SHORT COMMUNICATION

Synthesis, porous structure, and underwater acoustic properties of macroporous cross-linked copolymer beads

Weihong Sun · Xin Yan · Xi Zhu

Abstract The macroporous and elastomeric beads from polyurethane acrylate (PUA), ethyl methacrylate (EMA), and styrene (St) are prepared by suspension polymerization using *n*-heptane as porogen and 1,2-divinylbenzene (DVB) as cross-linking agent. The scanning electronic microscope results show that the beads of PUA–EMA–St cross-linked copolymers have many large pores on their surfaces and interiors, and the macroporous sizes are dependent of the copolymer composition and the dosages of cross-linking agents and porogen. Average porous diameters decrease as the dosages of DVB increase and the contents of PUA and porogen decrease. The cross-linked copolymers have two kinds of beads (one with many larger holes on the surface and another with much smaller pores or without pore), when the ratio of PUA to EMA and St is from 6/4 to 4/6. The macroporous and elastomeric beads can improve the underwater acoustic absorption properties of the polyurethane/epoxy (PU/EP) blend elastomer, and the underwater acoustic properties of the composites based on PU/EP blend elastomer and the beads depend mainly on the amounts of the beads and the dosages of porogen.

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Introduction

Porous or macroporous polymer microspheres, or micro-particles, or microbeads have been extensively investigated in recent years because of their numerous potential applications, including as absorbents, cosmetics, foams, drug delivery, enzyme immobilization carriers, chromatographic materials, solid-supported reagents and catalysts, damping materials, and airborne acoustic absorption materials [1–6]. They can be prepared by physical and chemical methods such as phase inversion [7], solvent evaporation [8], spray drying [9], emulsion polymerization [10–12], suspension polymerization [13–15], dispersion polymerization [16], precipitation polymerization [17, 18], and interfacial polymerization [19]. In most cases, polymers suitable for producing microspheres are usually hard or glassy ones due to the requirement of porous stabilization for mechanical resistance [20]. However, hard or glassy polymer microspheres are unfavorable to damping acoustic absorption due to their bad damping at room temperature. The ideal polymer microspheres as acoustic absorption materials should have more and larger pores and higher damping. Therefore, novel elastomeric beads with large pore size and high damping are desired for acoustic adsorption applications.

Vinyl-terminated polyurethanes (such as polyurethane acrylate (PUA)) as reactive macromonomers can be used for preparing UV-curable coatings and adhesives [21–25].

Their cross-linked copolymers with methyl methacrylate have good damping properties [26–28]. In this article, the macroporous beads from PUA, ethyl methacrylate (EMA), and styrene (St) are prepared by suspension polymerization using *n*-heptane as porogen and 1,2-divinylbenzene (DVB) as cross-linking agent and used as acoustic particles, and their pore structures and influences on underwater acoustic absorption properties of PU/EP blend elastomer are investigated.

Experimental

Main materials

Ethyl methacrylate and styrene were washed with diluted NaOH solution and deionized water for eliminating inhibitor and dried with anhydrous calcium chloride. Polypropylene glycol with molecular weight of 2,000 (PPG-2000) was dewatered at 100 °C under reducing pressure (0.95 MPa). Hydroethyl acrylate (HEA) and toluene diisocyanate (TDI) were distilled under reducing pressure for purification. 1,2-Divinylbenzene, *n*-heptane, 2,2-azobisisobutyronitrile (AIBN), sodium chloride, poly-vinyl alcohol (PVA), calcium phosphate, and bisphenol A-type epoxy resin (EP) with epoxy value of 0.51 eqiv/100 g were used without further purification. The *p*-cresol-terminated polyurethane prepolymer (PU) were synthesized as described in reference [29]. The synthesized adduct of ethlylenediamine and butyl acrylate (mole fraction ratio was 1/1) was used as a curing agent for EP and PU.

Preparation

The synthesis of polyurethane acrylate

PUA was synthesized by the reaction of NCO-terminated polyurethane prepolymer with HEA. One hundred seventy-four grams of TDI was added into a 1-L three-neck flask equipped with a stirrer, a condenser, a dropping funnel, and a drying tube, then 1,000 g PPG-2000 was added to the 1-L flask by dropping funnel under stirring (the molar ratio of NCO/OH is 2/1) and kept reaction for 3 h at 75 °C to obtain the NCO-terminated polyurethane prepolymer. The content of NCO, determined by dibutylamine titration method, was 3.65%. HEA (121.21 g; (the molar ratio of OH/NCO is 1.1/1)) was then added into the polyurethane prepolymer and kept for 3 h at 70–75 °C to give the PUA macromonomer.

The scheme synthesis of polyurethane acrylate:
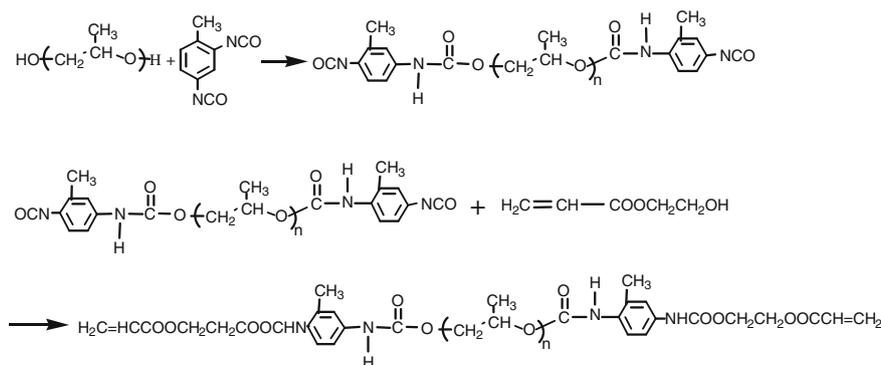
The preparation of PUA–EMA–St cross-linked copolymer beads

Macroporous beads of PUA–EMA–St cross-linked copolymers were prepared by radical suspension polymerization in a 500-mL three-neck flask equipped with a stirrer, a condenser, and a thermometer. The monomer phase containing quantitative 70 g PUA, 15 g EMA, 15 g St, 2.5 g DVB, 1 g AIBN, and 60 g *n*-heptane was suspended in the aqueous phase consisting of 560 mL deionized water, 1 g PVA, 0.5 g sodium chloride, and 0.5 g calcium phosphate.

The polymerization was performed at 65–70 °C for 3 h and at 75 °C for 3 h under constant stirring. After completion of the reaction, the milk white beads were filtered and washed well with water and ethanol, eluted with ethanol, and dried under vacuum at 70 °C. The mass ratio of the oil phase to the aqueous phase is 0.25; the mass ratios of AIBN, PVA, and calcium phosphate to the total monomer are 0.01, 0.005, and 0.005, respectively; the mass ratio of *n*-heptane to the total monomer is usually 0.6 except in special labels; and the mass ratio of sodium chloride to deionized water is 0.05.

The reaction equation of the preparation of PUA–EMA–St cross-linked copolymer beads as follows:

$$H_2C=HCCOOCH_2CH_2COOCHN \bigcirc \overset{CH_3}{} N-\overset{O}{C}-O+CH_2\overset{CH_3}{CH}O)_n-\overset{O}{C}-\overset{H}{N}\bigcirc \overset{CH_3}{}-NHCOOCH_2CH_2OOCCH=CH2$$

$$+ \quad CH_2=C-COOC_2H_5 \quad + \quad \bigcirc CH=CH_2 \quad \longrightarrow$$
$$\qquad\quad CH_3$$

$$-[C-H_2C-H_2C-HCCOOCH_2CH_2COOCHN\bigcirc\overset{CH_3}{}\overset{H}{N}-\overset{O}{C}-O+CH_2\overset{CH_3}{CH}O)_n-\overset{O}{C}-\overset{H}{N}\bigcirc\overset{CH_3}{}-NHCOOCH_2CH_2OOCCH-CH_2-CH_2-CH]_n^-$$
$$COOC_2H_5 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\bigcirc$$
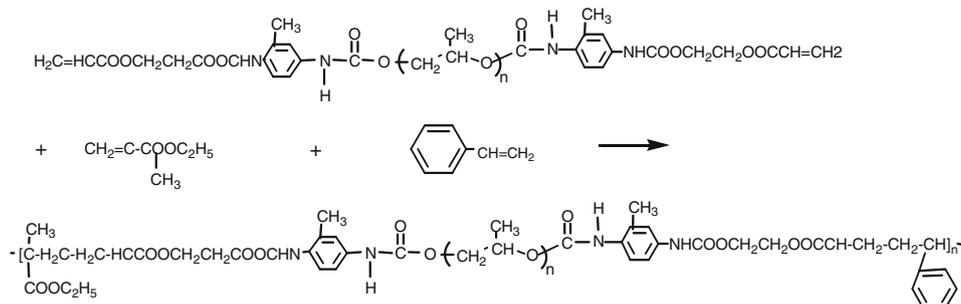
The preparation of the composites based on PU/EP blend elastomers and macroporous resin beads

PU and EP were heated in an oven at 50 °C for 1 h and mixed well under stirring (the weight ratio of PU to EP is 75/25). The PUA–EMA–St macroporous beads and a little of antifoam agent (polysiloxane) were added into the PU/EP mixture and mixed well, then degassed under vacuum for about 30 min (until bubble ceased). Stop degassing, the curing agents with 9% of the mixture weights were added to the mixture and mixed under stirring at a lower rate. The final mixture was degassed under vacuum and then poured into a columni-form mold made from Teflon and cured for 24 h at

Fig. 1 SEM images of the beads of PUA–EMA–St (70/15/15) cross-linked copolymers with different dosages of porogen. a 0%, b 30%, c 60%, and d 100%
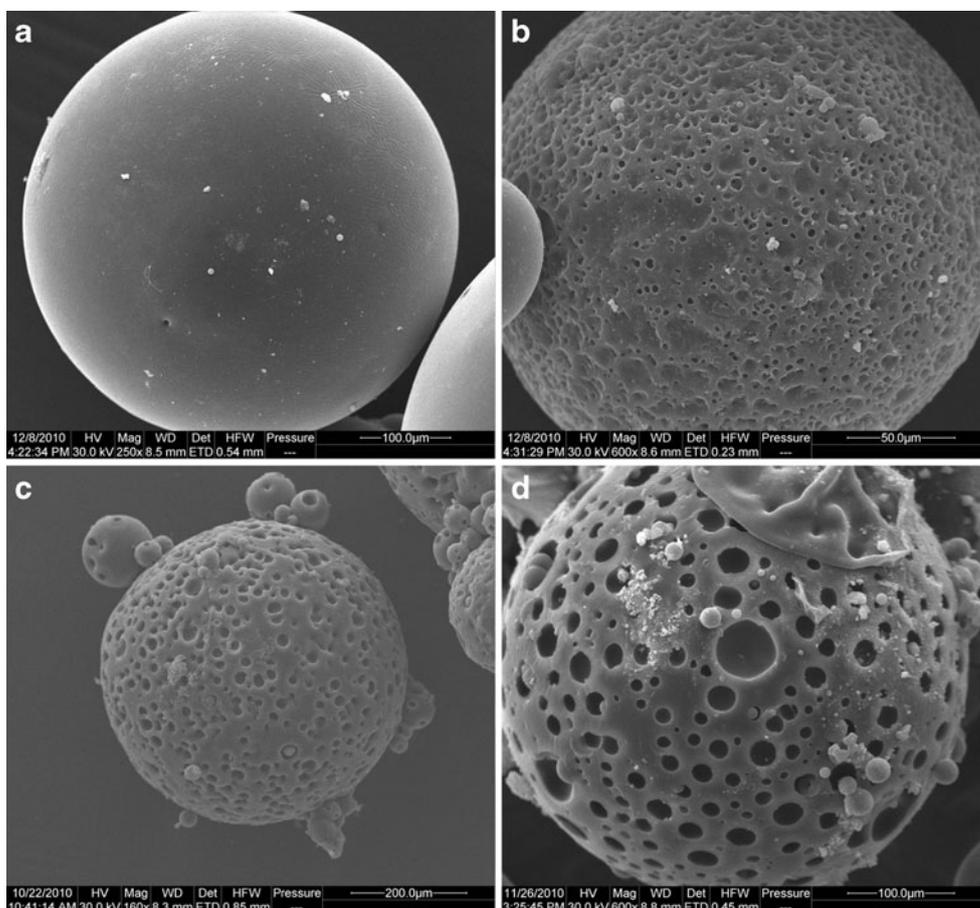
Table 1 The porous parameters of PUA–EMA–St (70/15/15) copolymer beads with different mass ratios of porogen

Porogen/ monomer (%)	Maximum diameter (μm)	Minimum diameter/(μm[a])	Average diameter (μm)
0	0	0	0
30	4.6	1	2.6
60	24	5	13.8
100	55	5	14.5

[a] In available magnified multiple

room temperature to give the composite samples with 56.2-mm diameter and 40 mm of thickness.

Characterization

Morphology and the porous structures test

The SEM images of the macroporous beads were recorded on Quanta 200 Field-Emission Scanning Electronic Microscope (the product of FEI Company, Netherlands). The macroporous beads in a dry state were put on a double-coated electronic tape with a gold coating of 10 nm, and then SEM images were taken under different magnification.

Measurements of underwater acoustic properties

The underwater acoustic properties were measured on a +57 pulse tube and corresponding equipments (as shown in Fig. 1) according to the Chinese standard GB/T14369-1993. The frequency is from 2 to 12 kHz and the water temperature is 26 °C except in the water temperature contrast experiment. The experimental set and a detailed description were given in reference [29].

Fig. 3 Underwater acoustic absorption coefficients of the PU/EP blend elastomer composites contains 10% PUA–EMA–St (75/15/15) copolymer beads with different porogen dosages

Results and discussion

The influence of the mass ratios of porogen to total monomer on pore structures and underwater acoustic absorption properties

Figure 1 shows the SEM images of the beads of PUA–EMA–St (70/15/15) cross-linked copolymers with different mass ratios of porogen to the total monomer (the mass ratio of DVB to PUA is 2.5/70). The corresponding pore parameters are listed in Table 1. It can be seen that the bead prepared without using porogen has no pore on its surface, and the maximum and number-average diameters increase as the mass ratio of porogen to the total monomer increases. The results indicate that the large pores are formed from *n*-heptane, which is immiscible with the copolymer. In order to observe the inner structures of the beads, two beads of the PUA–EMA–St copolymer with 60% of the mass ratios of *n*-heptane to the total monomer

Fig. 2 SEM images of the slice surfaces of two beads of PUA–EMA–St (70/15/15) copolymer with 60% of the mass ratios of *n*-heptane to total monomer

Fig. 4 SEM images of the PUA–EMA–St copolymer beads with different DVB dosages **a** 0%, **b** 5%, and **c** 10%
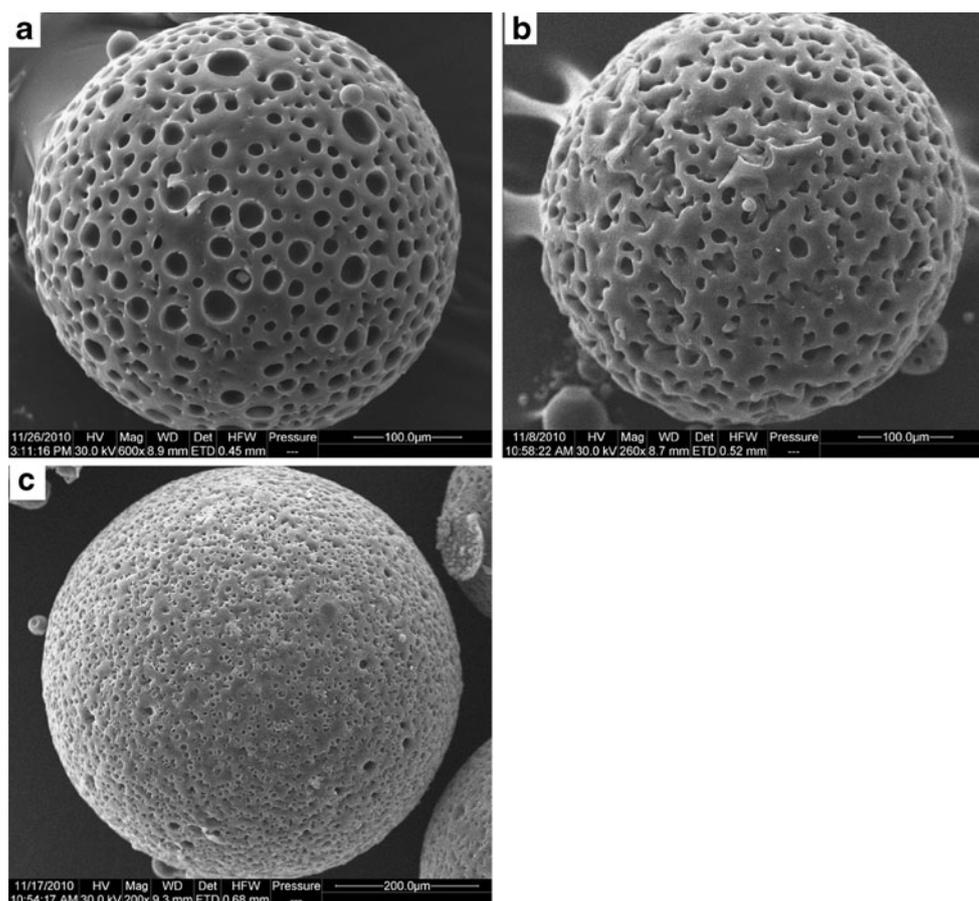
were cut into halves respectively; the SEM images of the sections were taken as shown in Fig. 2. The images show that many pores also exist within the beads. It is very interesting that a very large hole exists within every bead.

Figure 3 shows the underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and 10% of the PUA–EMA–St (75/15/15) copolymer beads with different dosages of the porogen. It can be seen that the elastomeric PUA–EMA–St copolymer beads can improve the underwater acoustic absorption properties of the PU–EP blend elastomer even without pores. When the porogen dosages are zero or lower

(30%), the synthesized copolymer beads have no pores or smaller pores, and the corresponding composites have higher underwater acoustic absorption properties at higher frequency. When the porogen dosages are increased from 60% to 100%, the synthesized copolymer beads have larger pores, and the corresponding composites have higher underwater acoustic absorption properties at lower frequency.

Table 2 The porous parameters of PUA–EMA–St copolymer beads with different DVB dosages

PUA/EMA/St/DVB	Maximum diameter (μm)	Minimum diameter (μm[a])	Average diameter (μm)
70/15/15/0	28	6	14.5
70/15/15/2.5	24	5	13.8
70/15/15/5.0	19	5	11.1
70/15/15/10	10	3	6.2

[a] In available magnified multiple
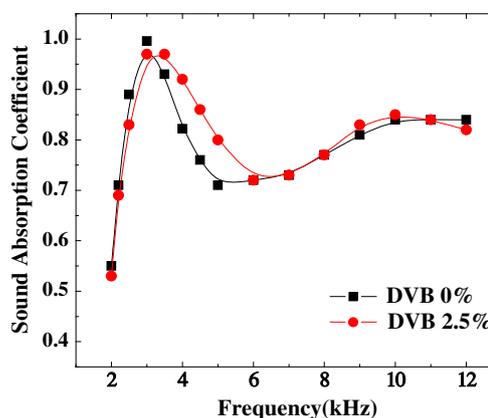
Fig. 5 Underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and 10% of PUA–EMA–St (75/15/15) copolymer beads with different DVB dosages

Fig. 6 SEM images of PUA–
EMA–St–DVB (60/20/20/2.5)
copolymer beads with larger
pores (**a**) and smaller pores (**b**)
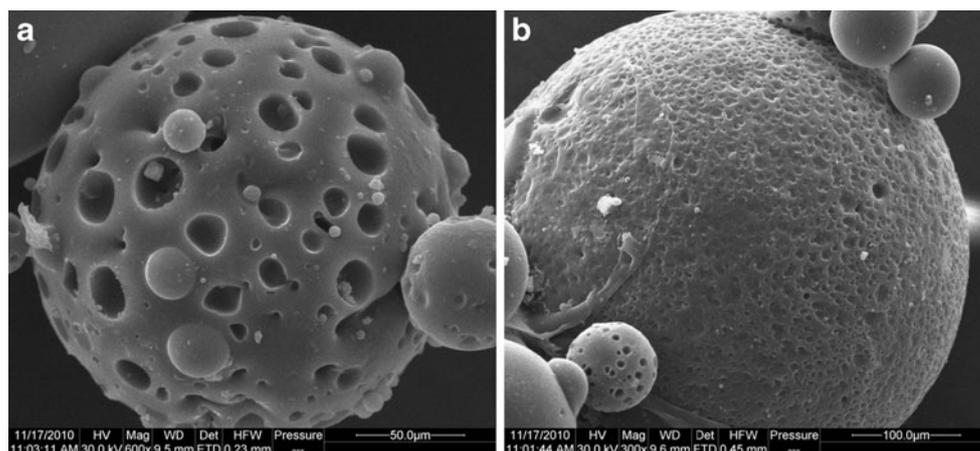
The results indicate that the pore size and amount have influences on the underwater acoustic absorption properties of the PU–EP blend elastomer.

The influence of DVB dosages on pores structures and underwater acoustic absorption properties

Figure 4 show the SEM images of the PUA–EMA–St (70/15/15) copolymer beads with different dosages of DVB. The corresponding pore parameters are listed in Table 2. The results indicate that the maximum, minimum, and average pore diameters decrease as DVB dosage increases. As known, the porogen *n*-heptane is a bad solvent for the cross-linked copolymers and phase separation may occur during the former period of polymerization. The large pores are formed from the accumulation of the porogen within the cross-linked chains; higher cross-linking degree can lead to smaller swelled degree to the cross-linked chains and results in forming smaller pores.

Figure 5 shows the underwater acoustic absorption coefficients of the composites based on PU–EP blend

elastomer (PU/EP=75/25) and 10% of the PUA–EMA–St (75/15/15) copolymer beads with different DVB dosages. The results show that the DVB dosages have a little influence on the underwater acoustic absorption properties of the PU/EP blend elastomer because of the small difference in pore parameters of the two beads (DVB=0 and 2.5).

The influence of the mass ratios of PUA to EMA–St mixture on porous structures and underwater acoustic absorption properties

Figures 6, 7, and 8 show the SEM images of the PUA–EMA–St copolymer beads with different mass ratios of PUA to EMA–St (1/1) mixture, respectively. The corresponding pore parameters are listed in Table 3. It can be seen that two types of beads exist: one is a sphere with many larger pores on its surface and another is a sphere with much smaller pores or without pores on its surface. The copolymers with the mass ratios of PUA to EMA–St mixture from 60/40 to 40/60 may form two phase structures (PUA soft phase and

Fig. 7 SEM images of PUA–
EMA–St–DVB (50/25/25/2.5)
copolymer beads with pores (**a**)
and without pores (**b**)
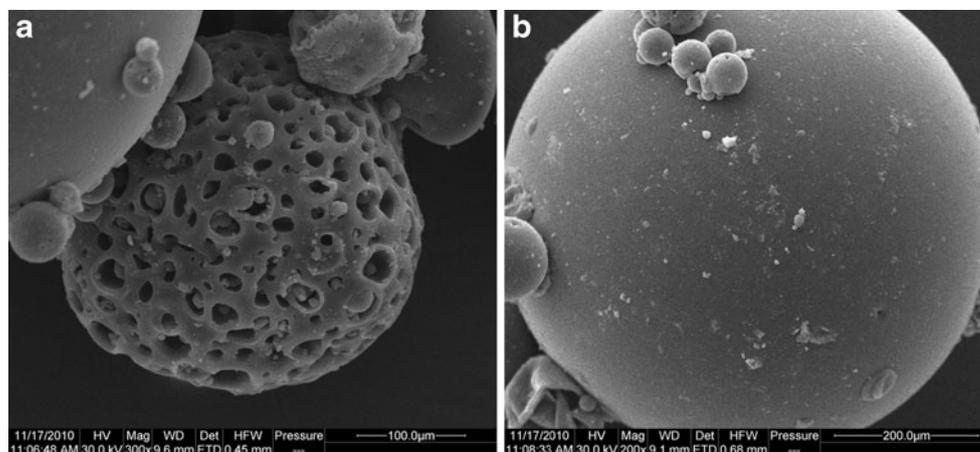
Fig. 8 SEM images of PUA–EMA–St–DVB (40/30/30/2.5) copolymer beads with pores (**a**) and without pores (**b**)
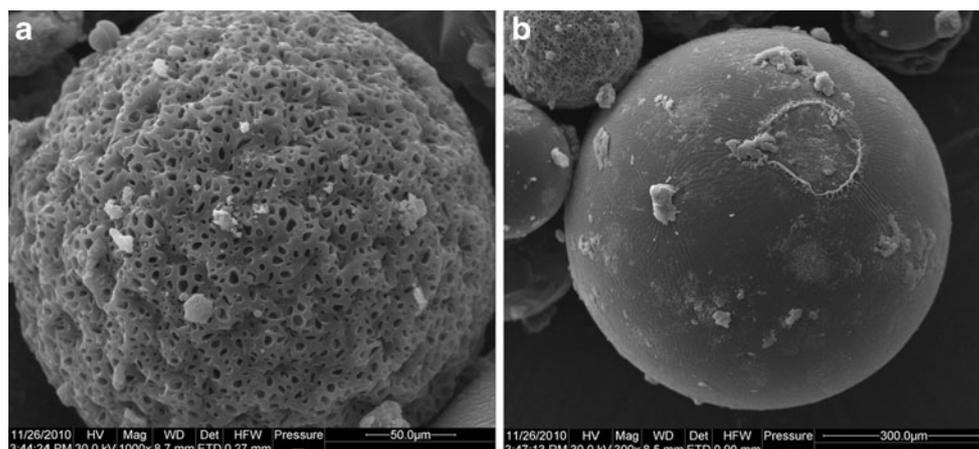
EMA–St copolymer hard phase) owing to the miscible limiting, which may lead to forming two different beads.

Figure 9 shows the underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and 10% of the PUA–EMA–St copolymer beads with different mass ratios of PUA to EMA–St (1/1) mixture. The results indicate that the influence of the mass ratio of PUA to EMA–St on the underwater acoustic absorption properties is not obvious. The composites with different mass ratios of PUA to EMA–St have almost the same average acoustic absorption coefficients except in the composite with 50/50 of mass ratios. The PUA–EMA–St (50/25/25) copolymer may have the most serious phase separation, which may cause that the corresponding composite has a bad acoustic absorption property.

The influence of the amounts of the PUA–EMA–St copolymer beads on the underwater acoustic absorption properties

Figure 10 shows the underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and different amounts of the PUA–EMA–St copolymer beads. The results indicate that

the PU–EP elastomer without PUA–EMA–St copolymer beads has the worst underwater acoustic absorption property, and the underwater acoustic absorption property of the elastomer can be improved with adding different amounts of the PUA–EMA–St copolymer beads because of their damping and scattering effects. The composite with 5% of the beads has higher acoustic absorption coefficients at higher frequency, and the two types of composites with 10% and 20% of the beads have higher acoustic absorption coefficients at lower frequency and almost the same average acoustic absorption coefficients. The results suggest that 10% of the amounts of the beads are enough for improving the underwater acoustic absorption property of the PU–EP elastomer.

Conclusion

Considering the requirements of acoustic adsorption micro-spheres for pore and damping, the macroporous and

Table 3 The porous parameters of PUA–EMA–St copolymer beads with different composition ratios

PUA/EMA/St/DVB	Maximum diameter (μm)	Minimum diameter (μm[a])	Average diameter (μm)
70/15/15/2.5	24	5	13.8
60/20/20/2.5	23	4	12.3
50/25/25/2.5	24	4	12.1
40/30/30/2.5	7	2	3.4

[a] In available magnified multiple
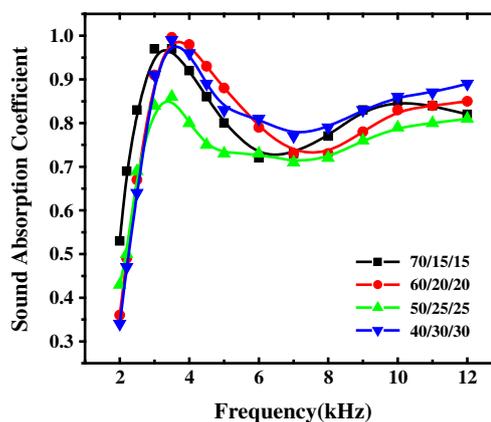
Fig. 9 Underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and 10% of PUA–EMA–St copolymer beads with different mass ratios of PUA to EMA–St (1/1) mixture
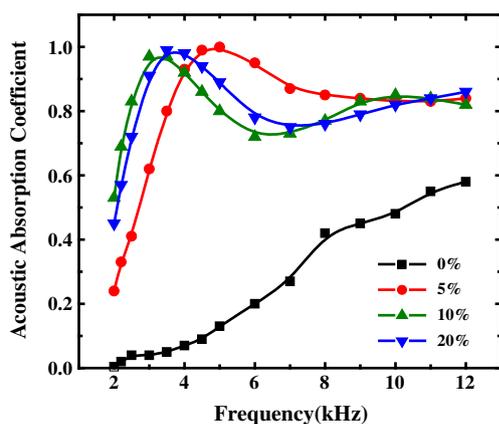
Fig. 10 Underwater acoustic absorption coefficients of the composites based on PU–EP blend elastomer (PU/EP=75/25) and different amounts of PUA–EMA–St copolymer beads

elastomeric beads from PUA, EMA, and St are prepared by suspension polymerization using *n*-heptane as porogen, and their porous structures are characterized by SEM. The PUA–EMA–St cross-linked copolymer beads have many pores on their surfaces and interiors, and the pore sizes are dependent of the copolymer composition and the dosages of cross-linking agents and porogen. These beads can improve the underwater acoustic absorption properties of PU/EP blend elastomers, and the underwater acoustic properties of the composites based on PU–EP blend elastomer and the beads depend mainly on the amounts of the beads and the dosages of the porogen.

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