Dynamic Mechanical and Underwater Acoustic Properties of the Polyurethane/Epoxy Resin Blend Elastomers Filled with Macroporous Poly(vinyl acetate-co-triallyl isocyanurate) Resin Beads

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ABSTRACT: Macroporous poly(vinyl acetate-co-triallyl isocyanurate) resin beads were prepared by suspension polymerization and used as acoustic particles for polyurethane (PU)/epoxy resin (EP) intercrosslinked elastomer matrices. The influences of the beads on the dynamic mechanical and underwater acoustic properties of the matrices were investigated. The results show that the underwater acoustic absorption properties of the matrices were improved by the beads, and this depended on the amount of the beads, the composition ratios of PU to EP, the bead diameters, the matrix thickness, and the water temperature. A comparison of the matrix with a 70/30 composition ratio of PU to EP to one without the beads showed that the average acoustic absorption coefficient of the composite with 5% beads increased from 0.38 to 0.55, and the peak value increased from 0.42 to 0.65, but the composites with 10 and 15% of the beads had lower acoustic absorption coefficients at low frequency and a much higher acoustic absorption coefficient at high frequency. The results also indicate that the beads with smaller diameters had a better enhancing effect on the underwater acoustic properties of the matrices. The results of the dynamic mechanical measurements showed that the damping properties of the composites depended on the composition ratios of PU to EP. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2359–2367, 2011

Key words: composites; elastomers; macroporous polymers; matrix; polyurethanes

INTRODUCTION

Covering a layer of anechoic tiles on a submarine surface is an important method for submarine acoustic stealth.1,12 The key part of the anechoic tiles is the underwater acoustic absorption material matching with the impedance of seawater as much as possible; this material is usually an elastomer or viscoelastic polymer containing various acoustic particles and/or acoustic structures.3,4 When the incident acoustic wave contacts the material, a part of the incident acoustic wave is reflected by the material surface, and the other enters into the material interior; the entry acoustic wave can be converted into heat energy by changes in the wave mode, scattering, and absorbing due to material damping and structure, except the transmitted acoustic wave.5–12 Polyurethane (PU) elastomer has excellent damping ability and can be used as a damping material and/or underwater acoustic absorption material.13–16 Its damping or underwater acoustic absorption ability can be controlled by molecular design, such as adjustment of the ratio of soft and hard segments,14,17 selection of different sorts of synthetic methods and materials,16,18 and blending with other polymers, such as epoxy resin (EP).19 EP can improve the mechanical and high-temperature damping properties of PU elastomers by the formation of interpenetrating polymer networks or other blend structures.19–23 Therefore, it is possible that PU/EP blends with higher composition ratios of PU to EP could be used as the matrices for underwater acoustic absorption materials.

To improve the underwater acoustic absorption properties of elastomeric or viscoelastic matrices, adequate porous fillers (e.g., microballoons, voids, cavities, particles) and acoustic absorption structures are usually introduced into the matrices.3,24–28 Generally, inorganic and rigid fillers can only reflect and
scatter sound waves, but porous polymer particles can attenuate sound wave because of their framework high-damping properties, except reflection and scattering. Recently, two research groups have discovered that porous polymer particles have good airborne acoustic absorption properties and can also improve the airborne acoustic absorption properties of PU foams, especially at low frequency. Whether porous polymer particles can improve the underwater acoustic absorption properties of the elastomer matrices or not is worth investigating. In this study, macroporous vinyl acetate (VAc)–triallyl isocyanurate (TAIC) copolymer beads were synthesized and used as acoustic particles for PU/EP blend elastomer matrices, and the dynamic mechanical and underwater acoustic properties were studied.

EXPERIMENTAL

Main materials

VAc (Shanghai Shanpu Chemical Co, Ltd., Shanghai, China) was distilled under reduced pressure to eliminate inhibitor. Poly(propylene glycol dioi) with a molecular weight of 2000 (PPG2000; Yueyang Petrochemical Co., Yueyang, China) was dewatered at 100°C under reduced pressure. p-Cresol (Shanghai Keda Chemical Co., Ltd., Shanghai, China) was distilled for purification. TAIC (Hunan Yixiang Chemical Co, Ltd., Changsha, China), bisphenol A type EP (with an epoxy value of 0.51 equiv/100 g, YueYang Petrochemical Co., Yueyang, China) was polyvinyl alcohol), and 1 g of calcium phosphate. The true density of the dried macroporous resin was estimated by a pycnometer method. The pore

Preparation of macroporous poly(vinyl acetate-co-triallyl isocyanurate) [P(VAc-co-TAIC)] resin beads (weight ratio = 70/30)

Macroporous P(VAc-co-TAIC) (70/30) resin beads were prepared by radical suspension polymerization in a three-necked flask equipped with a stirrer, a condenser, and a thermometer. The monomer phase containing 70 g of VAc, 30 g of TAIC, 1 g of initiator (2,2-azobisisobutyronitrile), and 50 mL of n-heptane was suspended in the aqueous phase consisting of 525 g of deionized water, 26 g of NaCl, 2.6 g of poly(vinyl alcohol), and 1 g of calcium phosphate. The polymerization was performed at 65–70°C for 7 h and at 75°C for 3 h under constant stirring. After completion of the reaction, the milk-white resin beads were filtered and washed well with water (3 times) and ethanol (3 times), kept in ethanol for 24 h, and dried in vacuo at 70°C. The product in perfect spherical beads was sieved, and the fractions with sizes of less than 0.2, 0.2–0.45, and 0.45–0.71 mm were used as acoustic particles.

Preparation of the composites based on PU/EP blend elastomers and macroporous resin beads

Blocked isocyanates can be deblocked and form urea in the presence of amines at lower temperature. Amines can also react with the epoxy groups in EPs at lower temperature. Hence, the blocked PU prepolymer and EP can be simultaneously cured and form an intercrosslinked PU/EP network in the presence of the curing agent (polymine) at room temperature.

PU and EP with weight ratios of 75/25, 70/30, and 65/35 were heated in an oven at 50°C for 1 h and mixed well under stirring. The macroporous resin beads and a little antifoam agent (polysiloxane) were added to the PU–EP mixture, mixed well, and then degassed in vacuo for about 30 min (until bubbling ceased). After degassing was stopped, 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 in vacuo and then poured into a columniform Teflon mold and cured for 24 h at room temperature to give the composite samples with diameters of 56.2 mm and thicknesses of 40 or 25 mm (the thickness of the samples in this study was 40 mm except the label).

Characterization and measurement

Characterization of the macroporous resin beads

The true density of the dried macroporous resin was estimated by a pycnometer method. The pore
volume and porosity were obtained by the monitoring of the mass gain of the resins in n-heptane.\textsuperscript{38} The true density of the macroporous resin was 1.2 g/cm\textsuperscript{3}, the pore volume was 0.468 cm\textsuperscript{3}/g, the porosity was 42.2\%, and the apparent density was 0.6 g/cm\textsuperscript{3}.

Morphology and the porous structures of the resin and composite sample were observed on a Quanta200 scanning electronic microscope (FEI Co., Eindhoven, The Netherlands). The resin and composite in a dry state were put on double-coated electronic tape with a gold coating of 10 nm, and scanning electron microscopy (SEM) images were taken under different magnifications.

Dynamic mechanical thermal analysis

The dynamic mechanical data from –60 to 100°C were obtained using a DMTA-V dynamic mechanical thermal analyzer (Rheometric, Scientific, Piscataway, NJ) at a heating rate of 3°C/min. Small rectangular bar specimens of 5.0 × 0.2 × 0.6 cm\textsuperscript{3} were tested in tension mode at a fixed frequency of 1 Hz. The loss tangent area (TA) was calculated by a summary of the recording tangent data per degree Celsius from –60 to 100°C.

Measurements of underwater acoustic properties

The underwater acoustic properties were measured on a +57 pulse tube and corresponding equipment (as shown in Fig. 1) according to Chinese standard GB/T14369-1993, similar with the method described in the literature.\textsuperscript{39} The frequency was from 2 to 12 kHz, and the water temperature was 26°C, except for in the water-temperature contrast experiment. The sample was soaked in water for 24 h before testing.

RESULTS AND DISCUSSION

Morphology of the resin beads and the composite

Figure 2 shows the SEM images of the surface and the cross section of the resin beads. It can be seen that the bead was accumulated by many smaller particles and had a lot of small pores in its surface, and the diameter range of the pores was 0.14–0.6 μm. Figure 3 shows the photo and vertical cross-sectional morphologies of the composite sample with 10\% of the resin beads. It can be seen that the resin beads were well dispersed in the PU–EP (70/30) matrix, and the single bead in the matrix had lots of holes in its interior.

Influences of the macroporous resin beads on the dynamic mechanical and underwater acoustic properties of the PU/EP blend matrices

The acoustic attenuation ability of materials is correlative with their structures, sorts and amount of
fillers, and acoustic absorbing structures. The relationship between the intrinsic acoustic impedance and acoustic absorption coefficient of a material is given as follows:\textsuperscript{2,7}

\[
\alpha = 1 - |R|^2 - |T|^2
\]

\[
1 - \left| \frac{(Z_1 + Z_2)(Z_2 - Z_3) e^{-ik_2d} + (Z_1 - Z_2)(Z_2 + Z_3) e^{ik_2d}}{(Z_1 + Z_2)(Z_2 - Z_3) e^{-ik_2d} + (Z_1 - Z_2)(Z_2 + Z_3) e^{ik_2d}} \right|^2
- \frac{4Z_1Z_2}{(Z_1 - Z_2)(Z_2 - Z_3) e^{ik_2d} + (Z_1 + Z_2)(Z_2 + Z_3) e^{-ik_2d}} \right|^2
\]  

(1)

where \( R \) is the complex reflection coefficient, \( T \) is the complex transmission coefficient, \( \alpha \) is the acoustic absorption coefficient, \( d \) is the thickness of the material, \( Z_1 \) is the intrinsic acoustic impedance of air (\( Z_1 = \rho_a c_a \), where \( \rho_a \) is the air density and \( c_a \) is the acoustic wave velocity in air), \( Z_2 \) is the intrinsic acoustic impedance of the material (\( Z_2 = \rho_c c_c \), where \( \rho_c \) is the density of the material and \( c_c \) is the acoustic wave velocity in the material), \( Z_3 \) is the intrinsic acoustic impedance of water (\( Z_3 = \rho_w c_w \), where \( \rho_w \) is the water density and \( c_w \) is the acoustic wave velocity in water), and the complex wave number \( (k_2) \) is defined as

\[
k_2 = \frac{2\pi f}{c_c} - i\beta
\]  

(2)

where \( f \) is the incident acoustic wave frequency, \( i \) is the imaginary unit and \( \beta \) is the acoustic attenuation coefficient. The acoustic impedances of water and air are basically invariable when the temperature and pressure are constant. It can, therefore, be seen from the equation that the acoustic absorption coefficient of the material at different frequencies depends on its intrinsic acoustic impedance, density and thickness, acoustic attenuation coefficient, and acoustic wave velocity in the material.

Figure 4 shows the temperature dependences of the damping factors and Young’s modulus of the PU/EP (70/30) blend matrix and its composite with 10% of the resin beads. It can be seen that the composite has a lower glass-transition temperature, higher damping factor at temperatures of less than 5°C, and lower Young’s modulus at temperatures of less than 44°C than the matrix. The TAs\textsuperscript{40} of the matrix and composite were 36.7 and 38.3 obtained from the testing data, respectively. The results indicate that the resin beads could improve the damping properties, especially the low-temperature damping properties. Introducing the beads into the matrix may have led to increases in the free volume and internal friction between the bead interface and polymer chains, which caused a decrease in the glass-transition temperature and an increase in damping at temperatures of less than 5°C. As the temperature increased, the free volume expanded, and the internal friction between the bead interface and polymer chains decreased. Hence, damping was mainly controlled by internal friction among polymer chains.

Figure 5 shows the underwater acoustic absorption coefficients and reflection coefficients of the composites with different contents of the macroporous resin beads (PU/EP = 70/30). It can be seen that the average reflection coefficient first decreased and then increased as the amount of the macroporous resin beads increased, and the acoustic absorption coefficient of the composite with 5% of the beads was obviously higher than that of the matrix in the whole frequency range (the lowest value was 0.42, the maximum value was 0.64, and the average value was 0.55), but the acoustic absorption coefficients of the composites with 10 and 15% of the beads were less at low frequency and much larger at high frequency than that of the matrix. The results show that an adequate amount of the macroporous resin bead could improve the underwater acoustic absorption.
absorption properties of the PU/EP matrices. The pores and holes existing in the beads, as shown in the SEM images, could have adjusted the acoustic impedance of the composites to match the water acoustic impedance, and the air inside the pores and holes caused viscous attenuation of the acoustic waves. In addition, the beads could have caused the mode conversion from longitudinal waves to highly damped transverse waves, and the multiple scattering among the beads could also enhance the energy dissipation.

By comparison with the PU/EP blend matrix (the amount of the beads is zero), the composite with 10% of the beads had a higher acoustic reflection coefficient and lower acoustic absorption coefficient at $f < 5$ kHz and had a higher acoustic absorption coefficient at $f > 5$ kHz, although it had a higher acoustic reflection coefficient at $f > 8$ kHz. The damping factors and Young’s modulus of the composite at 26°C, as shown in Figure 4, were less than that of the matrix. In addition, the apparent density (0.6 g/cm$^3$) of the beads was less than that of the matrix, the density of the composites was, therefore, less than that of the matrix. Decreases in the modulus and density led to an obvious decrease in its acoustic impedance, which caused the acoustic

Figure 4  Dynamic mechanical spectra of the PU/EP (70/30) blend matrix and its composite with 10% of the resin beads: (a) tan δ–temperature curves and (b) Young’s modulus ($E$)–temperature curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5  Underwater acoustic properties of the composites with different contents of the beads (PU/EP = 70/30): (a) acoustic absorption coefficient and (b) acoustic reflection coefficient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
impedance of the composites to be much less than that of the matrix and less than that of water (the acoustic impedance of the matrix was perhaps slightly larger than that of water). The relative acoustic impedance mismatching and lower damping factor resulted in a higher acoustic reflection coefficient and lower acoustic absorption coefficient at \( f < 5 \) kHz. As known, complex acoustic impedance is dependent on frequency, and its imaginary part is correlated to the damping factor.\(^{2,4,7,13}\) Hence, the acoustic reflection and absorption coefficients displayed the characteristics of frequency dependence.

**Influences of the weight ratios of PU to EP on the dynamic mechanical and underwater acoustic absorption properties**

Figure 6 shows the temperature dependences of damping factors and Young’s modulus of the composites with different weight ratios of PU to EP (the amount of resin beads was 10\%). It can be seen that the composites with weight ratios of PU to EP of 75/25 and 70/30 had only single loss factor peaks and lower Young’s moduli, but the composite with the weight ratio of PU to EP of 65/35 had two loss factor peaks and a higher Young’s modulus. This indicated that the component compatibility became wrong and the degree of phase separation increased when the weight ratio of PU to EP was 65/35. The TA values of these composites were 36.3, 38.3, and 34.1, as obtained from the testing data. The results show that the composites with the weight ratio of PU to EP of 70/30 had the best damping properties, and the composites with the weight ratio of PU to EP of 65/35 had better high-temperature damping properties, although its TA value was the lowest.

Figure 7 shows the underwater acoustic absorption coefficients and reflection coefficients of the composites with different weight ratios of PU to EP (the amount of the resin beads was 10\%). It can be seen that the composite with the weight ratio of PU to EP of 75/25 had a higher acoustic absorption coefficient at low frequency, and all acoustic reflection coefficients display periodic features with frequency; the extreme value peaks shifted toward lower frequency as the content of PU increased. This was because the damping factors and modulus of the composites depended on the composition ratios and temperature or frequency, as shown in Figure 6, which caused the underwater acoustic absorption coefficients and reflection coefficients to be interrelated with the composition ratios. On the basis of the Williams–Landel–Ferry equation and the data in Figure 6, the order of the damping factors at 26°C and 2–12 kHz was 70/30 > 75/25 > 65/35, and the order of the modulus at 26°C and 2–12 kHz was 65/35 > 70/30 > 75/25. Hence, the order of the acoustic impedance was 65/35 > 70/30 > 75/25 when the composites had almost same density, and the order of the average acoustic reflection coefficient was 75/25 > 70/30 > 65/35, as shown in Figure 7. However, the acoustic absorption coefficient of the composite with the weight ratio of PU to EP of 65 to 35 was not the highest because of its lowest damping factor.

**Influences of the bead diameters on the underwater acoustic properties**

The sizes of bead diameters have an obvious influence on the propagation of the acoustic wave and, thus, an effect on the underwater acoustic properties.
of composites. Figure 8 shows the underwater acoustic absorption coefficients and reflection coefficients of the composites with 10% different diameter sizes of the beads (PU/EP = 70/30). As shown in the figures, the composite with the beads of diameter size of less than 0.2 mm had a lower acoustic reflection coefficient and higher acoustic absorption coefficient than the other two, and the composites with beads with diameter sizes of 0.2–0.45 and 0.45–0.71 mm had almost the same acoustic absorption coefficients. This was because the bigger beads may have led to an increase in the heterogeneity of the composites and acoustic reflection coefficient. In addition, the extreme value peaks of the acoustic reflection coefficient–frequency curves shifted toward the low frequency with increasing diameters of the beads.

**Influence of the water temperature on the underwater acoustic properties**

Temperature had an obvious influence on the modulus and damping factor of the matrix and, thus, affected the underwater acoustic properties of the composites.
Figure 9 Underwater acoustic properties of the composites (PU/EP = 75/25) at 26 and 12°C: (a) acoustic absorption coefficient and (b) acoustic reflection coefficient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite. Figure 9 shows the underwater acoustic absorption coefficient and reflection coefficient of the composite (PU/EP = 75/25, the amount of the beads = 10%) at 26 and 12°C. As shown in the figures, the composite at higher temperature had a lower acoustic reflection coefficient and a higher acoustic absorption coefficient than itself at lower temperature. As shown in Figure 6 and discussed in an earlier section, the composite had a much higher damping factor at 12°C than itself at 26°C, which caused the composite to have a higher acoustic reflection at 12°C. In addition, changes in the modulus and density with temperature also influenced the acoustic impedance of the composite.

Influence of the thickness on the underwater acoustic properties

As shown in eq. (1), the thickness of an acoustic absorption material has a great deal of effect on its underwater acoustic properties because the intrinsic acoustic impedance and acoustic reflection coefficient of the material at different frequencies not only depend on its modulus, density, and acoustic wave...
velocity at different frequencies but also on its thickness. Figure 10 shows the underwater acoustic absorption coefficient and reflection coefficient of the PU/EP (70/30) blend matrices with thicknesses of 40 and 25 mm. Both the acoustic absorption coefficient and acoustic reflection coefficient increased as the thickness increased. The lower acoustic absorption coefficient and reflection coefficient, especially when the thickness was 25 mm, indicated that the elastomer had a higher acoustic transmission property.

CONCLUSIONS

Macroporous P(VAc-co-TAIC) resin beads improved the underwater acoustic absorption properties of PU/EP intercrosslinked elastomer matrices and depended on their amount and diameter size, the composition ratios of PU to EP, the thickness, and the water temperature. The beads with smaller diameters had a better enhancing effect on the underwater acoustic properties of the matrices. In a comparison with the matrix with a 70/30 composition ratio of PU to EP to one without the beads, the composite with 5% beads had higher damping properties, its average acoustic absorption coefficient increased from 0.38 to 0.55, and the peak value increased from 0.42 to 0.65. However, the composites with 10 and 15% beads had lower acoustic absorption coefficients at low frequency and much higher acoustic absorption coefficients at high frequency. The damping properties of the composites depended on the composition ratios of PU to EP.

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