Preparation and Damping Properties of Simethicone PU Microsphere

Jun Liu1,2,*, Cong Tang1, Tammam Kaid1, Yuguo Zhuo2, Li Wang3 and James Ren1

1Department of Maritime and Mechanical Engineering, Liverpool John Moores University, Liverpool L3 3AF, UK
2Department of Environmental Engineering, Hebei University of Environmental Engineering, Qinhuangdao, 066102, P.R. China
3School of Engineering, University of Bolton, Bolton BL3 5AB, UK

*Corresponding author

Abstract. Microspheres are an important material group with increased uses in mechanical, civil and environmental engineering. The microspheres with polyurethane as the wall material and dimethyl silicone oil as the core material were successfully prepared by interfacial polymerization method, which was incorporated into epoxy resin to enhance the damping properties. The new material was characterized by scanning electron microscopy and infrared spectroscopy. Results show that the microspheres had good sphericity and smooth surface. Dynamic mechanical thermal analysis showed that the incorporation of microspheres can elevate the damping performance of the epoxy resin.

1. Introduction

Microspheres are an important material group with many beneficial properties including low density, high specific surface area, good heat-insulation, and large useful inner spaces. Hollow polymer microspheres are widely used in materials for machinery, building, and environmental infrastructures. Typical cases included inertial confinement fusion (ICF) targets, fillers, high-performance coatings, insulating materials, and increasingly as advanced damping materials [1-4]. In civil engineering, small hollow plastic spheres are used to replace entrained air, which offers toughness and flexibility and prevents the concrete from freeze-thaw damage [4, 5]. To meet the demands for different applications, a broad range of manufacturing processes has been developed such as single emulsion, double emulsion, polymerization, phase separation, spray, all of which have found applications in different areas [6-9]. The research work reported on polymer microspheres has covered synthesized and natural biodegradable system, the diversity of plastics available has led to enhanced development of microsphere technologies and future applications.

One of the rapidly increasing application fields of microspheres is in the use of making damping materials, mostly in the form of composites. Damping materials are critical for vibration management and noise reduction, which is essential for the operation and maintenance of equipment, vehicles, buildings and environmental systems. Many different material systems have been developed with enhanced damping and insulating capacities [8-9]. Polymer composites are widely used in many engineering and civil applications. The high damping capacity of polymer-based composites is due to the viscoelastic behavior of the polymeric matrix in particular at the region of the glass transition temperature. The damping behaviors of materials can be tuned by properly choosing constitutive
parameters of composites such as fiber aspect ratio, stacking sequence and constituents properties. Many complex material systems are being developed for damping applications, including interpenetrating polymer networks (IPNs) that are polymer alloys consisting of two or more polymers in a network form. The network was held together by permanent entanglements with only occasional covalent bonds between the chains of two different types of polymers [10]. Recent work has also reported the use of carbon nanotubes (CNTs) [11]. Microcapsule technology offers a new opportunity for the development of damping and insulating materials, and the microcapsules can be incorporated into various substrates to improve the damping and other functional performances. However, there is limited literature about the damping properties of PU microspheres-reinforced epoxy composites, which potentially could offer a new route in further improving the damping abilities of composites. In recent years, work on polyurethane damping material was mostly focused on epoxy, polystyrene interpenetrating polymer networks or foam, and the reports on damping microspheres were limited. It is essential to develop a suitable material system and investigate the effect of microspheres on the damping properties.

In this study, microspheres with polyurethane (PU) as the wall material and dimethyl silicone oil as the core material were successfully prepared by interfacial polymerization method, which was incorporated into epoxy resin to enhance the damping performance.

2. Methods and Experimental

2.1. Methods

It is known that Tuned Liquid Damper (TLD) can be effectively used to reduce vibration, it is important to investigate the use of such a system in damping property improvement. In this paper PU microspheres, as the damping materials were designed and prepared, the effect of the materials on the damping properties of epoxy resin was studied. Fig.1 schematically shows the TLD as a model with simethicone as the core.

![TLD model](image)

**Figure 1.** The design model of microspheres.

2.2. Experimental

The sample was produced through an interfacial polymerization method with simethicone as the core and PU as the wall material [9]. Morphologies of microspheres were assessed by SEM (HITACHI S4800-II) at 15 kV. Before the test, samples were treated by spraying gold powder. Thermal behaviors were analysed by STA449C thermal analyzer from 20°C to 900°C. Fourier transform infrared (FTIR) analysis was examined on an E55+FRA106 FTIR (Bruker, Germany) spectrometer between 400 and 4000cm⁻¹. Dynamic mechanical thermal analysis was tested on DMAQ800 (TA, USA) analyzer between 2°C and 200°C.

3. Results and Discussions

3.1. FTIR Analysis

Fig. 2 shows the FTIR of simethicone and simethicone PU microspheres. There are two kinds of vibrations in the infrared spectroscopy, including deformation and stretching vibration. The absorption wave-number ranges from 4000cm⁻¹ to 400cm⁻¹, with the corresponding wavelength varies from 2.5μm to 25μm. Within this scope, different functional groups could be detected. 4000cm⁻¹ to 400cm⁻¹ also belongs to the characteristic frequency zones.
Silicon oxygen bond can be found from 1100 cm\(^{-1}\) to 1000 cm\(^{-1}\), which represents simethicone in Fig. 2(a). At 3278 cm\(^{-1}\) -NH, the functional groups were distinguished, at 2978 cm\(^{-1}\) -CH\(_3\) functional groups were found and around 2270 cm\(^{-1}\), the asymmetric vibration characteristic peak of -NCO functional groups were detected, all of which were associated to polyurethane, as shown curve (b) in Fig. 2. However, two peaks around 1600 cm\(^{-1}\) represent the C=O functional groups, indicating the coexistence of polyurea and polyurethane and the peaks about 1050 cm\(^{-1}\) suggest that dimethyl simethicone was capsuled by the polyurethane in Fig. 2(b).

3.2. Morphology

Fig. 3 shows the morphology of the composites. It shows that most of PU microspheres are in regular spherical form or partially broken microsphere with a distinctive core-wall structure. The surface of the microspheres was smooth. Part of PU microspheres with irregular shape indicates that the strength of the wall was low. Detailed observation and quantitative analysis reveals that the microspheres had a high sphericity, with a particle size between 14 and 136 \(\mu m\), a minimum particle size of 14 \(\mu m\), and the average particle size is about 50 \(\mu m\).
3.3. Thermal Analysis

Table 1 lists the data comparing the thermal properties of (a) simethicone; (b) simethicone PU microspheres. The weight loss data of two microspheres were analyzed. The data shows that the maximum weight-loss of these two microspheres was divided into two stages. The initial weight loss temperature (Tonset) of the two microspheres was very close, while the final weight loss temperature (Toffset) of microspheres with core was much higher than the value of the microspheres without core, which suggests that the stability of the microspheres was improved after adding the core material. When the temperature reached the maximum weight loss temperature (Tmax), the mass fraction corresponding to microspheres with core was significantly higher than that of core-free microspheres, but the final residual mass fraction (w) of the core-microspheres was significantly lower than that of the coreless microspheres. This indicates that the coreless microspheres were coated with more ethyl acetate than that for the core-microspheres, which indicates that the core-microspheres had fully covered the simethicone.

| Sample         | Tonset/℃ | Tmax/℃ | Toffset/℃ | w/% |
|----------------|----------|--------|-----------|-----|
| Without core   | 230      | 340    | 580       | 13.6|
| With core      | 225      | 355    | 705       | 8.6 |

3.4. Damping Properties Analysis

Table 2 summarised the dynamic thermal analysis data of composite samples. It shows that the high damping temperature range (tanδ greater than 0.3) of pure epoxy resin was 97-113 ℃ and the highest tan δ value was 0.376. When the epoxy resin is doped with microspheres, the glass transition temperature (Tg) increased and the high damping temperature range (Tdomain) was expanded. As the amount of microspheres increased in the mixture, the peak value of the loss factor (tanδ) first increased and then decreased. The Tg gradually increased, and Tdomain exhibited no significant change. When the amount of microcapsules reached 5%, tanδ reached a maximum value of 0.563. At this time, the high damping temperature range was 107-134 ℃, indicating that the incorporation of microspheres improved the damping performance of the epoxy resin, but when the amount of microspheres exceeded 5% and reached 10%, tanδ value began to decrease again. This was due to the excessive incorporation of microcapsules, which led to poor dispersion and destroyed the original structure of the material, thus reduced the damping properties of the composite.

| Addition content/% | tanδmax   | Tg/℃ | Tdomain/℃ |
|--------------------|-----------|------|-----------|
| 0                  | 0.376     | 105  | 97-113    |
| 3                  | 0.512     | 114  | 100-128   |
| 5                  | 0.563     | 120  | 107-134   |
| 10                 | 0.478     | 126  | 114-140   |

The works show that the microspheres are effective in controlling/improving damping behaviors. A full explanation of the effect of the microsphere requires complex analysis. Modelling a small volume of liquid is difficult through conventional computation fluid dynamics analysis, which required full scale atomic/molecular modeling [12-14]. The size analysis shows that one area which can be improved is the uniformity of the size of the spheres. Spheres with different sizes may provide advantages in some situations such as gradient materials, but a larger size range domains may make it difficult to accurately design the composite for damping applications. Future work will investigate both the production process of spheres and the mixing of the composites to improve the size distribution and statistically manage the mixing of the spheres in the matrix [15-17]. Apart from damping behavior, microspheres can also be used in self-repair materials which are important for building materials such as concretes [16-17]. Future work will explore these approaches to improve the understanding of the damping mechanism and
combine the damping performance of such a system in more complex materials systems such as building materials and geopolymers.

4. Conclusions
In this work, polyurethane microspheres as damping materials were designed and prepared. The effect of the materials on the damping properties of epoxy resin was studied. The morphologies of the microspheres and the composites were analyzed by SEM. Thermal and damping behaviors were characterized by TG and dynamic mechanical thermal analysis. The works showed that spheres had a good sphericity and smooth surface, and its average particle size was 50 μm. When 5% of prepared microspheres were added, the composites had better damping behaviors than the virgin plastic material. The high damping temperature range increased by 10-21°C, indicating that the addition of the microspheres enhanced the damping behaviors of the composites.

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