SELF-HEALING OF THERMOPLASTIC POLYMER BY LIVING POLYMERIZATION

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Keywords: thermoplastics, self-healing, living polymerization, microcapsules

ABSTRACT

Autonomic self-healing thermosetting polymers or elastomers have been substantially studied, in which polymerization of the healing agents released from pre-embedded capsules serves as the key issue. As for thermoplastics, another major class of polymeric materials, however, researches on their self-healing approaches are less reported.

Here in this work we show the feasibility of a healing chemistry based on living polymerization (that excludes the possibility of chain transfer and termination) for thermoplastics. Monomer-loaded microcapsules are dispersed in a living polymer matrix that contains living chain ends. When the fluidic monomer is released upon cracking, it is easily polymerized at room temperature wherever it meets the matrix. Then, the newly formed macromolecules, which are covalently attached to the interface, fill the interstitial space of cracks and fuse with the matrix into one, offering satisfied healing efficiency. No catalyst is required for resuming chain growth in the system. The repair processes are carried out without the necessity for manual intervention.

Details of the microcapsules preparation, matrix synthesis and types of controlled radical polymerization (atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT)) are discussed. It is hoped that the results would serve as solid basis for the development of self-healing thermoplastic polymers.

1. INTRODUCTION

So far, there are only a few reports on preparation of self-healing thermoplastics. In the authors' lab, a novel approach is proposed, which employs living thermoplastic polymer as the matrix filled with monomer-loaded microcapsules as the healing agent provider. Because the living polymer carrying active end groups is capable of resuming polymerization at room temperature when fresh monomer is supplied, cracks can be covalently re-bonded by the copolymerization product of the released monomer and the matrix. Such self-healing might combine both micron-scale and molecular scale rehabilitations [1]. Considering the versatility of living polymerization and manoeuvrability of microencapsulation techniques, most thermoplastics would thus be converted into self-healing ones accordingly.

2. MATERIALS

Glycidyl methacrylate (GMA, A.R.) used as the core healing agent to be encapsulated was purchased from Tianjin Damao Chemical Co., China. Melamine (M, A.R.) was provided by Shanghai Linfeng Chemical Co., China. Formaldehyde (F, A.R., 37 wt.%) was supplied by Guangzhou Donghong Chemical Co., China. Methyl methacrylate (MMA), used for making the composite's matrix, was purchased from Tianjin Damao Chemical Co., China. It was washed with sodium hydroxide aqueous solution (5 wt.%), thereafter three times with water, dried over magnesium sulphate, and evaporated to dryness in vacuum. The thermally decaying initiator 2,2´-azoisobutyronitrile (AIBN) was recrystallized twice from ethanol. The synthesis of cumyl phenyldithioacetate (CPDA) was undertaken according to the previously reported protocols [2]. It proceeded by a Grignard reaction of benzyl chloride with carbon disulfide and subsequent reaction of the resultant phenyldithioacetic acid with α-methylstyrene, then recrystallized from methanol as orange crystals.

3. RAFT POLYMERIZATION OF MMA AND PREPARATION OF SELF-HEALING PMMA COMPOSITES

Bulk polymerization was conducted in a two-neck flask. MMA (25.0 g, 0.25 mol), CPDA (0.119 g, 4.16□10-4 mol) and AIBN (0.068 g, 4.16□10-4 mol) were mixed and stirred using a magnetic stirrer. The solution was deoxygenated by purging with argon for 30 min. Considering that CPDA mediated MMA polymerization can be performed at different temperatures from 25 to 45 ºC and higher rate of polymerization is achieved at higher temperature, MMA polymerization was conducted at 45 ºC for a prescribed time with continuous stirring to accelerate the preparation process of specimens. Samples were taken at regular intervals, and the reaction mixture was chilled and diluted with tetrahydrofuran (THF). The resultant polymer was obtained as a yellow powder after three times of dissolving in THF and precipitating from a 10-fold excess of methanol and finally dried in a vacuum oven at 40 ºC for 24 h.

Microcapsules containing GMA was prepared via in-situ polymerization with melamine-formaldehyde resin as the shell material. The details have been reported elsewhere. For making self-healing PMMA composites, the microcapsules have to be compounded with the polymerized MMA. In a typical run, MMA (25.0 g, 0.25 mol), CPDA (0.119 g, 4.16×10^{-4} mol), and AIBN (0.068 g, 4.16×10^{-4} mol) were charged into a two-neck flask and deoxygenated by purging with argon for 30 min. Then, the flask was immersed in an oil bath at a preset temperature of 45 ºC. After 22-24 h, a given proportion of GMA-loaded microcapsules (average diameter = 133.4 μm, core content = 77.7 %) were incorporated into the flask under argon atmosphere and stirring. The mixture was then poured into closed silicone rubber moulds and kept for 96 h at ambient temperature to obtain cured specimens..

4. RESULTS

To confirm the living property of PMMA, an intuitional experiment was conducted at ambient temperature. Firstly, CPDA mediated MMA polymerization was carried out in a tube. Then, GMA monomer was poured onto the solidified PMMA surface and polymerization started at ambient temperature in the atmosphere of argon. After completion of the polymerization of GMA monomer, MMA was added. Finally a rod-

like material with sandwich structure was obtained (Figure 1). When the addition order of the monomers is changed, a rod with similar sandwich structure was also produced. The results demonstrate that the CPDA mediated polymerized product of MMA indeed has the capability of re-initiation of polymerization at ambient temperature. When GMA released from broken microcapsules encounters the fractured surface of living PMMA, copolymerization must occur, re-connecting the damaged sites.

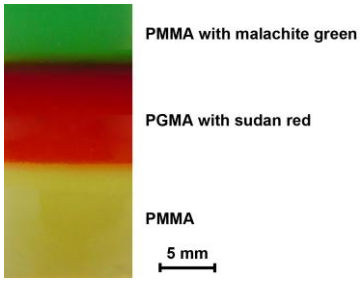

Figure 1: Multilayer sandwich structure formed by successively adding GMA and MMA monomers onto living PMMA. Sudan red and malachite green dye were incorporated for coloring.

Figure 2 shows time dependence of healing efficiency of the self-healing PMMA composites. With a rise in healing time, the healing efficiency increases and eventually reaches the equilibrium of about 100% when the time exceeds 72 h. It means that recovery of impact strength at room temperatures needs at least 72 h. More importantly, the idea of self-healing of thermoplastics via RAFT polymerization proves to be feasible.

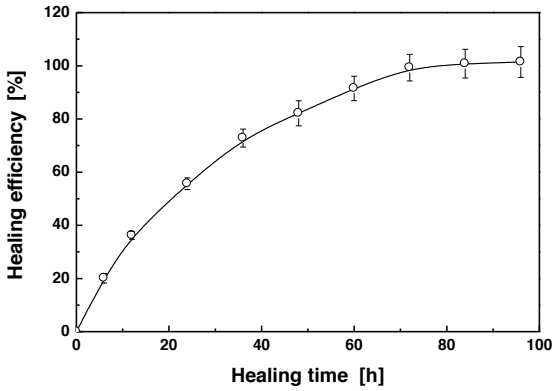

Figure 2: Healing efficiency of PMMA composites containing 15 wt.% GMA-loaded microcapsules as a function of healing time at 25 ºC.

5. CONCLUSIONS

The present work proves that RAFT polymerization is applicable to self-healing thermoplastics based on the strategy of microencapsulation. Restoration of impact strength at room temperature without manual intervention is observed in the living PMMA composites filled with GMA-loaded microcapsules.

ACKNOWLEDGEMENTS

The authors thank the support of the Natural Science Foundation of China (Grants: 51273214, 20874117, 51073176 and U0634001), Doctoral Fund of Ministry of Education of China (Grant: 20090171110026), and the Science and Technology Program of Guangdong Province (Grant: 2010B010800021, 2010A011300004).

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