



Polyurethane foaming with engineered CO₂-releasing nanoparticles: From the thickening effect to the industrial applications of the blowing agents

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ARTICLE INFO

Article history:

Received 17 November 2017

Received in revised form

29 March 2018

Accepted 2 April 2018

Available online 3 April 2018

Keywords:

Polyurethane foams

Polyethylenimine

CO₂ adducts

Global warming

Nanoparticles

ABSTRACT

We explored polyurethane (PU) foaming with CO₂-releasing nanoparticles from CO₂ adducts of poly(propylene glycol) (PPG)-grafted polyethylenimines. The amphiphilic nature of these CO₂ adduct macromolecules drives the formation of nanoparticles in the white components (i.e. foaming mixtures without isocyanates), with the hydrophobic PPG side-chains stretching outward. The outermost PPG terminal groups intimately contact the foaming mixture and thus largely determine the particle size, while the side-chain polymerization degree, ranging from 1 to 5, plays a minor role. The blowing agents with methoxyl terminal groups increased the viscosity of the white components very rapidly due to the small particles dispersed therein (e.g. 63–65 nm after 7 d aging) that caused a strong thickening effect. Normal PU foams could only be obtained within 1 h of white-component aging. Longer aging made the wall of the growing bubbles difficult to flow due to the strong thickening effect and the nanoparticles in the wall further weakened the wall while releasing CO₂, both contributing to the failure of blowing. In contrast, the blowing agents with butoxyl terminal groups demonstrated a very slow increase in the viscosity and the pot life of the white components could be prolonged up to 90 d, due to the relatively large dispersed-particles (e.g. about 200 nm at aging for 60 d). The CO₂ content as high as ~25% has been achieved in the blowing agents with the shortest side chains whose polymerization degree $n = 1$. The PU foams obtained had densities below 50 kg/m³ and compressive strengths over 230 kPa, both satisfying the demands of many industrial applications.

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1. Introduction

Polyurethane (PU) foams are the most-used cellular materials, whose traditional blowing agents are climate-changing substances. For example, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been banned because they can destroy the stratospheric ozone layer [1], while the currently used hydrofluorocarbons (HFCs) possess strong greenhouse effect [2,3], causing global warming. Recently, a series of unsaturated hydrofluoroolefins (HFOs, e.g. 1-chloro-3,3,3-trifluoropropene) have been introduced, due to their minor impact on both ozone loss and

global warming [4–7]. However, their final degradation products, such as trifluoroacetic acid and hydrofluoric acid [8,9], can pollute soil and water. Additionally, all of these physical blowing agents are volatile organic compounds (VOCs), whose concentrations in air have been strictly regulated in some cases, such as their use in cars and airplanes.

Water can react with isocyanates to generate CO₂ to blow PUs in a climate-friendly manner. However, this foaming reaction usually results in abundant rigid urea linkages in the PU chains if too much water is used, conferring the final PU foams their friability and weak interfacial adhesion [10]. In addition, high dosage of water may shorten the shelf life of the white components (i.e. foaming mixtures without isocyanates) if hydrolysis-sensitive ingredients are involved, such as organophosphate flame retardants and plasticizers [11].

In response to the aforementioned problems that are associated with conventional blowing agents, we recently explored a series of

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CO₂ adducts from polyethylenimines (PEIs) grafted with various hydrophobic side chains [12–15]. These adducts can release CO₂ to blow PUs during the exothermic PU polymerization. The hydrophobic modification is necessary, as the unmodified CO₂ adducts are too hydrophilic to disperse into the foaming mixtures. One hydrophobic side chain is poly (propylene glycol) (PPG) monobutyl ether with $M_n = 340$ Da, the optimized grafting rate of which is about 11% in terms of good raw material compatibility and high foaming efficiency [13]. Another side chain belongs to the family of alkyls with carbon number from 4 to 16 [14,15]. Among the resultant CO₂ adducts, that with a C₈ alkyl (2-ethylhexyl) side chain and a grafting rate of about 13% is the most effective blowing agent [15]. Apart from their environmental friendliness, these latent CO₂ blowing agents can be used in the same way as traditional ones, such as HFCs, without changing too much the foaming process. In comparison, foaming with liquid or supercritical CO₂ requires high pressure and delicate manipulation of the foaming process [16–18].

The previous undertakings mainly focused on the syntheses of CO₂-releasing blowing agents based on modified PEIs. Basically, these blowing agents are particles suspending in the foaming mixtures, while traditional HFCs are dissoluble liquids. Little is known regarding the effects of the dispersed particles on the foaming process. Moreover, the reported PU foams blown by these CO₂ adducts still possess relatively high densities (>60 kg/m³) that need to be further lowered for some practical applications (e.g. 30–60 kg/m³ for thermal insulations [13]).

In this study, we aimed primarily to improve the CO₂ content of the blowing agents from PPG-grafted PEIs (PPG-PEIs) by reducing the side-chain length. Unexpectedly, we observed a thickening effect caused by the CO₂-releasing nanoparticles dispersed into the foaming mixture. This effect and the particle size play fundamental roles in the foaming process. A deep understanding of the foaming process is essential for the evolution of these CO₂-releasing blowing agents towards their industrial applications.

2. Materials and methods

2.1. Synthesis of CO₂ adducts

The chemical structures of hydrophobically modified PEIs (R-PEIs) and their CO₂ adducts (R-PEI-CO₂s) are shown in Fig. 1A. A branched PEI serves as the main chain. The side chains are derived from monoalcohols of propylene glycol monomer, dimer, or trimer, with butoxyl or methoxyl terminal groups. Simply put, these side chains are called PPG oligomers, even in case of the polymerization degree $n = 1$. The nomination of the final products is based on the side-chain structure (see Fig. 1A).

The family of bPPGn side chains contain an additional member where n approximates to 5 (the precise average value is 4.58). The corresponding final products are designated as bPPG5-PEI and bPPG5-PEI-CO₂, whose synthesis has been detailed in the literature [12]. The same method was used to synthesize all the R-PEIs and their CO₂ adducts in this study. In brief, monoalcohols of propylene glycol oligomers (>95% in purity, from Sigma-Aldrich, USA) were reacted with epichlorohydrin (99%, Kelong Chemical Reagent Plant, Chengdu, Sichuan, China) to obtain the corresponding PPG glycidyl ethers, which were then grafted onto the branched PEI ($M_w = 25$ kDa, Sigma-Aldrich, USA) via a ring-opening reaction between the glycidyl ether group and the PEI amino groups. The molar ratio of both reactive groups was set as 1:9, meaning that the theoretical grafting rate was 11.1% for all R-PEIs.

To synthesize R-PEI-CO₂s, viscous R-PEIs spread on watch glasses were purged with CO₂ flow for 5 min (the compressed CO₂ with 99% purity was purchased from Sichuan Qiaoyuan Gas Co., Ltd, Dujiangyan, Sichuan, China) and the resultant solids were ground

into powder, followed by further reaction with CO₂ at 0.5 MPa in an enclosed steel flask until a constant weight was reached (it took about 4 h). Exceptionally, mPPG1-PEI and unmodified PEI absorb CO₂ very slowly. Their 30% ethanol solutions were purged with CO₂ flow for 5 min as well, and the white precipitates were dried under vacuum for 96 h at room temperature, followed by grinding into powder and saturating with CO₂ to obtain mPPG1-PEI-CO₂ and PEI-CO₂.

2.2. Dispersibility of CO₂ adducts

Each CO₂ adduct (0.2 g) was mixed separately with 6 g of the blank white component (Table 1, without blowing agent) with magnetic stirring at 300 rpm for 1 min. Thereafter, both the macroscopic and microscopic (200 \times) images were recorded by a digital camera and an Olympus BX 43 light microscope (Olympus, Japan), respectively. The morphological change was observed using the same instruments after aging the samples for 2 d and 7 d.

To further observe the CO₂-adduct particles at 7-d aging, each white component (Table 1, containing 2.8 g blowing agent) was diluted 600 times with ethanol, spread on copper grid, dried at 60 °C for 1 min, and stained with 1% phosphotungstic acid for 1 min prior to observation under a LIBRA 200 FE (Carl Zeiss, Germany) transmission electron microscope (TEM), operated at an accelerating voltage of 200 kV. Also, the particle size and particle size distribution of the same white component in ethanol (0.1%, w/v) was measured by dynamic light scattering on a Nano ZS90 Zetasizer (Malvern Instruments Ltd., Malvern, UK). Before the measurement, the ethanol suspension was filtered through a Rephile glass membrane with pore size of 0.7 μ m (Rephile Bioscience Ltd, Shanghai, China) to remove dust contaminant.

The viscosity change of each white component with aging time was measured using an NDJ-1 Rotational Viscometer (Shanghai Balance Instruments Factory, Shanghai, China).

2.3. Preparation of PU foams

The PU foam formulations are listed in Table 1, where the only change is the blowing agent used. In the blank foams without blowing agents added, the water impurity in the raw materials could serve as a blowing agent as well. The crosslinkers, glycerol and triethanolamine, were bought from Kelong Chemical Reagent Plant (Chengdu, Sichuan, China). The rest materials other than the blowing agents were available from Chengdu Advanced Polymer Technology Co., Ltd. (Chengdu, Sichuan, China). To prepare the PU foams, the raw materials constituting the white component (Table 1) were magnetically stirred at 300 rpm for 1 min and aged for a certain period (e.g. 7 d) at room temperature in a silica gel desiccator. Then the black component, polymeric 4,4'-diphenylmethane diisocyanate (PMDI), was added, and the mixture was stirred at 1000 rpm for 25 s. Thereafter, the freely rising foaming mixture was placed in an oven at 80 °C for 5 min. Finally, the foams were cooled to room temperature and stored in a desiccator for at least 4 d prior to any characterization.

Additional bPPG1-PEI-CO₂ blown foams were prepared after aging the white component for 0, 30, 60, 90 and 120 d, to reveal the long-term foaming performance. The blank foams with no added blowing agent, prepared at the same time, served as controls. The morphology and viscosity of the corresponding white component were recorded as well, using the same methods as those described in Section 2.2.

2.4. Characterizations

The details are shown in Supporting Information. Both ¹H NMR

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