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COMMUNICATION

Thermo-moldable Self-healing Commodity Plastics with Heat Resisting and Oxygen-insensitive Healant Capable of Room Temperature Redox Cationic Polymerization†

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Commercially available polystyrene is coupled with self-healability by exploiting a novel healing chemistry of redox cationic polymerization. In this system, iodonium bis(4-methylphenyl) hexafluorophosphate (IBH)/glycidyl methacrylate (GMA) loaded microcapsules and NaBH₄ particles are embedded in the matrix through compression molding. The healant is oxygen insensitive and heat resistant so that it meets the requirement of remendable thermoplastics.

Self-healing polymers are extensively investigated recently.¹⁻⁶ The target materials to be healed can be divided into two groups according to their sources: commercially available polymers and tailor-made polymers. In view of application, imparting self-healing ability to the former would be more favorable because there is no need to change their macromolecular structures. However, the relevant researches mostly deal with cured epoxy,⁷⁻⁹ and a few other polymers (like poly(ethylene-co-methacrylic acid) (EMAA),¹⁰ poly(methyl methacrylate) (PMMA),^{11,12} polystyrene (PS),¹³ PMMA/PS blends,¹⁴ polyester,¹⁵ vinyl ester resin,¹⁶ polydimethylsiloxane (PDMS),¹⁷ and polysulfides¹⁸) as well.

Comparatively, thermoplastics (especially commodity plastics), which are widely used in tremendous applications, are less studied. The reported healing approaches are mainly based on encapsulated solvents¹¹ or plasticizer.¹² Chain diffusion and entanglement across the interface caused by solvent effect are responsible for crack healing. Although self-healing has been enabled in the materials, they used to be fabricated by solution casting rather than thermo-processing already adopted in industry. Evidently, it is a bottleneck that restricts mass production of self-healing thermoplastics.

To tackle the problem, we synthesized multilayer microreactors carrying reactants for room temperature atom transfer radical polymerization (ATRP) and compounded the

microreactors with PS.¹⁹ The microreactors survived melt shear mixing and hot compression molding, and the resultant PS composite was self-healable owing to autonomous ATRP of the released monomer (glycidyl methacrylate, GMA) when the propagating cracks damaged the microreactors.¹³ Nevertheless, the healing agent is challenged by the fact that the lower oxidation state copper Cu(I) of the ATRP catalyst in the microreactors would be easily oxidized to Cu(II). That is, the healing reaction would not proceed due to deactivation of the ATRP catalyst if the fracture surface were exposed to air.

Recently, Crivello described a novel cationic redox system with diaryliodonium salt as oxidant and dialkylborane as reducing agent, which can initiate cationic polymerizations of vinyl and heterocyclic monomers at room temperature.²⁰ It was believed that dialkylborane reduced diaryliodonium salt liberating a strong Lewis acid. Then, the Lewis acid, in combination with a trace of protogen like water, triggers polymerization of the monomer by a cationic process. Compared with ATRP, redox cationic polymerization (RCP) seems to be more suitable for functioning as a healing chemistry for thermoplastics by virtue of the stable redox initiator, as well as its oxygen insensitivity, compatibility with a wider range of monomers, and fast polymerization.

Inspired by these advantages of RCP, we formulate the following healing approach for thermoplastics, in hopes of tolerating the high temperature processing as well as overcoming the oxygen inhibition. Iodonium bis(4-methylphenyl) hexafluorophosphate (IBH) cooperates with NaBH₄, constituting a redox cationic initiator for polymerization of GMA. In actual operation, IBH is dissolved in GMA, and then the solution is encapsulated by poly(melamine-formaldehyde) (PMF). Finally, the IBH/GMA-loaded capsules and NaBH₄ particles dispersed in PS matrix are compression molded to form self-healing PS (Figure 1a). Like other extrinsic self-healing materials, polymerization product of the released GMA upon capsules

rupture is supposed to reconnect cracks in PS. Hereinafter, the feasibility of our design is verified.

Before examining the effectiveness of the healing system, we should ascertain whether room temperature RCP of GMA is allowed to proceed under the catalysis of IBH and NaBH_4 . Accordingly, rheological measurement of the mixture of IBH/ NaBH_4 /GMA was conducted. From Figure 1b it is seen that with increasing time the storage shear modulus, G' , loss shear modulus, G'' , and complex viscosity, η^* , initially decrease and then increase. Originally, the high viscosity results from the uneven distribution of NaBH_4 particles in the system, which gradually decreases together with G' and G'' because of the shear induced homogenization. Afterwards, these parameters increase sharply with time, which must be attributed to the polymerization of the mixture. The deduction is supported by the fact that (i) loss tangent, $\tan \delta$, peaks up at the turning point, and (ii) the tested suspension between the parallel-plate clamps was solidified after the experiment. It is thus known that GMA can be polymerized by the IBH- NaBH_4 initiator at room temperature within ~3 h.

To understand the chemical structure of the polymerized product of the mixture of IBH/ NaBH_4 /GMA, its FTIR spectrum is shown in Figure 1c with those of GMA and IBH/GMA solution as references. By comparing the curves of GMA and IBH/GMA, it can be seen that the characteristic absorptions of GMA at 1720 cm^{-1} (C=O), 1640 cm^{-1} (C=C), and 908 cm^{-1} (epoxy group) remain unchanged in IBH/GMA, suggesting that GMA keeps stable with IBH. As for the polymerized product of IBH/ NaBH_4 /GMA, however, its peak profiles are different. For purposes of quantitative estimation of the changes, we define the area ratio of $v(\text{C=C})/v(\text{C=O})$ as α , and that of $v(\text{epoxy})/v(\text{C=O})$ as β . Accordingly, α_0 and β_0 represent the corresponding peak area ratios of the spectrum of IBH/GMA, while α_1 and β_1 denote those of the spectrum of IBH/ NaBH_4 /GMA. The calculation results in Figure 1c indicate that C=C has been greatly consumed, and epoxy group also has a small diminution after the reaction. It means that C=C of GMA is much more active than epoxy group during RCP under current conditions, yielding the random copolymer (Figure 1d).

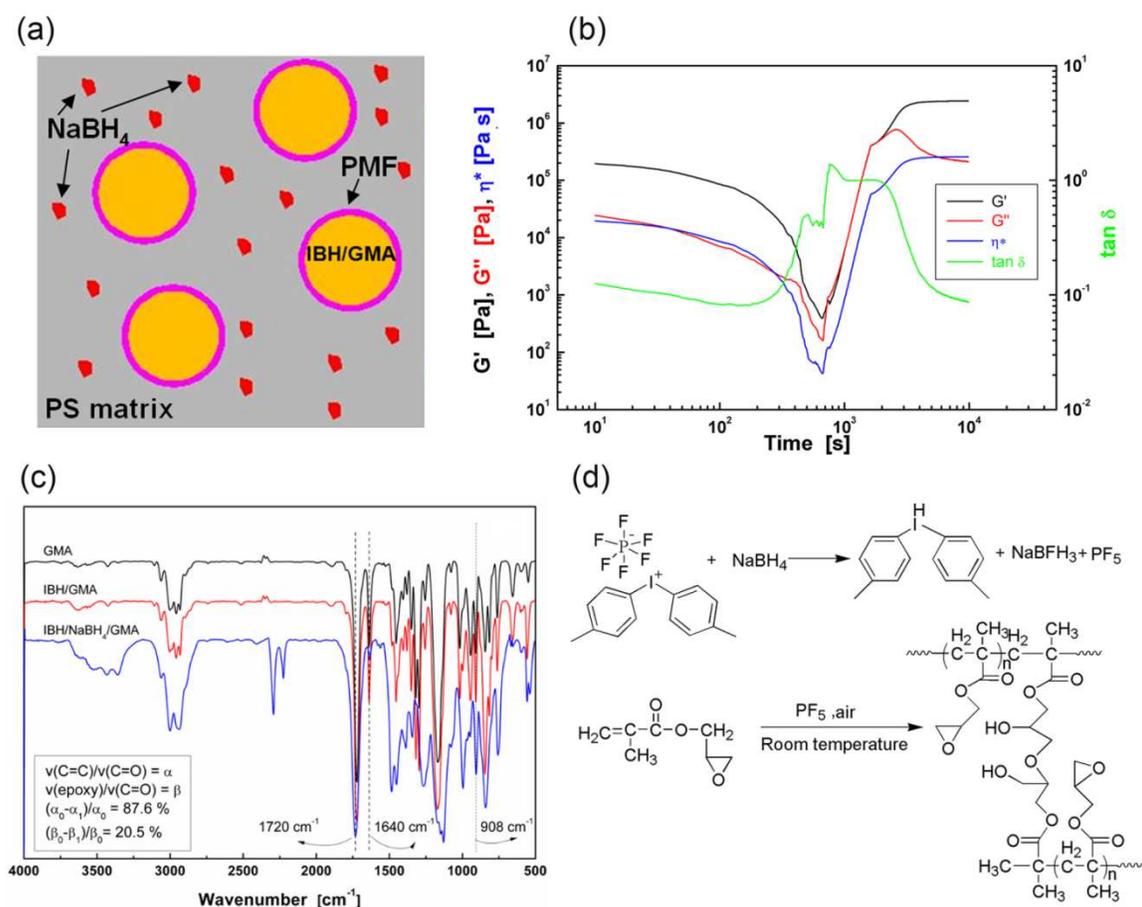


Figure 1. a) Design of the self-healing PS, b) time dependent rheological behaviors of IBH/ NaBH_4 /GMA mixture (IBH: NaBH_4 :GMA=3:3:100 by mol), c) FTIR spectra of GMA, IBH/GMA solution (IBH:GMA=3:100 by mol) and the polymerized product of IBH/ NaBH_4 /GMA mixture (IBH: NaBH_4 :GMA=3:3:100 by mol) that had reacted at 25°C for 3 h, and d) redox cationic polymerization of GMA.

Although IBH/ NaBH_4 /GMA has shown its capability of polymerization, the optimal proportions of the redox cationic

initiators in self-healing system are still unknown. Therefore, two groups of verification tests were done, during which manual

infiltration of the chemicals to the fracture surface of PS specimens for healing plays the key step. In this study, healing ability was assessed by impact test,²¹ and healing efficiency was characterized by the percentage recovery of impact strength. Figure 2a shows the influence of content of NaBH₄ embedded in PS matrix on the healing efficiency at a constant concentration of IBH in GMA. It is seen that the healing efficiency increases with increasing the content of NaBH₄, and almost levels off at above 3 wt%. Figure 2b further reveals the effect of IBH concentration in GMA under a fixed content of NaBH₄ in PS. The maximum healing efficiency of 100% is obtained for 2 wt% IBH. Accordingly, it can be concluded that the self-healing PS should be made by incorporating 3 wt% NaBH₄ particles, while the encapsulated IBH/GMA had better contain 2 wt% IBH. One thing needs to be mentioned. That is, the measurement error of the healing efficiency at NaBH₄ = 1 wt% in Figure 2a is much greater than the others. This should result from the difficulty of even distribution of the low concentration NaBH₄ particles in PS, which affects the uniformity of polymerization degree of the healing agent at the interface.

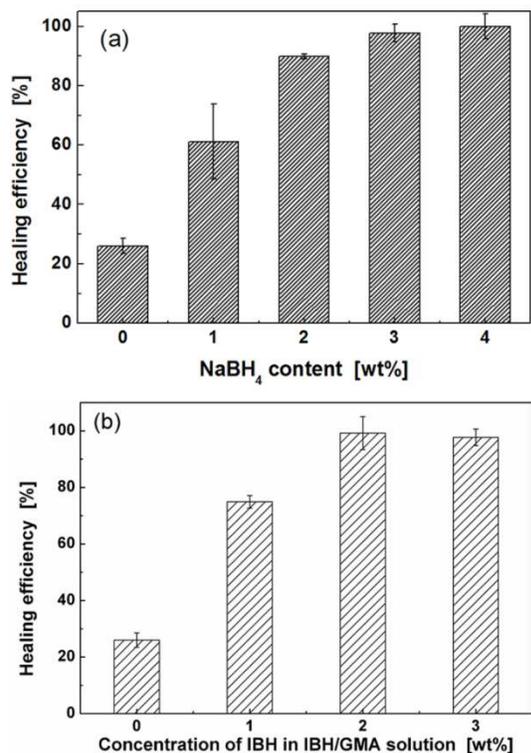


Figure 2. a) Dependence of healing efficiency of PS on content of pre-embedded NaBH₄ particles. IBH/GMA solution (concentration of IBH = 3 wt%) was injected onto the fractured surfaces of the specimens for healing. b) Dependence of healing efficiency of PS on concentration of IBH in IBH/GMA. 3 wt% NaBH₄ particles were pre-embedded in PS. IBH/GMA solution was injected onto the fractured surfaces of the specimens for healing. Healing of the fractured specimens was conducted at 25 °C in air for 24 h.

In fact, Figure 2a exhibits a healing efficiency of around 25% in the absence of NaBH₄. Similar result is also perceived in Figure 2b when IBH concentration is zero. It demonstrates that the solvent effect of GMA can only arouse minor healing effect,^{13,22}

while the polymerization of GMA mainly accounts for the rehabilitation of damaged PS.

On the basis of the above investigation, PMF-walled microcapsules containing IBH/GMA were prepared by in-situ polymerization (Figure S1 and S2, Electronic Supplementary Information (ESI)). Figure 3a shows FTIR spectrum of the microcapsules as well as those of the core and shell substances. The peaks assigned to PMF at 3390 cm⁻¹ (N-H, O-H), IBH at 1400 and 1475 cm⁻¹, and GMA (refer to the discussion of Figure 1c for its detailed peak positions) appear on the spectrum of IBH/GMA loaded microcapsules. Moreover, elements F, P and I are found in the remaining inclusion of broken capsule by EDS analysis (Figure S3, ESI), confirming the presence of IBH inside the microcapsules. These results manifest that the microcapsules have been made as designed.

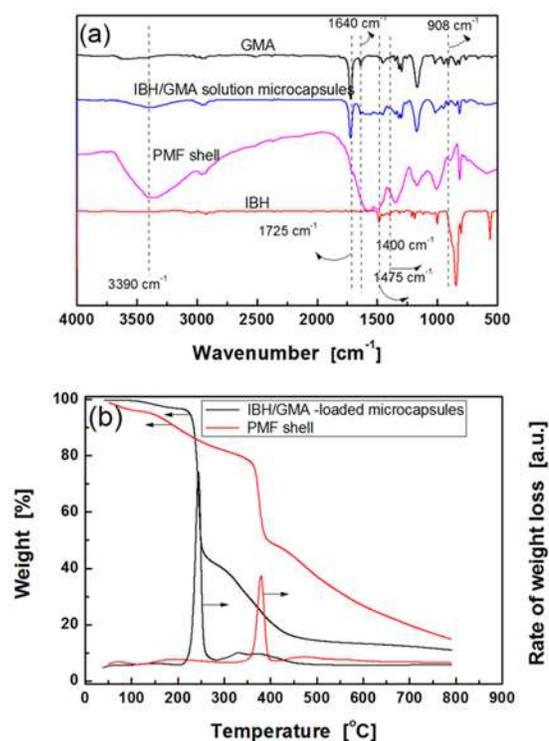


Figure 3. a) FTIR spectra of GMA, IBH, PMF, and IBH/GMA-loaded microcapsules. Concentration of IBH in IBH/GMA: 2 wt%. b) Thermogravimetric curves of IBH/GMA-loaded microcapsules and PMF shell.

We also measured the thermal degradation behavior of the microcapsules. There is no obvious weight loss below 200 °C (Figure 3b). This ensures the thermal stability of the healing capsules during thermo-processing with PS. Meanwhile, when the IBH/GMA-loaded microcapsules were ground with small amount of NaBH₄, the released fluid was quickly solidified (Figure S4, ESI). Evidently, the activity of IBH in GMA is maintained after encapsulation.

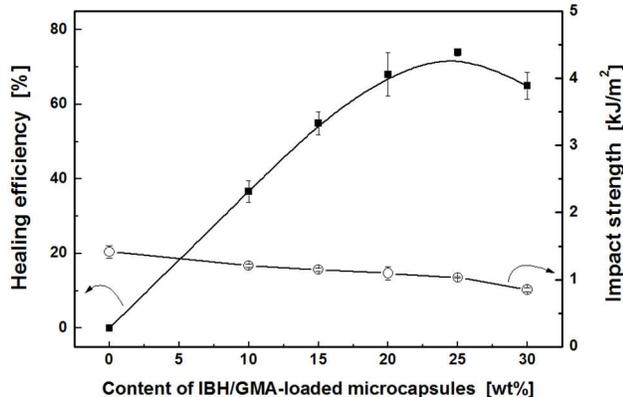


Figure 4. Dependences of impact strength and healing efficiency of authentic self-healing PS composite on content of IBH/GMA-loaded microcapsules. 3 wt% NaBH₄ particles were embedded in PS, while the IBH concentration in IBH/GMA was 2 wt%. Healing of the fractured specimens was conducted at 25 °C in air for 24 h. Impact strength of unfilled PS = 1.40 kJ/m².

Figure 4 illustrates the dependences of impact strength and healing efficiency of self-healing PS composite on content of IBH/GMA-loaded microcapsules. Here the content of NaBH₄ particles is fixed at 3 wt% as suggested by Figure 2a. With increasing the capsules content, impact strength of the composite slightly decreases. Basically, the reduction of impact strength is not significant. In the case of 20 wt% IBH/GMA-loaded microcapsules and 3 wt% NaBH₄ particles, for example, the impact strength of the PS composite is 20 % lower than that of neat PS. Similar embrittlement effect was reported in previous works concerning fluid-loaded microcapsules/polymer composites,^{13,22} but the percentage decline of impact strength of the solution cast PS composite was much more remarkable, i.e. ~60 % as compared to unfilled PS.²² When looking at the dependences of the composites' flexural properties on healing capsules content (Figure S5 and S6, ESI), we can find that at the filler loadings of 20 wt% IBH/GMA-loaded microcapsules and 3 wt% NaBH₄, the rates of reduction are ~18 and ~20 % for flexural modulus and flexural strength, respectively. It means that the present self-healing composites still have moderate mechanical properties for possible application, and appearance of the healing agent nearly does not change the deformation habit of PS. It is worth noting that the strength of the base polymer should not be greatly decreased due to incorporation of the healing capsules. Otherwise, the technique is unlikely to be used in engineering practice. Therefore, we should alleviate the negative influence of the capsules addition on mechanical properties of the matrix to the greatest extent.

As for the self-healing efficiency, it increases linearly with increasing the microcapsules' content until the highest value of ~78% is achieved at microcapsules' content of 25 wt%. The data evidence that the thermo-molded self-healing PS composite can indeed take effect at room temperature. The redox cationic initiators and the healing system are sufficiently stable under hot compression and air exposure. Besides, the effect of healing time on healing efficiency was also measured (Figure S7, ESI). It is found that the healing proceeds rapidly at the beginning and

the speed gradually slows down with time. The healing efficiency approaches to ~40 % within 45 min and reaches the equilibrium at about 180 min. According to these results, the healing time for our experiments set at 24 h can ensure complete polymerization of the healing fluid.

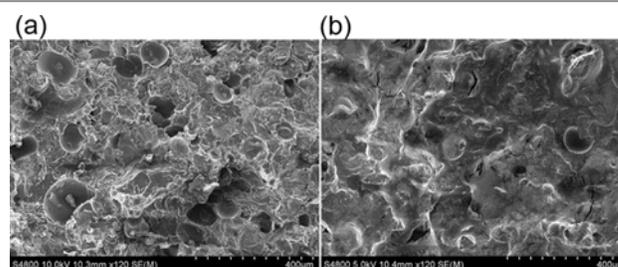


Figure 5. a) SEM microphotos of fracture surface of a virgin self-healing PS composite. The healing agent released from the broken microcapsules was immediately removed by ethanol. b) SEM microphoto of refracture surface of a healed self-healing PS composite. IBH/GMA-loaded microcapsules: 10 wt%, NaBH₄ particles: 3 wt%.

The SEM image in Figure 5a shows that there are quite a few concaves on the fracture surface of the PS composite, which are the halves left by the broken microcapsules. The intact edges of the concaves imply that the microcapsules were not damaged when the composite was made. In contrast, the refracture surface of a healed PS composite seems to be covered by a thin membrane (Figure 5b), which should represent the polymerized healing agent. It is this film that reconnects the cracked PS and restores the strength of the latter. EDS result of the membrane confirms the existence of IBH and NaBH₄ (Figure S8, ESI). That is, the redox cationic polymerization product of GMA successfully provides PS with self-healability.

Redox cationic polymerization proves to be an effective healing chemistry for air-insensitive room temperature self-healing of commercially available thermoplastics. Oxidant IBH together with its boron-based reducing agent NaBH₄ composes an ideal redox cationic initiator. By using the thermally stable IBH/NaBH₄ initiator system, commodity plastics PS filled with IBH/GMA-loaded microcapsules and NaBH₄ particles can be fabricated by conventional compression molding. Additionally, the damaged PS composite can be healed in air at room temperature without manual intervention. This study expands the family of healing chemistries for preparing self-healing thermoplastics processable at elevated temperature.

Further effort should be made to use the residual (unreacted) epoxide groups of the polymerization product of IBH/NaBH₄/GMA, so that bonding strength of the healing membrane would be increased and fewer healing capsules are required. When the repaired part is stronger than the matrix, repeated healing would be available at the sites with intact healing capsules. Moreover, the composite with lower concentration capsules would be less weakened than before.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, SEM micrographs, size distribution and EDS analysis of IBH/GMA solution-loaded microcapsules, photo of solid plate produced by ground microcapsules and NaBH₄ particles, flexural stress-strain curves of PS and its composites, effect of healing capsules content on flexural properties of the composite, healing efficiency as a function of healing time, and the EDS analysis of the re-fractured specimen surface. See DOI: 10.1039/c000000x/

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Thermo-moldable Self-healing Commodity Plastics with Heat Resisting and Oxygen-insensitive Healant Capable of Room Temperature Redox Cationic Polymerization

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By virtue of a novel healing chemistry of redox cationic polymerization, commercially available polystyrene compounded with IBH/GMA loaded capsules and NaBH₄ particles and molded through hot compression is proved to be self-healable at room temperature in air.

