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One-Pack Epoxy Foaming with CO_2 as Latent Blowing Agent

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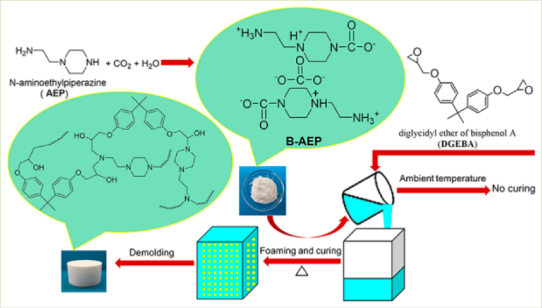
S Supporting Information

ABSTRACT: In this work, we have successfully developed a novel approach to epoxy foaming using CO_2 as the latent blowing agent. The active amine groups of a commercially available curing agent for epoxy resin are blocked by CO_2 to obtain ammonium carbamate. The prepared ammonium carbamate can be decomposed by heating. Above 100 °C, CO_2 is released from the amine groups and acts as the blowing agent, while the amine compound is used as the curing agent and cures the epoxy resin. The ammonium carbamate combines the functionalities of latent blowing agent and curing agent. The one-pack epoxy foaming formulation has good storage stability under ambient conditions. The thermoset epoxy foams prepared from the one-pack formulation have low density, good mechanical properties, and thermal stability, competitive with the epoxy foams prepared by other methods. This novel approach is simple, environmentally benign, and cost-effective, which represents a promising direction in the development of epoxy foaming technologies.



Polymer foams are a class of unique materials used in many fields, such as parts weight reduction, heat and sound insulation, and impact resistance protection.[1] There are also promising new applications emerging, such as low dielectrical materials,[2] gas capture and storage, catalyst carrier, separation,[3] and bioscaffolding.[4,5] Blowing agent plays a critical role in foaming processes, and it is usually evaluated with respect to its foaming efficiency, cost, and environmental effect. CO_2 is an outstanding candidate as a blowing resource due to its low cost and human and environmentally benign characteristics. However, CO_2 cannot be used directly because it is in a gas state under normal conditions. Moreover, it is difficult to handle and has low solubility in polymers. Supercritical CO_2 has been used to facilitate gas-loading by soaking process and a subsequent dropping in pressure leads to the development of foaming. The foaming of thermoplastic polymers by supercritical CO_2 is well reported.[6,7] However, little work is focused on thermoset polymers.[8] The foaming of thermoset polymers requires curing process to occur soon after bubbling with a very small time gap. The decomposition temperature of blowing agent and the working temperature of curing agent must match. If curing occurs first, bubbling cannot develop because the polymer matrix loses flowing and deformation ability. If bubbling occurs first without successive curing, bubbles collapse.

Epoxy resin-based foams have attracted much attention because of their broad range end-use applications such as automotive, electronics encapsulation, and sealing adhesive. Epoxy foams have excellent rigidity, adhesive strength, absence of shrinkage, and moisture resistance.[1] However, most foaming processes developed so far for epoxy resin employed hazardous chemicals as foaming agent, for example, azodicarbonamide.[9,10] Hydrogen gas generated from reaction of hydrogen-containing polysiloxane and amine curing agent has also been used as blowing source for epoxy resin.[11] Hydrogen gas is flammable and additional amount of amine curing agent is required. Curing agent must be carefully selected to match working temperature of the blowing agent. Environment-friendly supercritical CO_2 is preferred in epoxy foaming but its application in producing foam monoliths has limited success.[8] Another issue is that most epoxy formulations need be stored and transported in two packs; otherwise, they will be gelled in a couple of hours. The transport of foam products of low density is not practical. The on-site formulation is also labor intensive, including weighing and stirring. One-pack foaming formulation with good stability at ambient temperature is thus most desirable but remains to be challenging, if not impossible.

Recently, the reversible reaction of tertiary amine and amidine compounds with CO_2 has attracted great attention in developing CO_2-switchable surfactants and polymers.[12−18] Primary and secondary amine compounds have much stronger interactions with CO_2 than tertiary amines, which is irreversible under an ambient condition. However, the resulting carbamate or carbonate salt can undergo reversible reaction upon heating, to release amine compounds and CO_2,[19] which inspired us to develop a single-pack epoxy foaming formulation reported in this work.

Herein, we propose a novel approach to prepare a latent foaming and curing agent for epoxy foaming. Gaseous CO_2 is first absorbed by an amine-based compound, which is a

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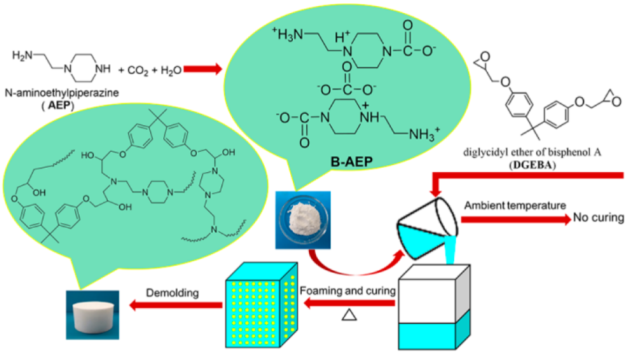
commercially available curing agent for epoxy resin, to obtain ammonium carbamate as blocked amine compound. The ammonium carbamate combines dual functionalities of latent curing agent and blowing agent for epoxy resin. It does not trigger curing and foaming below its decomposition temperature, which allows design of one-pack epoxy formulation. If the curing temperature of amine compound is lower than the decomposition temperature of its blocked counterpart, upon heating to above the decomposition temperature, ammonium carbamate releases CO_2 and returns to its amine form as curing agent to produce epoxy foam materials. In principle, this idea completely addresses the temperature matching issue in foaming and curing.

For proof of the concept, we chose a commercial curing agent, N-aminoethylpiperazine (AEP; Scheme 1) in this work.

Scheme 1. Schematic Process for Foam Preparation



AEP can cure epoxy resin from room temperature to 200 °C. The reason for selecting AEP is that it combines primary, secondary and tertiary amine groups in a single molecule. It captures more CO_2 for foaming because only primary and secondary amines have active hydrogen atoms and can act as curing groups for epoxy resin, but all three amines absorb CO_2.[19,13] Scheme 1 illustrates this simple, environment-benign, and cost-effective approach.

After reaction with CO_2, the liquid AEP turned into a white solid powder. The active amine groups of AEP were blocked. The chemical structure of the blocked AEP (B-AEP) was characterized. Two strong NH_2 stretching peaks were found at 3357 and 3273 cm^{-1} in FTIR spectrum of the original AEP (Figure 1a,b), representing the asymmetric and symmetric vibrations, respectively. Two peaks at 2938 and 2810 cm^{-1} were derived from the C−H stretching absorption of $-CH_2-$ group. In-plane N−H stretching absorption peak was observed at 1582 cm^{-1}. The CH_2 bending vibration was at 1457 and 1403 cm^{-1}. The strong and broad peak at 1141 cm^{-1} was attributed to C−N stretching modes. Out-of-plane NH_2 bending was observed as a blunt peak at 821 cm^{-1}. The medium-sized peak at 1000 cm^{-1} came from the C−C stretching vibrations of piperazine ring.[20] For B-AEP, the peaks related to N−H vibration at 3357 and 3273 cm^{-1}, as well as C−H stretching absorption at 2938 and 2810 cm^{-1}, disappeared while a strong platform-like peak appeared in the range of 1660−1410 cm^{-1}, indicating the presence of ammonium carbamate species.[21] Piperazine ring C−C peak at 1000 cm^{-1} became stronger. Some new peaks at 802, 779, and 655 cm^{-1} were observed (Figure 1b). It revealed that amine groups were blocked and AEP was turned into ammonium carbamate. ^1H NMR (Figure 1c) spectra show that chemical shift of protons from α-methylene of the primary ammonium was moved from 1.16 to 1.66 ppm.[22] Chemical shift of protons from the piperazine rings and α-methylene of the tertiary amines remained unchanged.

Further study revealed that only amines with strong basicity like aliphatic amines could capture CO_2 to prepare ammonium carbamate salts. Aromatic amines with weak basicity like 4,4′-diaminodiphenylmethane cannot react with CO_2 to obtain solid salt under normal conditions.

The thermal decomposition behavior of B-AEP is of key importance for its use as the latent blowing and curing agent. It must have good stability at room temperature and decompose quickly at an elevated temperature to release active ingredients. B-AEP is adequately stable with onset temperature of decomposition (with 1% weight loss) at 108 °C, as determined by TGA (Figure 2a). As revealed by the derivative thermogravimetric analysis (DTG) curve, there were three stages in B-AEP degradation, while only one stage in AEP degradation. The first and second peak temperature of DTG of B-AEP was 149 and 169 °C, respectively, indicating that CO_2 and water was completely released from ammonium carbamnate.[12,14] The total mass loss of B-AEP in the first and second stage was 45%. AEP experienced 17% weight loss at the same temperature because of volatilization. Deducting the volatile component of AEP gave an estimate of 33% CO_2 content in B-AEP. If B-AEP has the molecular structure of $AEP{\cdot}xCO_2$, x can be estimated as 1.4, based on 33% CO_2 release. Considering that there were one primary amine, one secondary amine, and one tertiary amine in each molecule of AEP (Scheme 1), the reaction of AEP with CO_2 and the

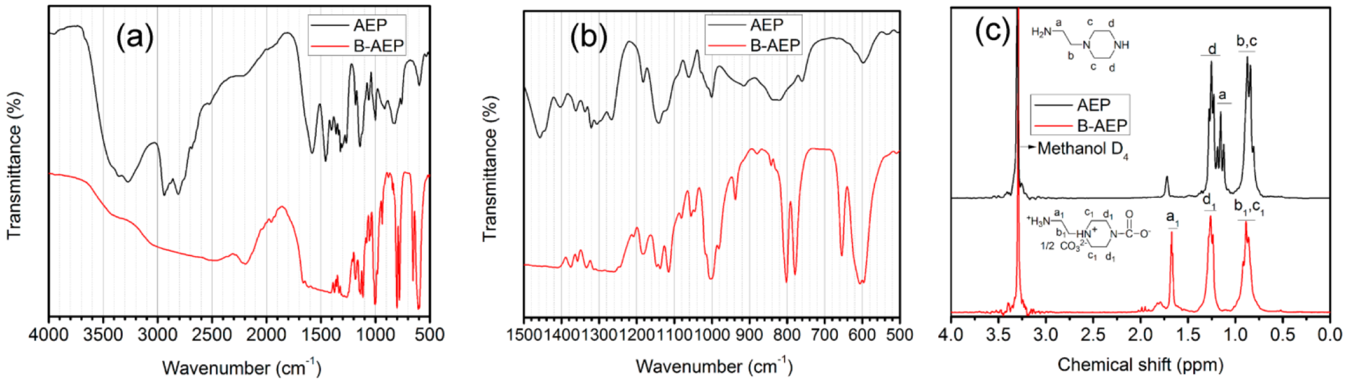


Figure 1. (a) FTIR spectra of AEP and B-AEP in 4000−500 cm^{-1}. (b) FTIR spectra of AEP and B-AEP in 1500−500 cm^{-1}. (c) ^1H NMR spectra of AEP and B-AEP.

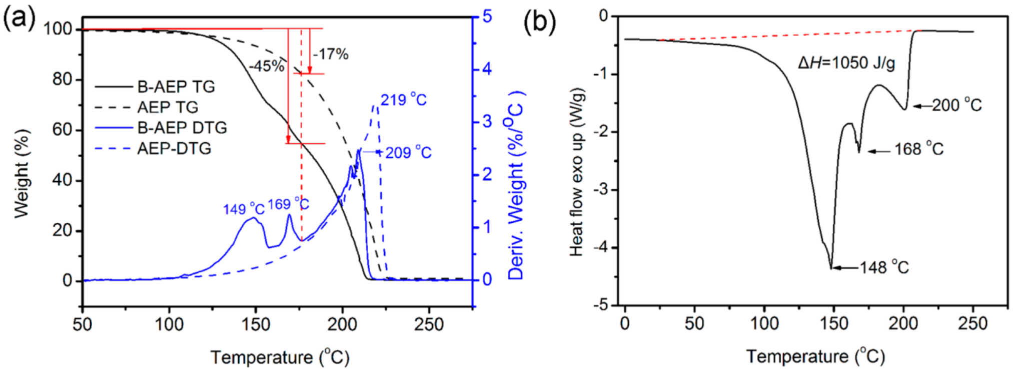


Figure 2. (a) TGA and DTG curves of AEP and B-AEP. (b) DSC curve of B-AEP.

structure of the product could be complicated. If all three kinds of amines took part in the reaction with CO_2, each AEP molecule would capture 1.5 CO_2, since every two amines capture one CO_2 molecule on average.[19] If only the primary and secondary amines took part in the reaction with CO_2, each AEP molecule would capture 1 CO_2 on average. The estimated value is 1.4 for x, suggesting that 80% of tertiary amine moieties were carbonated. A possible molecular structure of B-AEP is given in Scheme 1. Actually, the reaction of tertiary amine with CO_2 must be assisted by water,[13] as shown in Scheme S1. However, the contribution from water was very limited in the anhydrous alcohol used in our work. The molecular structure of B-AEP could be equivalently expressed as AEP·1.4CO_2. The amine hydrogen equivalent weight (AHEW) is grams of curing agent containing one equivalent of (latent) N−H groups. The average molecular weight of B-AEP is 190.8 (129.2 + 1.4 × 44). Hence, AHEW of B-AEP is 63.6, which is calculated as 190.8 divided by number of latent N−H group, that is, 3. The DSC curve of B-AEP (Figure 2b) revealed three decomposition peaks, coinciding well with its TGA data with some variation of the peak temperatures. The decomposition of B-AEP was highly endothermic and could thus alter the curing exotherm of epoxy resin.

After elucidation of B-AEP chemical structure and composition, epoxy formulations based on AEP and B-AEP were prepared to verify the role of B-AEP. A simple and pure epoxy resin, diglycidyl ether of bisphenol A (DGEBA), was selected as the matrix. The feeding ratio of DGEBA curing formulation was designed to give stoichiometric balance of amine protons and epoxide groups for both AEP and B-AEP. The exothermal behavior resulting from the ring-opening of epoxide during the epoxy resin curing was detected by differential scanning calorimetry (DSC). The AEP/DGEBA formulation exhibited a curing onset temperature of about 30 °C and an exothermal peak at 98 °C (Figure 3).

The curing onset temperature of B-AEP/DGEBA was shifted to about 100 °C and the exothermal peak was shifted to 131 °C. The increased curing onset temperature and peak temperature were attributed to the unblocking of B-AEP, that is, CO_2 and AEP release, followed by DGEBA curing. The exothermic heat, that is, the absolute value of enthalpy change ΔH, was obtained from the peak area of the thermogram. The exothermic heat from B-AEP/DGEBA was much smaller than that from AEP/DGEBA. This was because of the endothermic decomposition of B-AEP as revealed in Figure 2b and the lower epoxy group content in B-AEP/DGEBA than in AEP/DGEBA. The results verified that B-AEP provided stability of epoxy formulation at room temperature and fast curing over 100 °C.

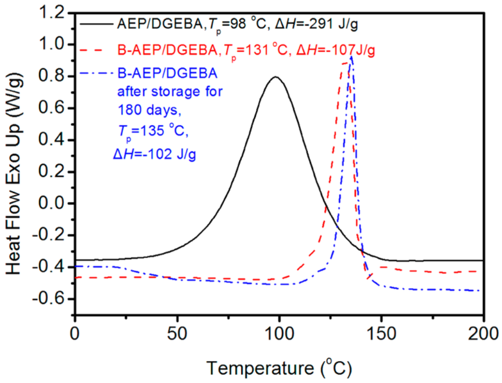


Figure 3. DSC curves of B-AEP/EP and AEP/EP formulations during nonisothermal curing process.

It is indeed an effective latent curing agent for epoxy resin, as hypothesized. Actually, the B-AEP/DGEBA resins prepared in our lab has been stored under an ambient condition for over half a year up to now, without any sign of curing or other change. Upon heating, it gave almost the same curing behavior as the freshly prepared formulation, shown in Figure 3. All the above results demonstrate that B-AEP is an effective latent curing agent for epoxy resin.

Foaming of DGEBA was attempted using B-AEP as the foaming and curing agent, fumed silica as the nucleating agent and PEG-*b*-PPG-*b*-PEG as the foam stabilizer. The formulation and basic properties of the foams prepared in this work are summarized in Table 1. The prepared foams (Figures 4a,b and S1) had the pore structure and morphology of closed cells with relatively big pore sizes and a broad size distribution. Some deformation to oval-shape of the pores could be observed. This might be caused by the relatively broad particle size distribution of the B-AEP powder and the low viscosity of the DGEBA resin. The viscosity of DGEBA above 100 °C, prior to curing, was very low and the bubbles could be coalesced. It is known that the cell growth is negatively correlated to the viscosity of polymer matrix.[23] Similar result was also reported by Stefani et al.[11] in preparation of epoxy foam using hydrogen gas as a blowing source, through the dehydrogenation reaction of hydrogen-containing polysiloxane and amine. In addition, the amount of released CO_2 depended on the type of amine used, that is, the number of amine groups. With the formulation fixed, it is difficult to control the amount of CO_2 released.

Typically, the compressive stress vs strain curve of the foam (Figure 4c) gave a high slope at the start, followed by a platform, with yield occurring at about 9% strain. The foam had

Table 1. Foaming Formulation, Condition, and Basic Properties of Foams Prepared

sample No.	formulation and condition[a]	$\rho_f{}^b$ (g cm^{-3})	P^b (%)	$d_{\mathrm{avg}}{}^b$ (μm)	σ^b (MPa)	E^b (MPa)
F1	1%/1%/120 °C	0.27 ± 0.02	77 ± 2	145 ± 86	3.1 ± 0.2	110 ± 10
F2	0.5% /2%/140 °C	0.32 ± 0.01	73 ± 1	111 ± 54	3.5 ± 0.3	136 ± 11
F3	0.5% /3%/140 °C	0.33 ± 0.01	72 ± 1	130 ± 55	3.3 ± 0.3	95 ± 9

[a] Foaming formulation and condition is express as filling level of PEG-*b*-PPG-*b*-PEG/fumed silica/foaming temperature. [b] ρ_f, P, d_{avg}, σ, and E are the foam density, porosity, average pore diameter, compressive strength, and compressive modulus, respectively. The density of bulk DGEBA thermoset is 1.17. $P = (1 - \rho_f/1.17) \times 100\%$.

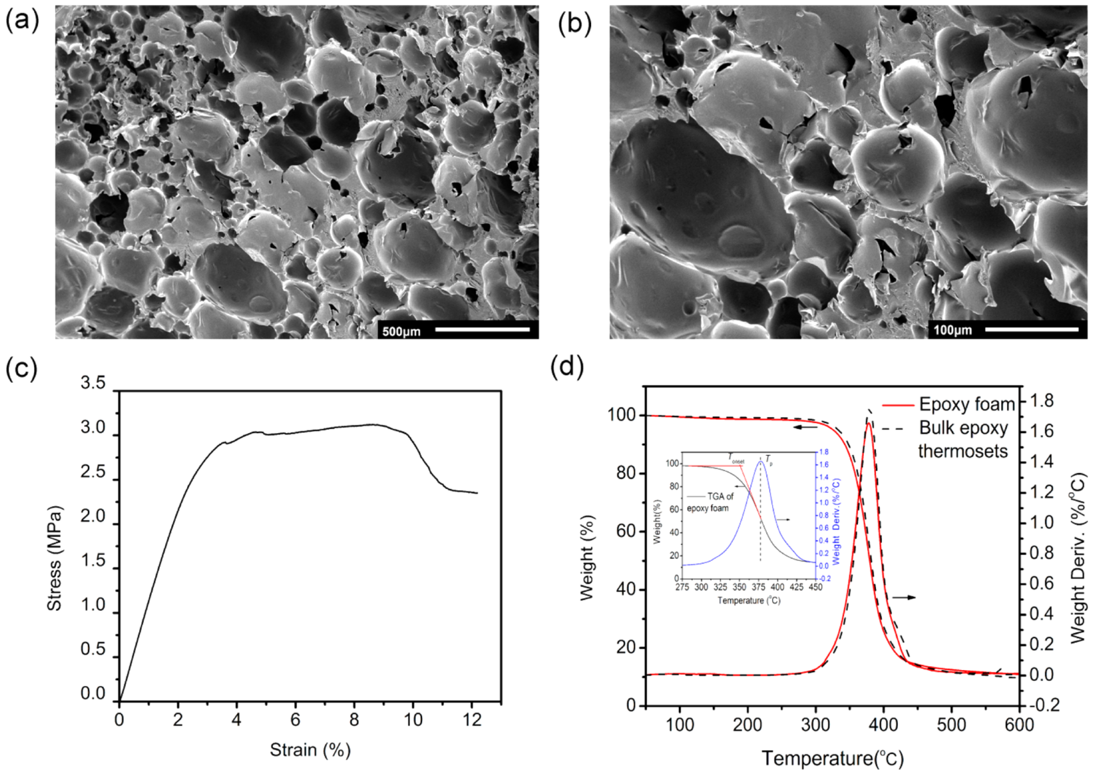


Figure 4. (a) Pore structure and morphology of the epoxy foam F1 with low magnification and (b) with high magnification (c) Stress vs strain curve in compressive testing of epoxy foam F1. (d) TGA and DTG curves of epoxy foam F1 and bulk epoxy thermosets. Inset shows the extrapolation method to determine onset weight loss temperature T_{onset}.

a good combination of rigidity and flexibility. The compressive strength of the foam with a density of 0.27 g/cm^3 reached 3.1 MPa and the compressive modulus reached 110 MPa, competitive with the literature data.[11,24,25] Adjustment of formulation could further improve performance of the prepared foams. (Figure S2). Figure 4d shows the TGA curves of the foam and the bulk epoxy thermosets prepared by AEP/DGEBA formulation. The extrapolated onset temperature T_{onset} was used to characterize the thermal stability following the recommendation of the American Society for Testing and Materials. The temperature corresponded to the point of intersection of the TGA baseline and the tangent line at the peak value of DTG curve. The T_{onset} values for the epoxy foam and bulk epoxy thermosets were 350 and 354 °C, respectively. Their peak temperatures of DTG were 377 and 379 °C, respectively. There was not much difference between the thermal stability of the two materials, indicating good curing efficiency of B-AEP for the epoxy resin.

To conclude, we have successfully developed a novel approach to epoxy foaming using CO_2 as the latent blowing agent. The active amine groups of a commercially available curing agent for epoxy resin are blocked by CO_2 to obtain ammonium carbamate, which has good stability in ambient temperature while can be decomposed by heating to release CO_2 as the blowing agent and amine compound as the curing agent for epoxy foaming. The one-pack epoxy foaming formulation has good storage stability under ambient conditions. Thermoset epoxy foams prepared from the one-pack formulation have low density, good mechanical properties, and thermal stability. This novel approach is simple, environmentally benign and cost-effective, which represents a promising direction in the development of epoxy foaming technologies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, B-AEP, foam preparation and characterization methods, Scheme S1, and Figures S1 and S2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00320.

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Notes

The authors declare no competing financial interest.

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