and 25.0 wt% TMPTA. Maximum strains for the lightly crosslinked samples exceed 700% while stresses at these large strains are relatively low. High strains of SMPs measured by crosshead displacement are not accurate due to slippage in and contribution from the grip sections as the polymer elongates. High strain measurements were taken in similar polymers systems with accurate video measurement of the strains which corresponded to roughly 40% of the strain measured by crosshead displacement alone [48]. High strain metrics were tabulated here to demonstrate the large difference in strain between the heavily crosslinked samples and the lightly crosslinked samples rather than to show precise large strain endpoints. In more heavily crosslinked samples such as the 25.0 wt% TMPTA blend, maximum strains are observed near 100% while the maximum stresses are nearly 4 times greater than those in the lightly crosslinked samples. As the blend concentration increases the residual strain after a shape-memory cycle decreases. Fig. 10 depicts the shape-memory cycle in a strain–temperature plane. When at least 12.5 wt% TMPTA is blended into the copolymer, no permanent strain is evident after one cycle while in the selected MA-IBoA copolymer blended with 3.00 wt% TMPTA, 3% strain remains in the sample after undergoing a shape-memory cycle in which the material was strained to 50%. Thus residual strain of 6% of the induced strain remains in the material after a single cycle.

4. Conclusions

A new method has been proposed and validated for accurately tuning the thermomechanical properties of network acrylates with shape-memory properties. Adjustment of rubbery modulus in the range from below 1 MPa to above 13 MPa was demonstrated. Rubbery moduli were tailored by varying both radiation dose between 5 and 300 kGy and crosslinker concentration between 1.00 and 25.0 wt%. T_g manipulation was independently shown between 23 °C and 70 °C in copolymers of MA and various other linear acrylates and acrylamides. Shape memory behavior was demonstrated by free strain recovery tests with recovered strains above 90% for all samples. The proposed method, *Mnemosynation*, could enable low cost mass-manufactured devices in complex shapes with tunable thermomechanical and shape-memory properties.

5. Experimental

5.1. *Materials*

Methyl acrylate (MA), isobornyl acrylate (IBoA), Triallylisocyanurate (TAIC®), trimethylolpropane triacrylate (TMPTA), *n*-isopropyl acrylamide (NiPAAm), acryloylmorpholine (AMO), 4-*tert*-butylcyclohexyl acrylate (*t*BCHA), 2-carboxyethyl acrylate oligomers (Mn ∼ 170) (CXEA) and photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were all ordered from Sigma–Aldrich, unless otherwise noted and used in their as received conditions without further purification.

5.2. *Synthesis of polymer networks*

Copolymers were synthesized by free radical polymerization using 0.1 wt% DMPA. For networks formed solely through free radical polymerization: 3 g mixtures of the monomers mixed with the photoinitiator were injected between glass slides separated using 1 mm glass spacers. For thermoplastics that would be subsequently irradiated: 35 g mixtures of linear builders and DMPA were poured into 100 mL polyethylene containers. Polymerization was performed using a crosslinking chamber with five overhead 365 nm UV bulbs (Cole–Parmer). Materials were cured for 1 h. Samples were either cut for testing or pelletized for further processing.

5.3. *Crosslinker blending*

Samples were blended with unreacted crosslinker (TMPTA or TAIC®) in a Brabender PlastiCorder. 35 g thermoplastic copolymer batches were pelletized and fed into the mixer and heated to between 150 °C and 220 °C. The liquid crosslinking agent was dripped into the mixing chamber. Samples were mixed for 7 min at which point the torque had leveled off to near 10 Newton-meters.

5.4. *Radiation crosslinking*

Samples blended with unreacted crosslinker (TMPTA or TAIC®) were injection molded or heated and pressed with a 12-Tonne

Carver Press into their desired shapes. Samples were packaged in air into sealed polyethylene specimen bags and sent to Sterigenics' Electron Beam facility in San Diego CA. Samples were exposed to either 5, 10, 20, 33, 50, 66, 100, 200 or 300 KGy as denoted. Samples were tested as received from Sterigenics.

5.5. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) in tensile loading was used to determine the T_g, onset of T_g and rubbery modulus of the networks using a TA Q800 DMA. Rectangular samples with dimensions of approx. $1 \times 5 \times 25$ mm^3 were cut and tested. The samples were thermally equilibrated at T_{low} for 2 min and then heated to T_{high} at a rate of 2 °C per minute at 1 Hz. Testing was performed in cyclic strain control at 0.2% strain. A preload force of 0.001 N and a force track setting of 125% were used. T_g was defined at the peak of tan delta. Samples were run in triplicate, and variations in T_g were within one standard deviation of 3–5 °C. The onset was calculated by the intersecting line method. The rubbery modulus was observed between $T_g + 24$ °C or $T_g + 50$ °C and noted as such in the representative figures.

5.6. Differential scanning calorimeter

The Q100 DSC from TA Instruments with an RCA cooling accessory was used to confirm shifts in T_g. Hermitic Aluminum pans were filled with polymer samples weighing between 3 and 15 mg. Nitrogen was used as the purge gas. Polymers were subjected to a Heat–Cool–Heat cycle to erase thermal memory. Samples were heated from ambient to 150 °C at 5 °C per min, then cooled to -25 °C at 10 °C per minute and heated at 5 °C per min to combustion near 320 °C. The intersecting line method was used to determine T_g.

5.7. Uniaxial tensile tests

Mechanical tensile tests were performed with the MTS Insight 2. Samples were cut to ASTM dogbone Type IV samples. Materials were strained isothermally at 10 mm per min using a 100N Load Cell in a variable temperature Thermal Chamber at the temperature specified. Grips were hand-tightened and the chamber was allowed to equilibrate for 10 min at the specified testing temperature. For samples tested above T_g, grips were often re-tightened after an initial heating above T_g to minimize slippage. Testing limitations regarding the size of the thermal chamber and slippage due to high strains led to lower bounds on max strain and max stress for samples of PMA-co-IBoA blended with 3 wt% TMPTA and subsequently irradiated with an electron beam.

5.8. Gel fraction tests

Vials were prepared with approximately 20 mL of acetone placed in each. Three samples of each polymer weighing between 80 mg and 110 mg were weighed and then placed in a separate vial. The vials were allowed to soak for 7 days to allow all non-crosslinked material to be removed from the network polymer. The polymer was then removed from the acetone and placed on preweighed weigh paper. The paper and polymer were then placed into a vacuum oven at 40 °C and 0.33 atm for 24 h to drive off the remaining solvent. The polymers and paper equilibrated to standard conditions in the ambient lab environment for 24 h. The samples were then weighed on the paper. The final polymer weight was determined by subtracting the weigh papers' original weight from the total weight.

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