Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 595–598 **595**
DOI: 10.1021/ma902021v

Self-Healing of Thermoplastics via Living Polymerization

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Received September 10, 2009
Revised Manuscript Received December 9, 2009

Autonomic self-healing polymers can be made by incorporating fluidic healant-loaded vessels. Crack-induced breakage of the tiny containers leads to delivery of the healant into damaged regions and trigger of repair through polymerization of the healant.[1] The method used to be applicable to thermosets or elastomers but has not yet been applied to thermoplastic polymers.

On the other hand, to ensure sufficient strength for long-term structural applications, establishment of covalent bonding between the separated parts during self-healing of cracks in polymers is desirable. This is because the adhesion generated by chemical bonds is much stronger than that produced by secondary forces (like van der Waals, hydrogen, and electrostatic forces). In this context, the repair strategy had better to be based on chemical reaction between healing agent and crack surfaces. For thermoplastic polymers, however, no therapy allowing autonomic self-healing is available. A healing agent like epoxy monomer[2] that is good at repairing cured epoxy usually cannot react with thermosplastics at room temperature. Actually, even in the case of thermosetting polymers, polymerization of healing agent could not bring about any covalent bond between healant and completely cured matrix. The existing healing methods do not enable the matrix to take part in the healing reaction. New concepts should be proposed accordingly.

Living polymerization is a process in which chain transfer and termination are removed.[3] It proves to be very useful in obtaining various types of tailor-made polymers with finely controlled molecular weight and molecular weight distribution. Because the resultant polymer carries living ends, chain growth is always allowed so long as monomer is available. It is therefore a popular method for synthesizing block copolymers since the polymer can be prepared in stages, each of which contains a different monomer. Being enlightened by this interesting characteristic, we suggest mixing microencapsulated glycidyl methacrylate (GMA) monomer (healing agent) with a living poly(methyl methacrylate) (PMMA) as matrix. Owing to the infinitely long lives of the molecules' ends of the matrix, as long as the monomer is released from the spheres as a result of crack initiation or propagation, the polymerization process of the healing agent will be started at ambient temperature wherever the monomer meets the matrix (Supporting Information Scheme 1). Then, the newly formed macromolecules, which are covalently attached to the interface, would fill the interstitial space of cracks and fuse with the matrix into one. In this way, the inert matrix that is passively healed in the case of thermosetting polymers turns to play an active role, simply as part of the healing agent (initiator). Since no catalyst is required for resuming chain growth in this system, naturally there is no question about catalyst deactivation.

Hereinafter we show the feasibility of this idea. First, atom transfer radical polymerization (ATRP), one of the most powerful control/living radical polymerization techniques,[4] is selected as the healing reaction. It has been known that polymers prepared by ATRP are highly chain end-functionalized and can participate in various postpolymerization modifications.[5] So far, a variety of monomers have been successfully homopolymerized in ATRP systems at ambient temperature, including methyl methacrylate (MMA),[6] benzyl methacrylate (BMA),[7] and glycidyl methacrylate (GMA).[8] Moreover, copolymerization of GMA with methyl acrylate can also proceed by ATRP at ambient temperature.[9] Considering the need of autonomic self-healing without manual intervention, therefore, we choose poly(methyl methacrylate) (PMMA) made by ATRP as the matrix polymer, in which microencapsulated GMA is dispersed as one-component healant. Compared to MMA, GMA is easier to be encapsulated via in situ interfacial polymerization because of its high boiling point (189 °C), low volatility, and low solubility in water. The similar polarity of PMMA and GMA facilitates wetting of GMA monomer on the surface of PMMA matrix and hence the subsequent copolymerization.

Living PMMA was synthesized at 25 °C by using ethyl 2-bromoisobutyrate (EBiB) as initiator and cuprous bromide (CuBr)/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA)/tetrabutylammonium bromide (Bu_4NBr) as catalyst (refer to experimental details in the Supporting Information). The role of Bu_4NBr is to increase solubility of the catalyst complex because Cu(II)/PMDETA is poorly soluble in MMA monomer. As verified by the ^1H NMR spectrum (Supporting Information Figure S1), the resultant PMMA is made indeed following the ATRP mechanism. The kinetic plot for monomer disappearance during polymerization of MMA (Figure 1a) reveals the linear time dependence of $\ln([M]_0/[M])$. It indicates that the polymerization is a first-order reaction with respect to monomer, while the concentration of the growing radicals remains constant. Side reactions like chain termination and transfer are negligible. Figure 1b further shows the variations of number-average molecular weight, M_n, and polydispersity, M_w/M_n, with conversion for the ATRP system presented in Figure 1a. Clearly, M_n increases linearly with conversion, and the polydispersity is rather low in all cases (1.08−1.15). These manifest that ATRP of MMA is a controlled/living process.

As mentioned earlier, it is expected that the fluidic healing agent (i.e., monomer) issued from the broken capsules is able to polymerize with the living matrix on its fracture surface so as to mend cracks. Therefore, the initiating activity of the resultant matrix should be verified prior to authentic healing experiments. To do that, bulk PMMA was first prepared by ATRP in a tube. Then, several acrylate monomers were poured onto it in random sequence. The typical procedures are described as follows. Ethyl methacrylate (EMA) was first added onto the aforesaid bulk PMMA, allowing polymerization of the monomer at 25 °C. Similarly, MMA was subsequently added onto the surface of solidified poly(ethyl methacrylate) (PEMA). The procedure was repeated for several times by using EMA, MMA, and GMA monomers. Eventually, a rod with a multilayer sandwich structure was obtained (Figure 1c). This experiment simulates the

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Published on Web 12/29/2009

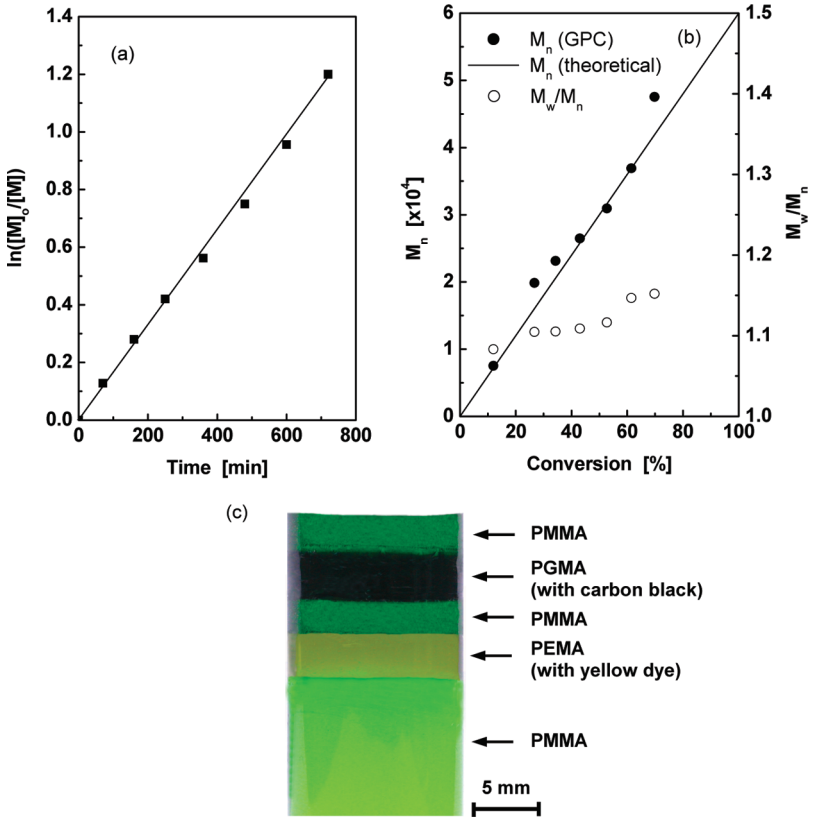

Figure 1. Characteristics of living polymerization of MMA. (a) $\ln([M]_0/[M])$ vs reaction time for ATRP of MMA in bulk at 25 °C. $[M]_0$ and [M] denote overall MMA monomer concentrations at times 0 and t, respectively. $[M]_0 = 0.24$ mol, $[EBiB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.40$ mmol, $[Bu_4NBr] = 3.2$ mmol. (b) Number-average molecular weight, M_n, and polydispersity, M_w/M_n, vs percent conversion for ATRP of MMA using the same recipe as given in (a). (c) Multilayer sandwich structure formed by successively adding acrylate monomers onto living PMMA. The yellow dye and carbon black were incorporated for coloring.

situation when released healing monomer meets the matrix and evidences that the macromolecules in either the base PMMA or the resultant polymers (like PEMA, PMMA, and PGMA shown in Figure 1c) remain active. The obscure interfaces between layers are indicative of diffusion of monomers and formation of copolymers. Clearly, the PMMA derived from ATRP can initiate polymerization of proper monomers whenever the monomers come into contact with the living polymer. It satisfies the requirement of the proposed self-healing via living polymerization.

As the main concern of our study lies in the self-healing capability of the proposed system, self-healing PMMA composites were fabricated by embedding GMA-loaded capsules (Supporting Information Figures S2−S6; diameter: 283 μm; core content: 94.6%; wall material: polymelamine formaldehyde (PMF)) during polymerization of the matrix (refer to Supporting Information). The ratio of Izod impact strengths of a healed and virgin specimen acts as the measure of healing efficiency.[10] It is seen from Figure 2 that our technical route works as planned. Initially, the healing efficiency increases rapidly with increasing healing time, attains ~89% after 12 h, and reaches the equilibrium at about 100% after 21 h. So, a conservative healing period of 24 h was used for the rest of the tests to ensure full healing under room temperature circumstances. Scanning electron microscopic (SEM) observation of fracture surfaces of the specimens indicates that the microcapsules are well adhered to the matrix (Figure 3a). After failure of the specimen, the spheres must be rapidly cleaved but not pulled out, giving off GMA, which was then converted into solidified membrane on the fracture surface (Figure 3b). Figure 4 further gives a live record of the surface polymerization of the released GMA on the living PMMA matrix in terms of in situ Raman spectroscopy. By using the C=O band

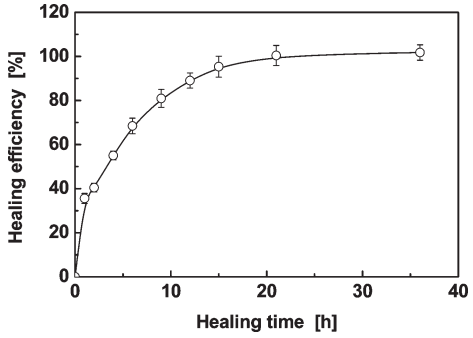

Figure 2. Healing behavior. Healing efficiency of PMMA composites containing 15 wt % GMA-loaded microcapsules (average diameter: 283 μm) as a function of healing time at 25 °C.

at 1725 cm^{-1} which is unaffected by the polymerization as internal standard, the time dependence of the peak intensity of C=C at 1638 cm^{-1} representing the methacrylate group is plotted in Figure 4b. Evidently, the amount of C=C decreases with time, which coincides with the trend exhibited in Figure 2 and can serve as a measure of the healing polymerization kinetics. It reveals that GMA flowed out of the broken microcapsules is able to undergo polymerization on the fracture surface of PMMA, accounting for the satisfied healing effect.

Considering that solvent might also help to heal cracks[11] in thermoplastics through swollen driven chain entanglement across the cracked planes and GMA is a good solvent for PMMA, the contribution of solvent effect of GMA to the healing capability should be understood. Accordingly, a mixture of GMA monomer

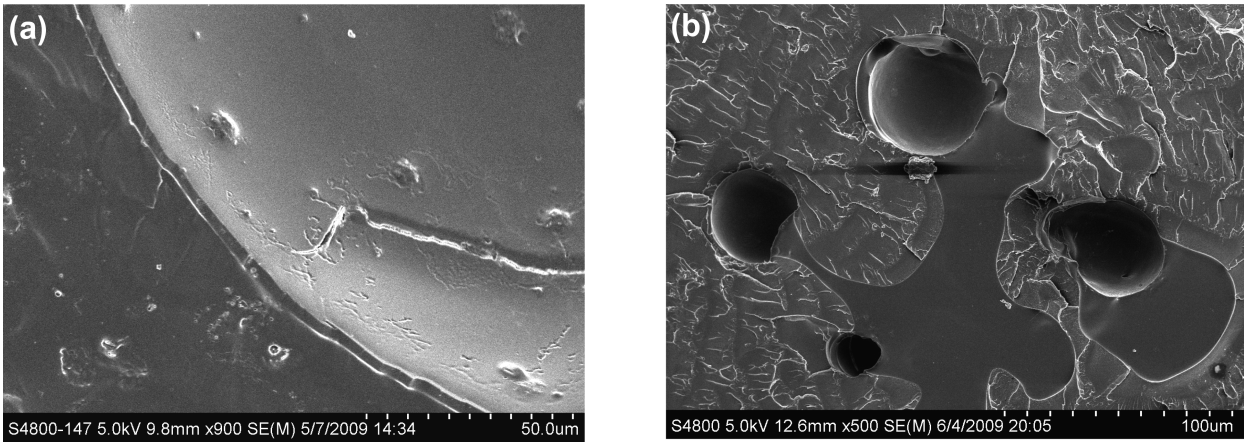

Figure 3. SEM micrographs of fractured surfaces of PMMA composites containing 15 wt % GMA-loaded microcapsules with an average diameter of 283 μm. (a) The specimen had been fractured by the first impact test and the released GMA had been immediately removed by solvent. (b) The specimen had been fractured by the first impact test, healed at 25 °C for 24 h, and then fractured again by the second impact test.

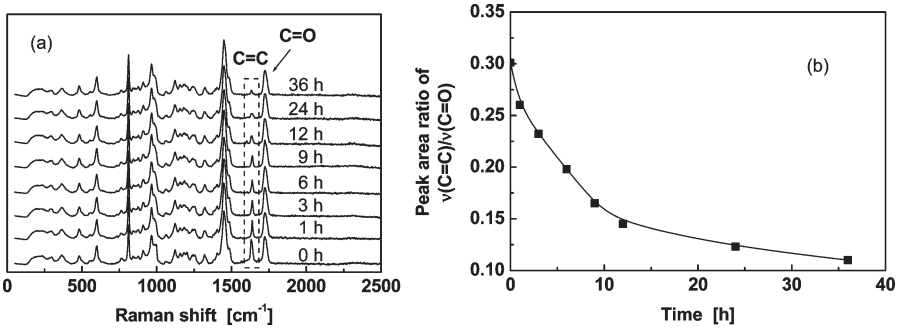

Figure 4. In situ confocal Raman microscopy observation. (a) The typical Raman spectra collected from the center of the fracture surface of a self-healing specimen with 15 wt % GMA-loaded microcapsules (average diameter: 283 μm). (b) Time dependence of the characteristic Raman peak area ratio, showing the consumption of GMA during polymerization.

and its polymerization inhibitor mequinol (which prevents GMA from participating in polymerization) was manually injected onto (i) fracture surfaces of living PMMA specimens and (ii) fracture surfaces of PMMA specimens that had been deactivated by hydrogen peroxide in advance (Supporting Information Figure S7). As a reference, GMA alone was also injected onto fracture surfaces of living PMMA specimens. All the control PMMA specimens used in this part of the experiment do not contain any GMA-loaded capsules. After rehabilitation at 25 °C for 24 h like the authentic samples, healing efficiencies (Supporting Information Table S1) offered by the solvent effect (i.e., the first two cases) were found to contribute little to the overall value (refer to the last case). It means that chemical reaction rather than solvent effect is the main contributor to crack repair. In fact, crack healing of thermoplastics simply using solvent might be not an appropriate option. Regardless of the low healing efficiency shown above, the solvent absorbed deep inside thermoplastics would hardly be desorbed, leading to obvious plasticization and property deterioration. Here in this work GMA plays the role of solvent at the beginning and then is polymerized very soon. Therefore, only the positive side of the solvent effect (i.e., wetting) is included.

In short, room temperature living polymerization proves to be an effective way to impart autonomic self-healing capability to thermoplastic polymers. Such a healing system helps to build up chemical bonding from the cracked planes and does not need the addition of catalyst in a polymeric matrix and manual intervention as well. Our preliminary tests demonstrate that the healing function of the present system remains unchanged after storage for one year as characterized by full recovery of impact strength (Supporting Information Figure S8). An additional potential advantage lies in the fact that the living matrix itself might allow self-healing of radiation (like ionizing, UV, and electromagnetic radiation) induced degradation because of recombination between the new free radicals and the macromolecular radicals on the matrix chain ends.[12] Consequently, multiscale self-healing at both micrometer and molecular levels that is critical for space applications could possibly be developed.

Acknowledgment. The authors are grateful to the support of the Natural Science Foundation of China (Grants 20874117, 50573093, and U0634001).

Supporting Information Available: Experimental details, characterization of the capsules and long-term stability, and results of control tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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