Optimising the Properties of Polymer Composites: Low Weight / High Strength Composites for Commercial Applications

M. Hayward*, J. Johnston*, T. Dougherty** and K. de Silva***

*Victoria University of Wellington, School of Chemical and Physical Sciences,
PO Box 600, Wellington, New Zealand, matilda.hayward@vuw.ac.nz
**Nuenz Limited, Lower Hutt, New Zealand
***Product Accelerator, University of Auckland, New Zealand

ABSTRACT

This paper presents our research on the use of dry, expanded, hollow polymer microspheres (PMS) as an additive in a commercial vinyl ester resin to reduce the density of the composite material. PMS were functionalised with hydroxyethyl methacrylate (HEMA) monomers as a method to maximise the interfacial adhesion between the dispersed PMS and the polymer matrix. Stronger interfacial adhesion is known to improve the mechanical performance of the composite material by reducing the number of interfacial voids, which can be weak points in the composite structure. The PMS and HEMA-functionalised PMS were compared via FT-IR to confirm that the functionalisation process was successful. During polymerisation, the surface-bound HEMA co-polymerised with the vinyl ester to form a strong interfacial bond between the surface of the spheres and the resin matrix. SEM imaging of the fracture surface of the composite confirmed improved interfacial adhesion. Mechanical testing showed an increase in the tensile strength and hardness of the HEMA-PMS composite compared to the unfunctionalised PMS composite.

Keywords: polymer composites, interfacial adhesion, polymer microspheres, vinyl ester

1 INTRODUCTION

Vinyl ester (VE) resins are thermosetting polymers, produced by the esterification of epoxy resins with a monocarboxylic acid group. They are cured via addition of a catalytic amount of an organic peroxide, such as methyl ethyl ketone peroxide (MEKP). Vinyl ester polymers have an excellent resistance to harsh and corrosive environments. This results in their wide-spread use as a resin for multiple applications in various industries such as marine composites, swimming pools and solvent storage tanks. Alongside corrosion resistance, which results in a significant reduction in maintenance time and costs compared to other polymer materials, vinyl ester resins also have favourable mechanical properties, a low viscosity and are low cost.[1,2] Fibre-reinforced polymer (FRP) composites, which use vinyl ester resins as the matrix material, are low-density with superior mechanical properties, such as strength and stiffness. Further improvements to the strength-to-weight ratio of the vinyl ester matrix are of constant interest to maximise the performance of the FRP composite in high-end commercial applications.

There are many examples in the literature of polymer composite materials filled with hollow glass [3,4] or ceramic microspheres. Tagliavia *et al*. studied the flexural properties of hollow glass particle – vinyl ester composites, and found an increase in the volume fraction of microspheres resulted in an increase in the specific elastic modulus of the composite, but a decrease in composite specific strength.[5] The authors have suggested this is due to interface de-bonding followed by matrix cracking which is prominent in composite structures.

PMS have an extremely low density and also exhibit high elasticity and low moisture absorption. PMS can be incorporated into a polymer composite to reduce the overall density, improve workability and increase resilience of the material.

Ahmad *et al.* demonstrated that the incorporation of polymeric hollow microspheres into a polymer composite can increase the resilience and elasticity of the composite.[6] Foon *et al.* studied the effect of epoxy-PMS in vinyl ester resins and found that an increase in PMS resulted in an increase in tensile, flexural and impact strength. This trend occurred up until 5 wt.% filler loading at which point the strengths decreased with an increase in filler content due to the onset of agglomeration of PMS.[7]

Sphere dispersion, adhesion and wettability can all be increased via surface functionalisation techniques. Addition of a compatible surface group with the resin can onset chemical binding between the additive surface and the resin allowing for further improvements to the composite performance, and also reduces agglomeration which means filler loading can be increased without decreasing the properties. In this paper, HEMA was used to functionalise the surface of the polymer spheres, which co-polymerises with the vinyl ester resin forming a strong adhesive bond across the composite interface.

2 EXPERIMENTAL

The PMS used for this study were EXPANCEL 461 DET 40 d25 provided by Akzonobel (New Zealand) with sphere diameters of 35-55 µm and true densities of 25 kg m^{-3}. 2-Hydroxyethyl methacrylate (97%) was from Sigma Aldrich. The vinyl ester resin was a commercial Derakane™ 8084

Epoxy Vinyl Ester Resin, provided by Adhesive Technologies (Auckland, New Zealand). The resin was catalysed by 1.5 % addition of 925H NOROX MEK-P catalyst.

The microspheres were dispersed in 3M H_2SO_4 solution and vigorously stirred for 6 hrs. They were then separated from solution via centrifugation and dried. The carboxylated-PMS were then dispersed into HEMA with a catalytic amount of H_2SO_4 and vigorously stirred at 60ºC for 5 hrs. The microspheres were then separated from solution via use of a centrifuge, washed in ethanol and left to dry at room temperature for >48 hours. The composites were made up at various volume fractions of PMS and HEMA-PMS. A measured volume of microspheres were dispersed into 200 ml of vinyl ester and mixed via an overhead mixer for 30 minutes at 2000 RPM. 3 ml (1.5%) of catalyst was added to the mixture and which was then further mixed with the overhead mixer for 1.5 minutes. The resin was then transferred into moulds and left to cure at room temperature for >24 hrs.

FT-IR analysis of the PMS was carried out via ATR-IR on a Bruker Tensor 27 FT-IR spectrometer between 4000 and 600 cm^{-1}. SEM was performed on the fracture surface of the composites using a JEOL 6500F field emission gun at 20 kV accelerating voltage. The sample surfaces were pre-coated with a 24 nm thick layer of carbon using a JEOL JEC-560 carbon coater.

Hardness measurements were taken using an industrial shore durometer (scale D) as per ASTM D2240 standard. Tensile tests were carried out using an Instron 3367 at a strain rate of 1.5 mm min^{-1}, using dog bone shaped samples according to ASTM D3039 standard.

3 RESULTS AND DISCUSSION

3.1 HEMA Functionalisation of PMS

The reaction mechanism for the functionalisation of the microspheres with HEMA is shown in Figure 1.

FT-IR analysis of the unfunctionalised and HEMA-functionalised microspheres was conducted to observe whether or not the functionalisation had been successful.

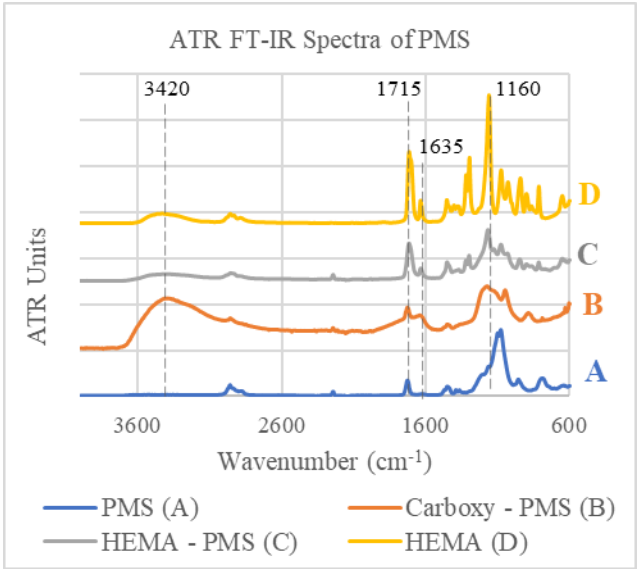

Figure 2. FT-IR spectra of functionalised PMS

Wavenumber (cm^{-1})	Compound	Assignment	Lit. Value (cm^{-1}) [8]
3420	B	OH stretch	3100-3500
1715	A, B, C, D	C=O (ester)	1700-1750
1635	C, D	$C=CH_2$	1600-1650
1160	C, D	C-O (ester)	1150-1210

Table 1. Peak assignment of FT-IR spectra

The appearance of a broad peak around 3400 cm^{-1} for the carboxylated spheres (Figure 2 B) is evidence for the formation of -OH groups as part of a carboxylic acid group on the surface of the microspheres. All spectra have peaks around 1715 cm^{-1} due to the presence of C=O groups, however this peak has a higher intensity for the HEMA-PMS (C) and the HEMA (D) spectra due to the presence of two acetate groups per molecule. Spectra C and D also display peaks at 1635 and 1160 cm^{-1} which are due to the vinyl group and the conjugated acetate ester respectively. The presence of the vinyl peak for both C and D confirms the successful functionalisation of the PMS with HEMA.

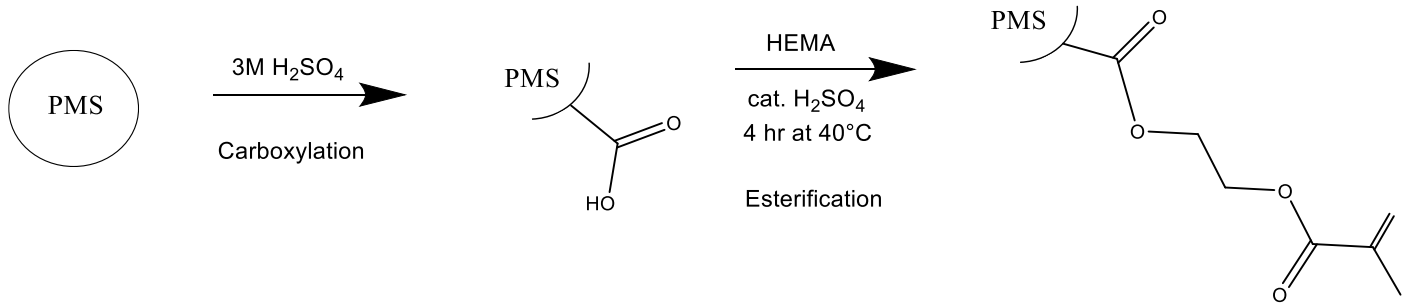

Figure 1. Reaction scheme for the functionalisation of HPMS with HEMA

3.2 HEMA-PMS Vinyl Ester Composite Analysis

The microspheres were then dispersed into the vinyl ester resin at various filler volume ratios and cured via addition of a catalyst.

The density of the composites were measured via the Archimedes method to quantify the reduction in composite density for each PMS volume fraction, these densities are shown in Figure 3.

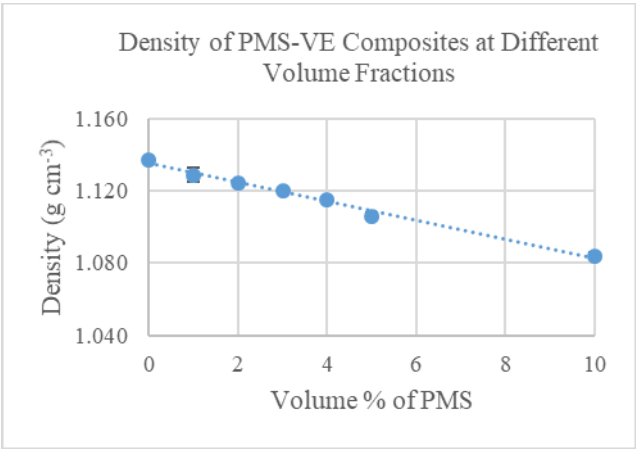

Figure 3. Density of PMS - VE composites

3.3 Mechanical Testing

The hardness values of the PMS - vinyl ester composite samples were tested via an industrial standard, Shore hardness (scale D), the results are shown in Figure 4.

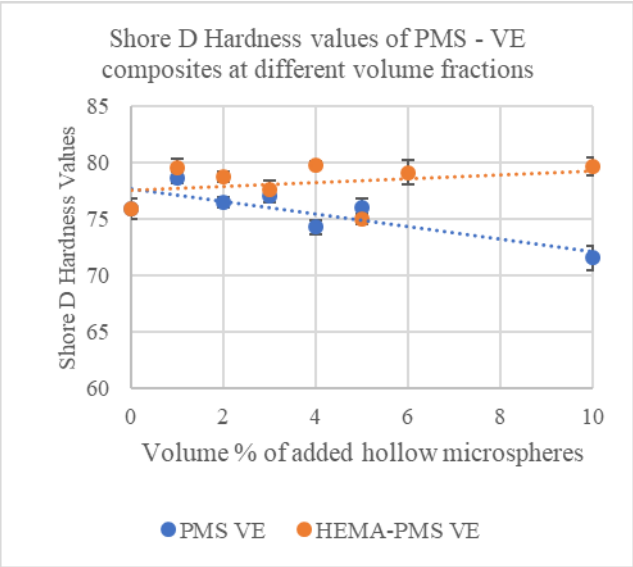

Figure 4. Shore D hardness results for PMS-VE and HEMA-PMS VE composites

The hardness values display a clear trend that for the unfunctionalised PMS composites, the Shore D hardness decreases with an increase in volume % of PMS. However, the HEMA-PMS VE samples maintain an approximately consistent Shore D hardness value as the microsphere content is increased from 1 to 10 vol.%.

The specific tensile properties, shown in Figure 5, were also measured to determine whether the microspheres effected the strength-to-weight ratio of the composite materials.

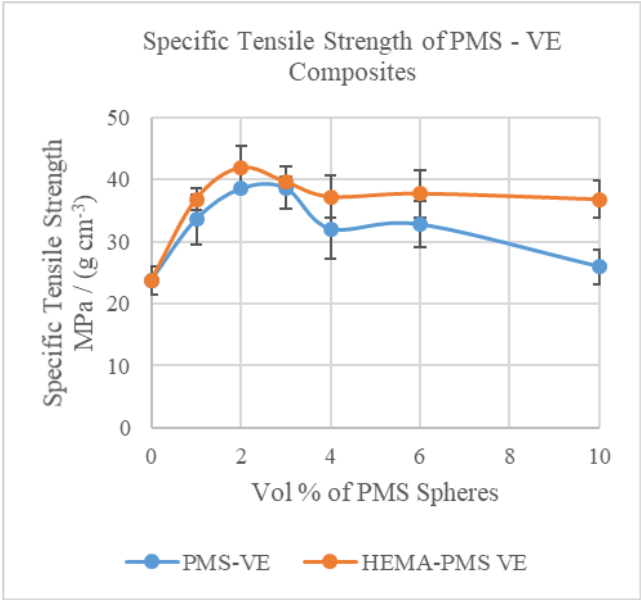

Figure 5. Specific tensile strength results for PMS-VE and HEMA-PMS VE composites

The results show that the best strength-to-weight ratio properties are observed at 2 vol.% sphere addition, at this loading the unfunctionalised PMS composites show a significant increase of 62% in specific tensile strength, and the HEMA functionalised PMS composites show an even higher increase of 76% compared to the neat vinyl ester resin. The trends also show that the HEMA functionalised composites have consistently higher tensile strengths than the unfunctionalised PMS composite at the same filler volume.

3.4 Microstructural Analysis

SEM analysis of the fracture surface of the composite materials (Figure 6) was used for visual analysis of the dispersion and adhesion of the spheres to the polymer matrix. The PMS composites displayed multiple examples of ‘sphere pull out’, where the microsphere additives were pulled out of the composite surface during the fracturing process. The unfunctionalised composites (Figure 6 A) also

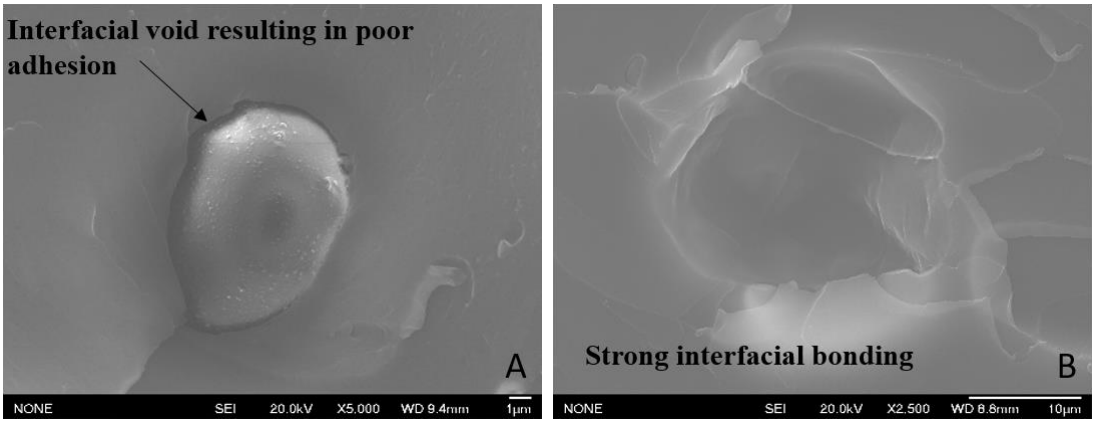

Figure 6. SEM images of fracture surfaces of PMS vinyl ester composite (A) showing interfacial voids, and HEMA-PMS vinyl ester composites (B) showing good interfacial adhesion.

displayed small gaps at the phase boundary which is known to result in a weaker composite performance. From the images it is evident that the functionalisation process removes the interfacial voids between the spheres and the vinyl ester matrix facilitating better resin-sphere contact and bonding, and hence increasing the bond strength across the interface.

4 CONCLUSION

Interfacial adhesion in polymer composites is a key contributing factor towards achieving optimum composite properties. In this work, polymer microspheres were incorporated into a vinyl ester resin in order to reduce the overall density of the material without compromising the mechanical properties of the composite material. In order to maintain optimum mechanical properties, the surfaces of the spheres were functionalised with HEMA monomers to maximise the interfacial adhesion and reduce the interfacial void content which can result in reduced composite performance.

Density measurements proved that PMS addition reduced the density of the cured polymer material and mechanical testing (tensile and hardness) of the composites showed that the surface functionalisation technique was successful in increasing the mechanical performance of the materials, with maximum performance at 2 vol.% PMS loading.

SEM images confirmed that HEMA functionalisation increased the interfacial adhesion in the composite, enhancing the wettability of the microspheres and reducing the interfacial void content.

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