A NOVEL STRATEGY OF SELF-HEALING THERMOPLASTIC POLYMERS VIA COVALENT BONDING IN LIVING MATRICES

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ABSTRACT

Autonomic self-healing thermosetting polymers or elastomers have been reported, in which polymerization of healing agents released from pre-embedded capsules serves as the key issue [1-3]. As for thermoplastics, another major class of polymeric materials, however, research achievements in self-healing fall behind those in the field of thermosets on the whole. Some works dealing with thermoplastics repairing bonded the cracked surfaces by heating-aided technique, but it is not an autonomic healing. Others restored crack surface in terms of solvents, which diffused into the matrices and fused the cracks, but they would reduce mechanical properties of the matrices due to plasticization effect. More importantly, these methods cannot build up chemical connection between the cracked parts.

Living polymerization is a process in which chain transfer and termination are removed. Because the resultant polymer carries living ends, chain growth is always allowed so long as monomer is added. Being enlightened by this interesting habit, here we show the feasibility of a healing chemistry based on living polymerization. Firstly, poly(methyl methacrylate) (PMMA) was prepared by atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT), respectively. Vinyl monomers (glycidyl methacrylate (GMA), for example)-loaded microcapsules were then dispersed in the PMMA matrix containing living chain ends. When the fluidic monomer was released upon cracking, it was easily polymerized at room temperature wherever it met the matrix. The newly formed macromolecules, which are covalently attached to the interface, filled the interstitial space of cracks and fused with the matrix into one (Figure 1). In this way, the living matrix played a role of macro-initiator, and no catalyst was required for resuming chain growth.

a b c

Figure 1: Schematic drawing of crack repair by living copolymerization of GMA released from the cracked surfaces of living PMMA matrix. a. Diffusion of released GMA monomer into living PMMA matrix, leading to swollen interlayer at the cracked surface. b. Growth of living polyglycidyl methacrylate (PGMA) chains from copolymer of PGMA and PMMA (i.e. PMMA-co-PGMA). c. Crack filled with PMMA-co-PGMA.

Living PMMA was synthesized at 25 ºC by using ethyl 2-bromoisobutyrate (EBiB) as initiator, and cuprous bromide (CuBr)/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA)/ tetrabutyl-ammonium bromide (Bu_4NBr) as catalyst. As verified by ^1H NMR spectrum, the resultant PMMA was made indeed following ATRP mechanism. GMA loaded capsules with diameter of 283 μm and core content of 94.6% was prepared by a two-step approach as reported elsewhere [2] (Figure 2). Self-healing PMMA composites were fabricated by embedding GMA-loaded capsules during polymerization of the matrix. The ratio of Izod impact strengths of a healed and virgin specimen was used to characterize the healing efficiency. It is found that the healing efficiency increases rapidly with increasing healing time up to an equilibrium value of about 100 % after 21 h (Figure 3). To perceive the contribution of solvent effect of GMA to the healing capability, a mixture of GMA monomer and its polymerization inhibitor mequinol was manually injected onto fracture surfaces of living PMMA specimens. After rehabilitation at 25 ºC for 24 h as the authentic samples, healing efficiency offered by the solvent effect was found to be about only one third of the total value.

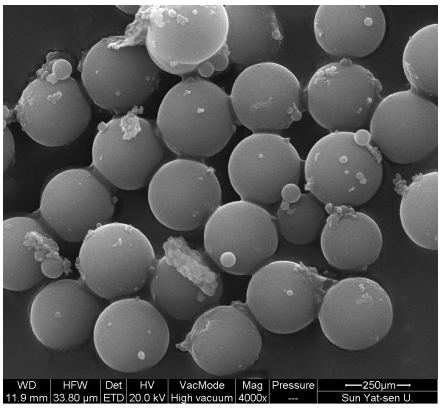

Figure 2: Scanning electron microscope (SEM) micrograph of GMA-loaded microcapsules.

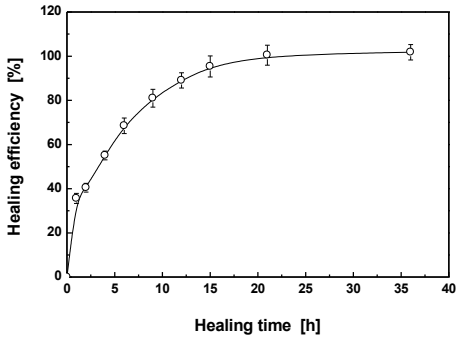

Figure 3: Healing efficiency of PMMA composites containing 15 wt.% GMA-loaded microcapsules as a function of healing time at 25 ºC.

In addition, we further prove that RAFT polymerization is also applicable to self-healing thermoplastics based on the strategy of microencapsulation. Full restoration of impact strength at room temperature without manual intervention is observed in the living PMMA composites filled with GMA-loaded microcapsules. Unlike the self-healing polymer made from ATRP that involves metal ions, the one using RAFT is coupled with robust vitality in air. As a result, it improves the feasibility of practical usage of self-healing thermoplastics via living polymerization.

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REFERENCES

[1] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown, S. Viswanathan, Autonomic healing of polymer compositesm; *Nature*, **409**, 2001; pp.794-797.

[2] L. M. Meng, Y. C. Yuan, M. Z. Rong, M. Q. Zhang, A dual mechanism single-component self-healing strategy for polymers, *Journal of Materials Chemistry*, **20**, 2010, pp.6030-6038.

[3] R. S. Trask, G. J. Williams, I. P. Bond, Bioinspired self-healing of advanced composite structures using hollow glass fibres, *Journal of the Royal Society Interface*, **4**, 2007, pp.363-371.