CHAPTER V
FORMATION OF THERMOSETS VIA MOLECULAR POCKET IN THERMOPLASTIC CHAIN: A SIMPLE AND DIRECT WAY TO NANOSPHERICAL THERMOSETS

5.1 Abstract

By simply curing thermosetting monomer of bisphenol A-based benzoxazine in thermoplastic of SEBS block copolymer, nanospherical polybenzoxazines as small as 150 nm with narrow size distribution are obtained in high yield (more than 80%). The homogeneous blends between a series of thermoplastics and benzoxazine monomers confirm that this specific condition allows simple and direct nano- or micro-spherical thermoset resin formation. The present work shows a good model of which the mechanism related to the thermoplastic block copolymer chains function as a molecular pocket where the thermoset curing proceeds to result in nano-sized or micro-sized spheres. The work also proves that this mechanism requires; (i) a particular block of thermoplastic copolymer which allows specific interaction with monomeric thermoset molecules, and (ii) the curing of thermosets in molecular assembly structure to confine the phase separation of thermoset prepolymer during curing

Keywords: SEBS; Benzoxazine; Thermoset Nanosphere; Molecular Pocket

5.2 Introduction

Molecular assemblies under their secondary interaction as a bottom-up method are well recognized as unique systems to provide nanoparticles.[1] In most cases, the preparations have to be carried out under multi-step reactions and the products obtained have to be treated under specific conditions to initiate and maintain nanoparticulation. In most cases, preparations of nanoparticles deal with the thermoplastic system due to the ease to control the morphology, However the preparations are complicated and involved with particular conditions, such as self-assembly of core-corona or amphiphilic polymer,[2] self-organization of block copolymers,[3] micelles, emulsions,[4] and template-aided structures.[5] Furthermore, most thermoplastic nanospheres have to be stabilized under the loosely bound secondary interaction which can be easily dissociated in the harsh conditions, such as pH[6] or temperature. In the case of thermoset nanospheres, there are some reports related to the thermoset formation, mostly are epoxy, in thermoplastic systems.[7,8]

The works paid attention on the phase separation of thermoset in droplets or spheroid granules.[9-11] It should be noted that, in the case of epoxy, the curing has to be done with some hardeners in viscous system and this brings non-unified phase separation to result in various morphologies depending on the mixture composition. Only low content of epoxy resin in the mixture system possibly provides a nano-spherical epoxy thermoset.[7,10] In other words, a significantly high amount of thermoplastic resin (more than 50% concentration) than that of thermoset monomer obstructs a large scale thermoset nanosphere production.

Polybenzoxazine (poly BZ) is a thermoset polymer prepared by simply mixing bisphenol based benzoxazine monomer (BZ), p-formaldehyde, and amine derivatives and leaving for curing at 150°C for 2 hours without any solvents.[12] Poly BZ is a self-thermally cured resin through oxazine-ring opening[13] which hardeners or other components for chemical curing reaction are not necessary.

In the past, inclusion phenomena are known as a molecular assembly that host molecules align themselves to provide specific channel for monomer entrapment

followed by inclusion polymerization which the stereoregularity is effectively controlled.[14] Based on this concept, here, we propose a novel strategy for thermoset resin formation under molecular self-assembly which the consequent specific nano-channel controls the curing system to be nanospherical thermoset fabrication. This process not only simple and direct polymerization to obtain nano-sized resins but also is a good model for large-scale production.

5.3 Experimental

5.3.1 Chemicals

SEBS triblock copolymer with 32 wt % styrene content, M_w of 77 000 g/mol and M_n of 60 000 with PDI of 1.28, measured by GPC, was provided by Asahi Kasei Chemicals Cooperation, Japan. Bisphenol-A, paraformaldehyde, cyclohexylamine , chloroform and toluene were purchase from Fluka, Switzerland. All chemicals were used without further purification.

5.3.2 Synthesis of BZ monomer

Bisphenol-A, cyclohexlamine and formaldehyde were mixing with mole ratio 1: 2: 4 with stirring at about 110°C for 45 minutes, solventless method to afford Pale-yellow solid. The solid product was grinded to powder and washed by cooled methanol several times before dry it at room temperature.

5.3.3 Preparation of SEBS-BZ blended film

BZ monomer and SEBS were mixed (50:50 wt%, namely S50BZ50) in chloroform and cast on teflon sheet before leaving at room temperature to evaporate chloroform and obtain pale-yellowish film.

5.3.4 Curing process and BZ-thermoset nanosphere extraction

The film was cured steply from 100°C to 190°C and keep at that temperature for 3 hours to obtain cured SEBS-polyBZ film. To extract the BZ-

thermoset nanosphere, that cured film was dissolved in chloroform with heating to remove SEBS template. The BZ-thermoset nanosphere was collected by centrifuge machine and washes several times with chloroform.

5.3.5 Characterizations

The chemical structure of BZ-thermoset nanosphere was confirmed by ATR FT-IR microspectroscopy equipped with a miniature-Ge IRE with contact area smaller than 50 micrometer. The nano-sphere morphology was observed by transmission electron microscope (TEM) Hitachi TEM Zero H-7650 with accelerating voltage of 100 kV. Two-dimensional nuclear magnetic resonance (2D-NMR) in nuclear overhauser effect spectroscopy (NOESY) mode and spin-spin lattice relaxation (T_1) measurement were conducted by an NMR Bruker Ultrashield Plus 500 MHz at room temperature.

5.4 Results and Discussion

The nano-spherical poly BZ was obtained from the following steps. Bz monomer and SEBS were mixed (50:50 wt%, namely S50BZ50) in chloroform and cast on teflon sheet before leaving at room temperature to evaporate chloroform and obtain yellowish film. The film was cured at 190°C for 3 hours to obtain cured S50BZ50 film. By comparing FT-IR spectra of the cured neat BZ and that of S50BZ50, it was clear that the curing or ring opening was completed as observed from the new OH band (3600-3200 cm^{-1}) and C-N-C (1249 cm^{-1}) (Fig. 5.1) together with the disappearance of characteristic absorption of oxazine moiety, stretching of C-O-C (1230 cm^{-1}) and trisubstituted benzene ring attached to oxazine ring (944 cm^{-1}). The film was immersed in toluene to dissolve SEBS and separate SEBS out of the film. At that time, yellowish colloidal particles were observed.

For S50BZ50, the BZ particles show a uniform morphology (Fig. 5.2 (c)) with a narrow size distribution in nanometer size (~500 nm) (Fig. 5.2 (h)). The FT-IR spectrum confirmed that the nanoparticles were poly BZ (see Fig. 5.1). A series of

films with different SEBS:BZ contents, i.e., 10:90 wt% (S10BZ90), 25:75 wt% (S25BZ75), 75:25 wt% (S75BZ25), and 90:10 wt% (S90BZ10) were prepared and the nanoparticles were collected in similar procedures to study whether SEBS and BZ contents have any effects on nanoparticle formation. Figure 5.2 (a-e) clearly shows that all contents give poly BZ nanospheres. The less content of BZ in SEBS, the smaller size of nanoparticles is obtained. For example, when the BZ content is as low as 10 wt%, the size of nanospherical poly BZ is as small as 150 nm.

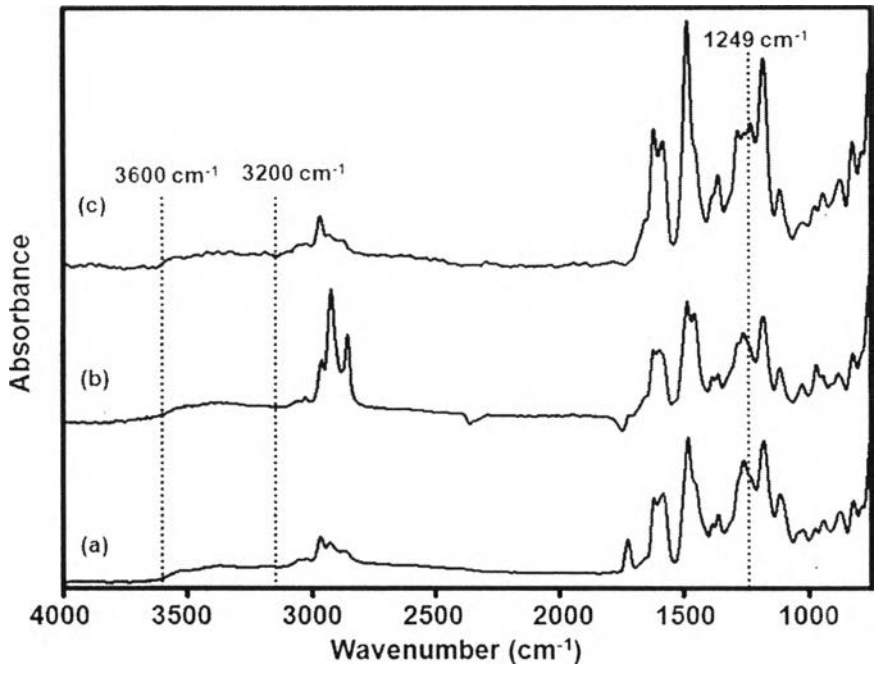


Figure 5.1 FT-IR spectra of :(a) cured neat-BZ resin, (b) cured S50BZ50 film, and (c) nanospheres extracted from S50BZ50 by toluene.

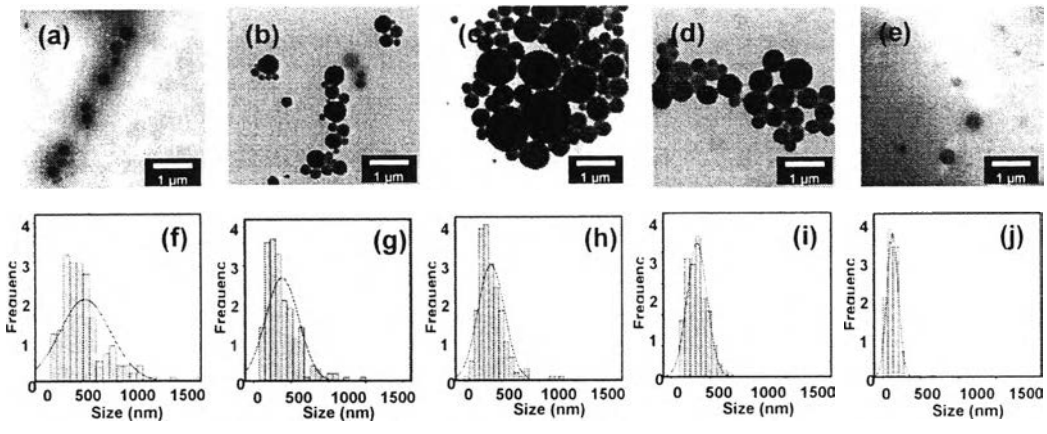


Figure 5.2 TEM micrographs (above images) and size distribution (below graphs) averaged from 200 spheres of BZ nanosphere for: (a) and (f) S10BZ90; (b) and (g) S25BZ75; (c) and (h) S50BZ50; (d) and (i) S75BZ25; and (e) and (j) S90BZ10.

To clarify the formation mechanism of nanospherical poly BZ, a series of polymers based on the similar aromatic structure but different T_g and T_m, such as polystyrene (PS), poly(butylene adipate-co-terephatalate (PBAT), polycarbonate (PC) were selected. In addition, chlorinated polyethylene (CPE) which represents the polymer with aliphatic chain and high polarity was also considered. Each polymer was mixed with BZ in various ratios followed by the similar heating profiles to the case of BZ/SEBS system to prepare the films. SEM micrographs showed that there were tiny particles of poly BZ only in the cases of PS and SEBS in high BZ-blending composition, i.e. S25BZ75 and PS25BZ75 (Fig. 5.3). The films obtained were further treated in other appropriate solvents, i.e. toluene or chloroform, to separate poly BZ thermosets. TEM micrographs revealed that PS25BZ75 gave the spherical poly BZ (Fig. 5.3) with the sizes of 1-10 μm. This microsphere formation indicated that PS and SEBS provide similar system for curing BZ. For PBAT, PC, and CPE, there were no spherical shaped poly BZs formed as identified by SEM and TEM. This leads to an assumption of the role of aromatic pendant group (benzene rings) in PS and in SEBS.

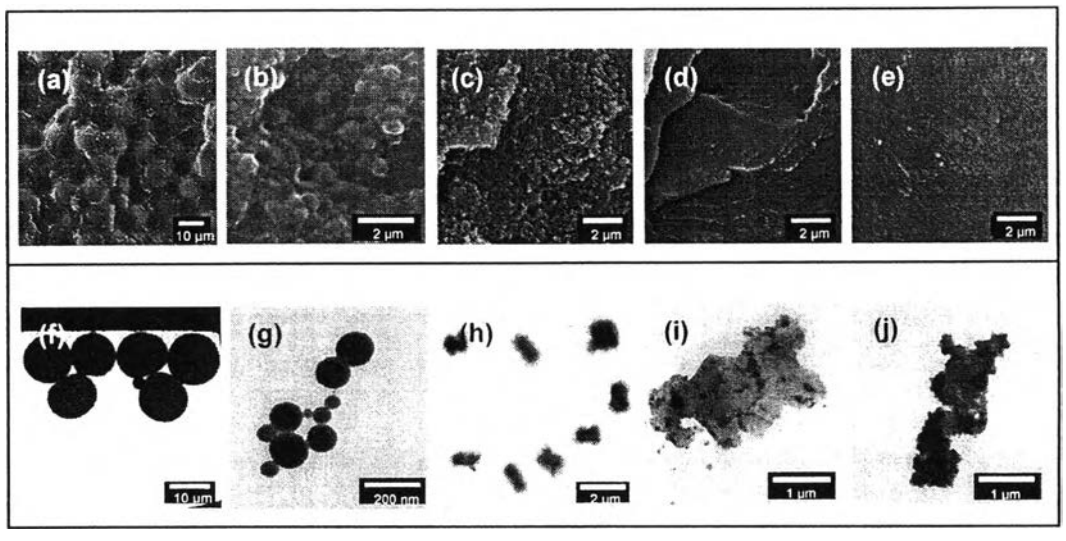


Figure 5.3 SEM images of the cured-film mixtures ((a)-(e)) and TEM images of the extracted BZ-thermosets ((f)-(j)) of: (a) and (f) PS25BS75; (b) and (g) S25BZ75; (c) and (h) PBAT25BZ75; (d) and (i) PC25BZ75; and (e) and (j) CPE25BZ75.

2D-NMR NOESY spectrum confirmed the interaction between aromatic proton of BZ monomer (δ = 6.63 ppm) and that of PS segments in SEBS chain (δ = 7.10 ppm) (Fig. 5.4). Here, the interaction between the aromatic pendant group and BZ monomer was evaluated by ^{1}H-NMR T_1 relaxation technique. The T_1 value of each aromatic proton in BZ monomer is found to be significantly reduced as the SEBS content increased; whereas those in other blended thermoplastic systems are found to be almost unchanged (Fig. 5.5). As evidenced above, the mechanism (Scheme 5.1) might relate to an assembly of BZ monomers under inclusion phenomena in PS segments of SEBS chains via π-π interaction among benzene ring. At that time, the SEBS might allow PS segment to form an aromatic pocket for the curing of poly BZ. The curing with the less surface tension results in spherical shape. As speculated, at high-temperature curing, those BZ monomers in molecular pocket fuse together during curing and finally become as large as the pocket size allowed, for example, 100 nm to 600 nm range. In similar, PS provides a micro-scaled pocket to allow polymerization of poly BZ in micrometer level. The size in nanometer or

micrometer level, then, might be derived from (i) the size of the aromatic pocket which polystyrene segment of SEBS is much less than PS polymer chain, (ii) the concentration of BZ monomer in the blend which the less concentration, the smaller the particles. For other polymers, i.e., PBAT, PC, and CPE, the aromatic rings are in the main chain and might not be able to form molecular pocket for BZ monomer. In other words, BZ monomers dispersed homogeneously in those polymer matrices (PBAT, PC, and CPE) without any specific interaction resulting in no particular forms generated after curing as seen from SEM and TEM.

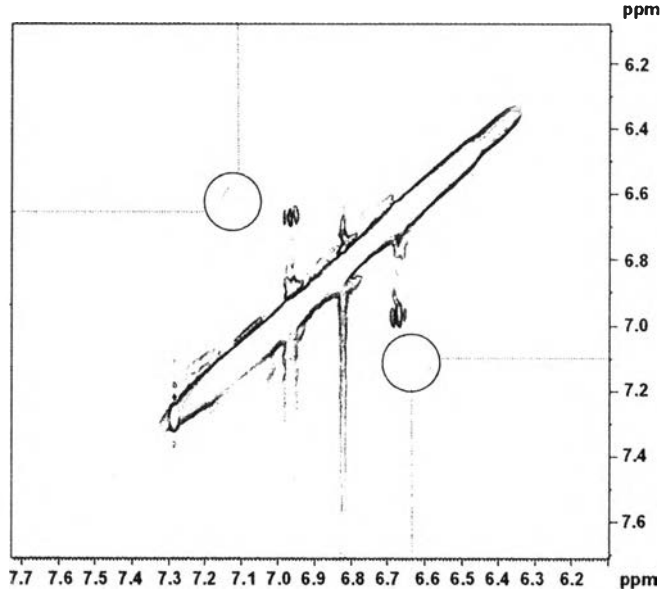


Figure 5.4 2D-NMR NOESY contour plot of a 3.9×10^{-3} %w/w of S50BZ50 in $CDCl_3$.

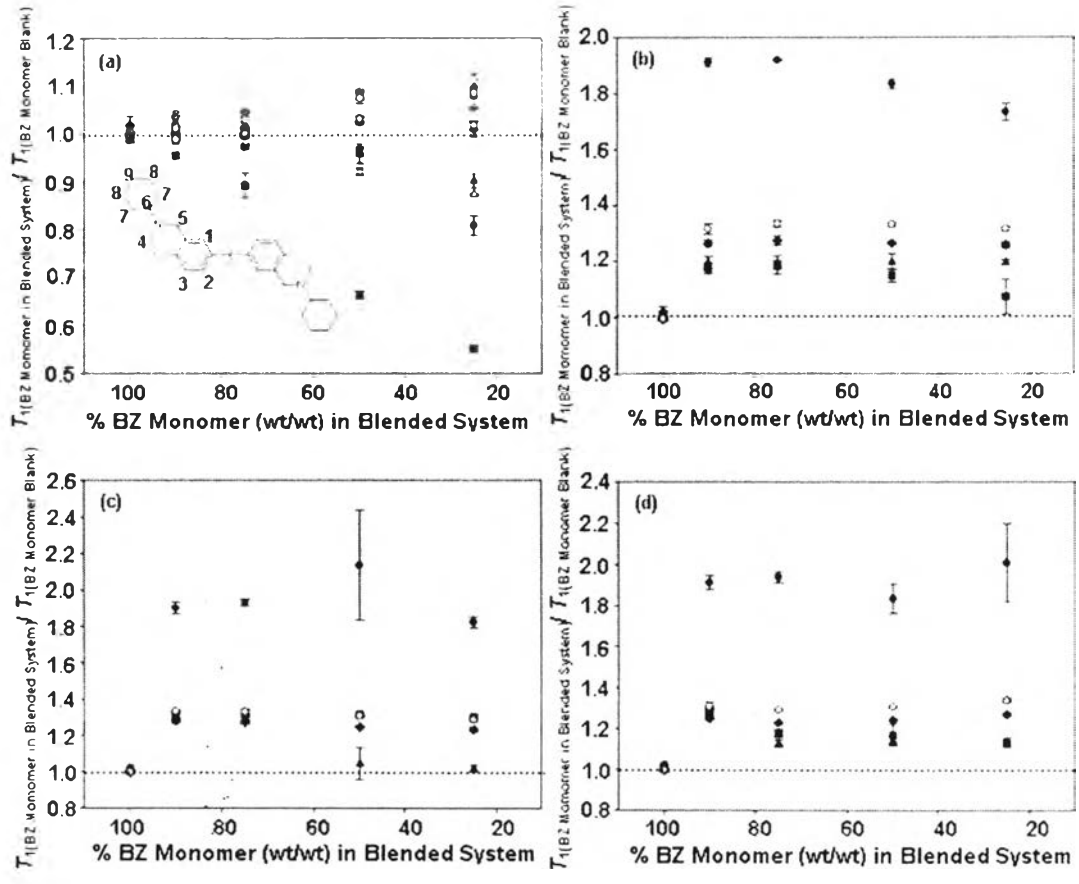
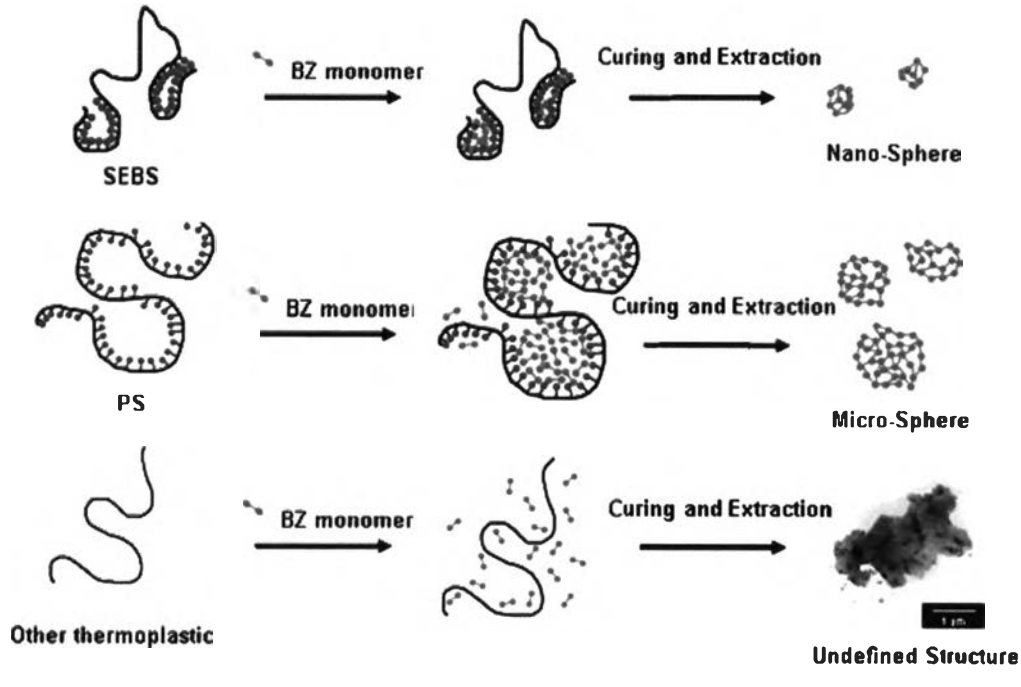


Figure 5.5 ^{1}H-NMR T_1 relaxation of BZ monomer of each proton in a 3.9×10^{-3} %w/w $CDCl_3$ for: (a) S50BZ50, (b) PBAT50BZ50, (c) PC50BZ50 and (d) CPE50BZ50. ^{1}H of BZ monomer represents (●) H1 δ 6.97 ppm, (▲) H2 δ 6.82 ppm, (■) H3 δ 6.68 ppm, (◆)H4 δ 4.97 ppm, (○) H5 δ 4.06 ppm, (△) H6 δ 2.78 ppm, (□) H7 δ 1.99 ppm, (◇) H8 δ 1.78 ppm and (◈) H9 δ 1.29 ppm.

It should be noted that BZ differs from epoxy in the way that the PS-BZ blends can be accomplished in prepolymer film form, followed by curing the film at the elevated temperature whereas the PS-epoxy starts curing from the viscous blending solution. Therefore, the unique point of this system is also related to the curing of BZ which is satisfied under the film form where the rigidity of the solid state plays an important role in controlling the molecular motion during curing

without significant movement to diverse the morphologies. As all mixing ratios between BZ monomer and SEBS yield poly BZ nanospheres above 80%, this leads us to a conclusion of a simple and direct nanosphere formation approach which can be expected for a large scale production.

Scheme 5.1 Suspected mechanism of nanospherical thermoset formation via molecular pocket of thermoplastic chains indicating the role of aromatic pendant group in PS and PS segments in SEBS chain for molecular assembly formation with BZ followed by the curing in nano-scaled or micro-scaled channel.



5.5 Conclusions

The present work shows a unique strategy to produce nanospherical thermoset resin in a simple and direct pathway from the model case of the blend

between benzoxazine monomer and SEBS. The styrene pendant group of SEBS and the benzene unit of BZ monomer form a specific π-π interaction to favor the molecular assembly structure and might allow the curing in nano-pocket structure of PS in SEBS (Scheme 5.1). As also seen in the case of PS and BZ monomer, the fact that poly BZ develops the microspheres explains very well how the conditions are suitable for either nano- or micro-sized spheres formation. The conditions for this mechanism are; (i) the specific interaction between thermoset monomer and thermoplastic chain and (ii) the specific phase separation such as a molecular pocket to control the curing under a confined space.

5.6 Acknowledgement

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5.7 References

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