



A new class of self-healable hydrophobic materials based on ABA triblock copolymer via RAFT polymerization and Diels-Alder “click chemistry”



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ABSTRACT

This investigation reports the preparation of a new self-healing ABA tri-block copolymer (BCP) poly(-furfuryl methacrylate-*b*-poly(dimethyl siloxane)-*b*-poly(furfuryl methacrylate) (PFMA-*b*-PDMS-*b*-PFMA) (FDF) via RAFT polymerization using PDMS-CTA as macro-RAFT agent. The formation of FDF triblock copolymer was confirmed by ¹H NMR, GPC and DSC analyses. The phase segregated domain morphology of the synthesized BCP films as a function of PFMA fraction was studied via an AFM. In this BCP, Diels-Alder (DA) click reaction was carried out between the reactive furfuryl group in PFMA unit as diene with different maleimides as dienophile. While the presence of the PFMA unit makes the triblock copolymer thermally amendable and the PDMS present in the matrix makes the BCP ideally suited for hydrophobic self-healing applications. The hydrophobic nature of the triblock copolymer was studied by water contact angle (WCA) measurement and the self-healing property was studied by DSC and SEM analyses.

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1. Introduction

Self-healing materials are an important class of smart materials which have got extensive attention among the material science community [1–7]. Self-healing polymers (SHPs) have several important advantages, as they can lead to autonomous healing of internal crack or damage generated in a polymer matrix and can restore the mechanical strength of the damaged part via autonomic healing, much like our skin.

Self-healing capability in a polymer can be achieved by two distinct approaches. In autonomous self-healing, the polymer network is embedded with microcapsules containing healing agent, which are released into the network when the microcapsule shell is damaged and perform the healing process. This is called the microcapsule approach of self-healing. On the other hand, stimuli-responsive healing systems need external stimuli to trigger the

healing process, which involve the bond breaking and bond rebuilding process. The main disadvantage of microcapsule approach is that microcapsule based approach can healed the polymer surface only once, but approaches based on reversible breaking and reformation of chemical bond can achieve healing over many cycles. White et al. reported the microcapsule embedded autonomous self-healing system which involved the use of dicyclopentadiene as healing agent and Grubb catalyst to form epoxy based healing system [8–10]. Stimuli responsive healing is triggered by various stimuli like light [11,12], pH [13,14], redox system [15–17] and heat [18,19]. Diels-Alder (DA) and retro-DA (rDA) system is one of the most studied self-healing system, where healing is triggered thermally [20–28]. The advantages of this system include its stability against oxygen, moisture and hysteresis free cyclic process. The furan and *N*-maleimide adduct is the most used DA and rDA system to prepare self-healing polymer offering cyclability at mild conditions. Acrylates bearing reactive furfuryl functional group are polymerized via conventional free radical polymerization (FRP) as well as living/controlled radical polymerization (CRP) process [29–38]. The furfuryl groups on the polymers are used to prepare cross-linked polymeric network via DA reaction

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using bismaleimide as dienophile. However, to the best of our knowledge, there is no report on the preparation of ABA triblock copolymers having self-healing as well as hydrophobic properties.

Block copolymers (BCPs) are macromolecules comprising of various sequences of blocks covalently bonded together with varying architectures like linear, branched, star, comb etc. [39] BCPs with immiscible blocks are very interesting, as they show nano-phase separated morphology. Suitable designs of BCP having different segments are very useful for multiple applications, such as thermoplastic elastomers, dispersing agents, emulsifiers, surfactants, surface coating, nanotechnology, electronics and drug delivery [40–44]. The microdomain structure of BCPs can be controlled by controlling block length, choice of solvent or changing temperature [45]. ABA triblock copolymers having an elastomeric middle block (B) and glassy end blocks (A) can act as a thermoplastic elastomer (TPE) [46,47]. Formation of well-defined reversible triblock copolymers is an attractive field of research, because of their several applications in the field of thermoplastic elastomers (TPEs), self-healing polymers, hydrophobic polymers and biomedical applications. Synthesis of ABA triblock copolymers bearing reactive furfuryl group remains a challenge, as furfuryl group undergoes several side reactions during polymerization [32,48].

This article describes the synthesis of a new well-defined triblock copolymer based on furfuryl methacrylate (FMA) via RAFT polymerization using polydimethylsiloxane (PDMS) as bifunctional macro-RAFT agent, followed by their post polymerization modification to prepare self-healable hydrophobic polymeric network via DA reaction between the furfuryl group and maleimides. Poly(dimethylsiloxane) (PDMS) which has several interesting properties like hydrophobicity, high thermal and oxidative stability, high gas permeability and excellent bio-compatibility is used as the middle block in the ABA type BCP in order to enhance flexibility, hydrophobicity as well as thermal stability [49,50]. PDMS blocks are incorporated into the polymer chains to prepare wide variety of materials with tunable properties. PDMS has very low T_g of about -120 °C i.e. having the most flexible backbone. As a result it can adjust the lowest surface energy configuration via a close packing of the pendent methyl groups at the PDMS/air interface. Thus PDMS increases hydrophobicity and thermal stability of many materials [51–55]. PDMS was also used to prepare self-healing polymers [56–59].

In the present work we focused on to prepare self-healing polymer having hydrophobic characteristics. The acrylic based self-healing polymers can be used in self-healing paint, coating and adhesive applications. If the material is hydrophobic in nature, it will form a water resistant thin layer over the substrates making them anti-fouling and anti-corrosive (if the substrate is a metal). In this case microcracks and/or micro-scratches on the surface are self-repaired by autonomic healing. At the same time the surface will be water-resistant, anti-corrosive and anti-fouling. So, we were interested in the development of polymers having self-healing as well as improved hydrophobicity. For that purpose the triblock copolymer of poly(furfuryl methacrylate)-*b*-poly(dimethyl siloxane)-*b*-poly(furfuryl methacrylate) (PFMA-*b*-PDMS-*b*-PFMA) was prepared via RAFT polymerization and modified via Diels-Alder reaction to prepare self-healing polymer having hydrophobic characteristics. The PFMA-*b*-PDMS-*b*-PFMA triblock copolymers were prepared via RAFT polymerization and their self-healing properties were studied by monitoring the healing of a scratch in the BCP film by SEM, optical microscopy (OM) analyses and their hydrophobicity was measured by WCA measurement.

2. Experimental

2.1. Chemicals

Polydimethylsiloxane, bis(hydroxyalkyl) terminated ($M_n \sim 5600$ g/mol), *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Sigma Aldrich, USA. Furfuryl methacrylate (FMA) was purchased from Sigma Aldrich and purified by passing through basic alumina column. 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTSPA), 4,4'-azobis(4-cyanovaleric acid) (ABCVA) and 1,1-(methylene di-4,1-phenylene)bismaleimide (BM) were also purchased from Aldrich. POSS maleimide isobutyl (POSS-M) was obtained from Hybrid Plastics, USA. *N,N'* Dimethylformamide (DMF) (Merck, India) was purified by vacuum distillation over CaH_2 . Dichloromethane (DCM) (Merck, India) was dried over $CaCl_2$.

2.1.1. Synthesis of macro-RAFT (PDMS-CTA) agent of PDMS

Macro-RAFT agent was synthesized by the esterification reaction of bis(hydroxyalkyl) terminated PDMS with carboxylic acid end-functionalized trithiocarbonate RAFT agent catalyzed by DCC/DMAP. The molar ratio of reagents [OH]:[COOH]:[DCC]:[DMAP] was selected as 1: 3: 4: 0.4. In this case 2 g of HO-PDMS-OH ($M_n = 5600$ g/mol, $\bar{D} = 1.35$) (0.35 mmol), 0.018 g of DMAP (0.14 mmol) and 20 mL dichloromethane (DCM) were added to a 50 mL two-neck round bottom flask under dried N_2 atmosphere. Then a solution of 0.4325 g CDTSPA (1.07 mmol) RAFT agent in 10 mL distilled DCM and 0.302 g DCC (1.4 mmol) in 10 mL distilled DCM solution were added dropwise into the reaction mixture of the round bottom flask under N_2 atmosphere. The flask was placed in an oil bath preheated at 40 °C and stirred for 24 h. Then the flask was cooled to room temperature and the reaction mixture was filtered to remove solid impurities. The solvent was evaporated under reduced pressure. 50 mL of *n*-hexane was added and the mixture was filtered for one more time. The resulting mixture was diluted by 100 mL of *n*-hexane and 50 mL of methanol was added to remove unreacted CTA and DMAP. This step was repeated three times. The hexane rich phase containing macro-RAFT agent was added dropwise into methanol for further purification. Again the macro-RAFT agent was dissolved in hexane and washed first with a saturated NaCl solution and then with distilled water. The solution was dried over magnesium sulfate, filtered and the hexane was eliminated under reduced pressure. A final pale yellow liquid product was obtained after drying in vacuum oven. ($M_n = 6200$ g/mol, $\bar{D} = 1.36$).

2.1.2. Synthesis of PDMS-based triblock copolymers (PFMA-*b*-PDMS-*b*-PFMA)(FDF)

In a typical polymerization reaction, FMA (1.34 g, 8.06×10^{-3} mol), PDMS-CTA macro-RAFT (1 g, 1.61×10^{-4} mol) and ABCVA (0.0113 g, 4.03×10^{-5} mol) and DMF (monomer: DMF = 1:1 by weight) were charged into a dried Schlenk tube with a magnetic stirrer bar. The solution was deoxygenated by bubbling N_2 at room temperature. The solution was heated at 80 °C for 5 h for polymerization. At the end of reaction, the reaction mixture was cooled to room temperature and precipitated into methanol. The final polymer was precipitated several times in methanol and then dried under vacuum oven at 40 °C. The final polymer was characterized by GPC, NMR and other analyses.

2.1.3. Modified polymeric network via DA reaction

The triblock copolymer, FDF-3 and 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) (1:1 mol ratio) were dissolved in chloroform in a 25 mL two neck round-bottom flask. The mixture was stirred at 50 °C for 24 h under N_2 atmosphere. The reaction mixture

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