Article

JOURNAL OF REINFORCED PLASTICS & COMPOSITES

Journal of Reinforced Plastics and Composites
29(20) 3066–3073

DOI: 10.1177/0731684410364681
jrp.sagepub.com
SAGE

The properties of vinyl ester composites reinforced with different types of woven fabric and hollow phenolic microspheres

L Yusriah, M Mariatti and A Abu Bakar

Abstract

This study compares the effects of hollow polymeric microspheres (PHMS) on specific mechanical properties and thermal properties of glass, basalt, and carbon woven fabric reinforced vinyl ester composites. The specific flexural and specific impact strengths of the composites were marginally increased with the addition of PHMS; however, it was at the expense of reduced specific flexural modulus. The thermal stability of the neat vinyl ester was improved with the addition of woven glass and carbon, but was consequently reduced with the further inclusion of PHMS. SEM observations identified the presence of the combined failure mechanism of fibers and PHMS. In short, the major reinforcing effect of the woven fiber-reinforced vinyl ester composites is governed by the type of fiber used, while the addition of PHMS enhanced the ductility of the composites.

Keywords

hollow phenolic microspheres, specific mechanical properties, thermal properties, woven fabric

Introduction

Composites are suitable materials that can be tailored to meet the needs of the applications by emphasizing the benefits of incorporating various types of reinforcements, such as fiber, to achieve their desired properties. Many studies have reported on the properties of woven fabric reinforced thermosetting polymers using various types of fibers ranging from synthetic to rock fibers. Ahmed and Vijayarangan[1] reported that woven glass fabric was found to have great extensibility, which increased the flexural strength of the jute/polyester composites. Chowdury et al.[2] conducted a study of epoxy composites reinforced with woven carbon fabric. They noted that carbon fibers formed kink bands on the failure surface of the compression side of the flexural specimen. The formation of kink bands was expected because carbon fibers are known to be brittle. In his work Ratna[3] also emphasized that carbon fibers are more brittle than glass fibers, which explains why woven carbon fabric-reinforced epoxy composites have lower impact strength than woven glass fabric-reinforced epoxy composites. Moreover, it was established that the impact failure of the composite occurred owing to carbon fibers breakage. According to Liu et al.,[4] epoxy composite reinforced with woven basalt fabric exhibited higher flexural strength compared to the corresponding woven glass fabric-reinforced epoxy composite despite the lack of any remarkable differences in the tensile, shear, and compressive strengths of both composites. Basalt fibers were also found to be suitable alternative material to glass fibers because basalt fibers possessed relative mechanical properties with the glass fibers. In addition, basalt fibers are fit for applications at moderately elevated temperatures.[5] Numerous studies have been made to investigate hybrid composites of particulate filler and woven fabric.[2,6] There were also several attempts to study the effects of hollow microspheres

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia.

Corresponding author:
M. Mariatti, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia
Email: mariatti@eng.usm.my

on the properties of various types of composites;[7,8] however, most of the investigations focused on hollow glass microspheres. Little is understood of the effects of incorporating hollow polymeric microspheres into woven fabric-reinforced composites. In this study, hollow microspheres were chosen because they contribute to lower density, high stiffness, and excellent compressive and good impact behavior.[9] Hence, this paper aims to investigate the specific mechanical and thermal properties of vinyl ester composites reinforced with glass, basalt, and carbon woven fabric, with the addition of hollow polymeric microspheres.

Experimental

Materials

The vinyl ester epoxy (VE) resin Hetron 922 used in this study was supplied by Ashland Specialty Chemical Company, Columbus, Ohio, USA. Methyl ethyl ketone peroxide (MEKP) was used as the hardener. The batch of hollow microspheres used in this study was made of phenolic (Phenoset), manufactured by Asia Pacific Microspheres Sdn. Bhd. Selangor, Malaysia, with an average particle size of 70–90 µm and density of 0.25 g/cm^3. Three types of plain weave fabrics were used in this study, namely, glass, basalt, and carbon fibers. The properties of the woven fabric are summarized in Table 1 based on technical data from the suppliers.

Preparation of composites

The amount of hollow polymeric microspheres (PHMS) fillers was fixed at 5 wt% and the woven fabric content was fixed at 40 wt% for all types of fibers. PHMS was gradually added into the VE resin while stirring the resin mixture. The mixture was stirred at 200 rpm for about 10–15 min using a mechanical stirrer. A 1% MEKP was later added into the mixture. All samples were manufactured using the hand lay-up and vacuum bagging technique. The laminates comprised of 3-ply woven fabric, which were cured at room temperature for 24 h and post-cured for another 4 h in the oven at 80°C.

Table 1. Properties of woven glass, basalt, and carbon fiber

Type of fiber	Supplier	Density (g/cm^3)	Areal density (g/m^2)	Coefficient of thermal expansion (ppm/°C)
Glass (Hybon)	PPG Industries	2.63	800	5.0–6.0
Basalt (TBR-400)	Kammeny Vek	2.67	400	3.5
Carbon (3 K)	Fibre Glast	1.85	193	2.10

Testing and characterization of composites

Three-point bending tests were carried out according to the standard method used for flexural properties (ASTM D790-98) using Instron 3366 with the cross-head speed set at 5 mm/min. The span-to-depth ratio of all specimens were fixed at 16 : 1. The unnotched Izod impact tests were carried out according to ASTM D-256-02 using a Galdabini 1890 impact tester. The morphological study on fracture composite surfaces was observed using a field emission scanning electron microscope performed with a ZEISS model SUPRA 35VP instrument. The composites' surfaces were mounted on aluminum stubs and coated with a thin layer of gold to eliminate electron charge accumulation during the examination. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Pyris Diamond TG/DTA Analyzer under nitrogen atmosphere at a heating rate of 20°C/min from 30°C to 700°C. Dilatometry was carried out to determine the coefficient of thermal expansion of the composites. The test was done using Linseis L75 dilatometer at the heating rate of 10°C/min from room temperature to 165°C.

Results and discussion

Mechanical and thermal properties

Flexural properties. The results of the tests on the specific flexural strengths of vinyl ester composites reinforced with various types of woven fabric are presented in Table 2. Based on the comparison for specific flexural strength of the composites in Table 2, vinyl ester composite reinforced with woven carbon fabric showed a remarkable 193% increase in specific flexural strength compared to that of the neat vinyl ester resin. The increasing trend in specific flexural strength is then followed by woven basalt and woven glass fabric-reinforced vinyl ester composites, respectively. It is understood that carbon fibers are known as excellent reinforcing materials with good specific strength and specific moduli in both compression and tensile,[10] which are the major reasons for woven carbon fabric-reinforced composites having a tendency to outperform glass and basalt-reinforced composites in terms of flexural strength.

In the case of the woven basalt, which showed improved specific flexural strength over woven glass fabric-reinforced composites, it is reported that basalt fibers have better compressive strength than glass fibers, while glass fibers have better tensile strength compared to basalt fibers.[11] According to Mingchao et al.,[11] specimens under flexural testing have complex stress states. The upper side of the specimen bears compressive stress and the lower side of the specimen bears tensile stress. Thus, flexural strength is contributed by both tensile and compressive strengths. Inasmuch as the flexural strength of the composites reinforced with fibers is predominantly governed by compressive strength than by the contribution of variations in tensile strength,[12] the composites reinforced with woven basalt fabric exhibited better specific flexural strength than that of woven glass fabric-reinforced composites. This finding is in accordance with works conducted by Liu et al.[4] and Mingchao et al.,[11] where composites reinforced with basalt fibers showed higher compressive strength and low tensile strength than composites reinforced with glass fibers and vice versa.

It is noted that the addition of 5 wt% of PHMS fillers had improved the specific flexural strength for vinyl ester composites reinforced with woven glass fabric and woven basalt fabric. The improved flexural strength with the addition of 5 wt% PHMS is attributed to the increase in plastic deformation of the matrix. According to Wouterson et al.,[13,14] PHMS fillers that are embedded in the matrix have the ability to facilitate enhanced plastic deformation of the matrix. In addition, the stress-strain curves of the woven fabric-reinforced composites for all types of fibers in Figure 1 proved that the incorporation of the 5 wt% PHMS fillers into the composites had slightly increased the strain of the composites.

It can be observed from Figure 1 that all stress-strain curves of the reinforced vinyl ester composites showed linearity before reaching the maximum stress. The vinyl ester composite reinforced with woven carbon fabric

Table 2. Comparison for specific flexural strength, specific flexural modulus, and specific impact strength of vinyl ester composites reinforced with glass, basalt, and carbon woven fabric with the addition of 5 wt% PHMS fillers

Sample	Specific flexural strength (MPa cm^3/g)	Specific flexural modulus (GPa cm^3/g)	Specific impact strength (J.m/kg)
Neat VE	63.75	3.07	5.47
VE/glass/PHMS 0%	93.04	5.72	68.17
VE/glass/PHMS 5%	117.60	5.50	92.89
VE/basalt/PHMS 0%	154.50	8.49	65.66
VE/basalt/PHMS 5%	131.67	6.44	117.01
VE/carbon/PHMS 0%	186.85	25.80	57.55
VE/carbon/PHMS 5%	148.30	17.05	54.06

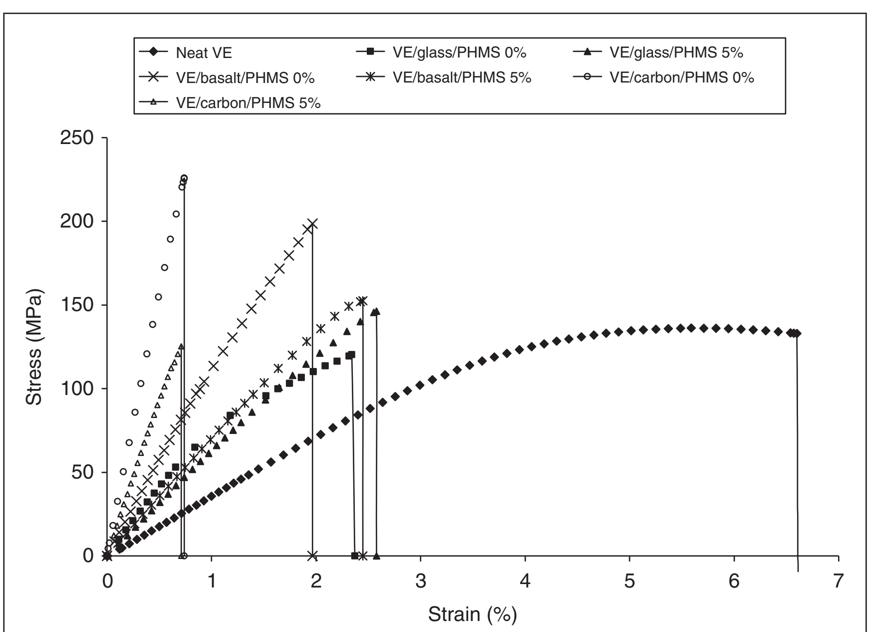

Figure 1. Stress-strain curves of neat vinyl ester, woven fabric reinforced vinyl ester composites, and PHMS-filled woven fabric reinforced vinyl ester composites.

had reduced strain, but had an increase in the failure stress of the composites compared to vinyl ester composites reinforced with woven glass and basalt fabric. The larger strain and lower initial slope of the stress-strain curves of the woven fabric-reinforced vinyl ester composites added with PHMS fillers suggest that the inclusion of PHMS fillers had caused improved ductile behavior of the composites.

Table 2 also shows the variations in the moduli of woven fabric-reinforced vinyl ester composites as a function of different types of fibers. The trend of enhancement in specific flexural modulus is similar with the trend shown in specific flexural strengths in Table 2, where the increment of modulus was in the order of carbon > basalt > glass reinforced vinyl ester composites. The woven carbon fabric-reinforced vinyl ester composites showed the highest modulus value of all composites. The high modulus of carbon fibers naturally gives rise to higher modulus of the woven carbon fiber-reinforced vinyl ester composites than that of composites reinforced with glass and basalt fibers. Previous works have suggested that the modulus of the composites is significantly influenced correspondingly by the modulus of reinforcing fibers used.[3,10,12] The same findings were obtained in research where the composites reinforced with carbon fibers showed higher modulus compared to glass fiber-reinforced composites.

On the other hand, the woven basalt fabric-reinforced vinyl ester composites showed only a slight increment in modulus than the woven glass fabric-reinforced vinyl ester composites. This is due to the fact that basalt and glass fibers are both silicates; thus, the modulus values are relatively similar. The basalt fiber, however, was slightly different from the glass fiber owing to crystalline structures that occurred in the basalt fiber, resulting from various conditions of the lava flow which, in turn, gave a slight improvement in the modulus of basalt fibers than that of the glass fibers. This was also proved by Deak et al.[15] in their work, where they reported that the moduli of continuous basalt fiber and glass fiber were comparable.

It can be seen from Table 2 that the modulus decreased for all types of woven fabric-reinforced vinyl ester composites upon the addition of PHMS fillers. The decrease in the modulus is believed to be due to the presence of porosity in the resin. Addition of particulate fillers in VE resin results in high resin viscosity which creates difficulty in mixing of the resin during processing hence increasing the amount of trapped gases in the resin. Increasing the porosity of the composites by incorporating hollow microspheres in the resin matrix is also observed by Palumbo et al.[16] due to the mechanical destruction of the microspheres during the composites processing.

Impact properties. The results of the impact test of composites reinforced with all three types of woven fabrics are summarized in Table 2. It was observed that there was a significant increase in specific impact strengths for woven glass- and basalt fabric-reinforced vinyl ester composites owing to the inclusion of PHMS. According to Siriwardena et al.,[17] the toughness of a filled material may either increase or decrease depending on the nature of the fillers. The increment in specific impact strength was due to the increase in toughness of the vinyl ester matrix, which was attributed to the toughening mechanisms induced by the PHMS fillers embedded in the matrix. Moreover, based on the SEM observations in Figure 2, the PHMS were able to experience ductile deformations under subjection of load, which is believed to provide better toughening effect in the PHMS-filled composites. It was reported that the inclusion of ductile fillers such as elastomeric and low modulus thermoplastic particles into the matrix is a common method used to modify epoxy-based matrix to increase impact strength and improve the ductility of the matrix.[18] The particulate type of fillers was able to reduce the internal stress of the matrix and constrain crack propagations in the matrix.[19] According to Lee and Yee,[20] there are three major types of micro-mechanical deformations occurring during the fracture process of thermosetting-filled composites, that is, the formation of step structures, debonding of the particulate glass beads, yielding of diffuse matrix shear, and micro-shear banding. These toughening mechanisms provide better energy absorption and resistance to crack propagations, hence results in improved impact strength. The SEM micrographs in Figure 2 represent the fracture surfaces of glass, basalt, and carbon woven fabric-reinforced vinyl ester composites filled with PHMS fillers. It is observed from Figure 2(a) that step structures are formed on the fracture surface of the composites filled with PHMS fillers. It is noted that the step structures were found to be dominant around the matrix surface that are embedded with PHMS fillers, indicating that the matrix has undergone enhanced plastic deformations owing to the inclusion of PHMS in the matrix. Furthermore, the step structures suggested that a very good bonding between PHMS fillers and the vinyl ester matrix exists. Figures 2(b), 2(c) and 2(d) show the deformed and fractured PHMS fillers in the matrix, which suggest that PHMS fillers also played the same role as that of the fibers in absorbing the impact energy applied to the composites. On the other hand, PHMS debonding and both PHMS and fiber fractures suggest that the impact energy was dissipated via the fractures and debonding of both types of reinforcements. There were also a few microspherical voids observed on the matrix surface, which resulted from the debonding of the PHMS. These voids

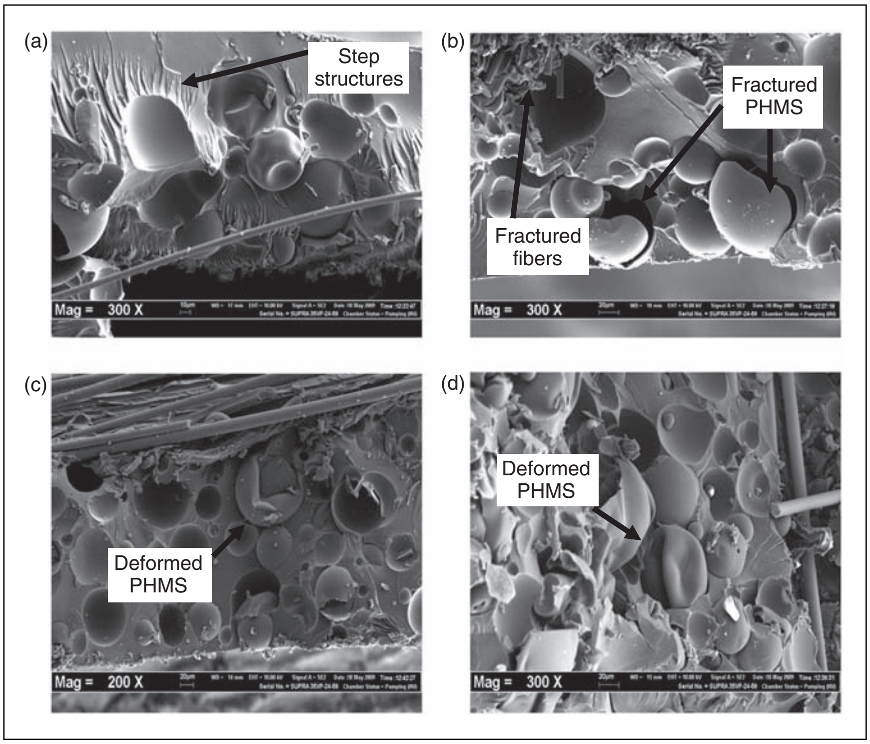

Figure 2. Various SEM micrographs of fractured surfaces of woven fabric reinforced vinyl ester composites with the incorporation of 5 wt% PHMS fillers (200× and 300× magnification).

Table 3. CTE and TGA values of neat vinyl ester, woven fabric reinforced vinyl ester composites, and PHMS-filled woven fabric reinforced vinyl ester composites

	CTE (ppm/°C)		TGA	
Sample	Above T_g	Below T_g	Initial degradation temperature (°C)	Residue (%)
Neat VE	75.9	71.8	340	9.3
VE/glass/PHMS 0%	23.7	24.6	360	42.4
VE/glass/PHMS 5%	16.4	17.3	310	38.6
VE/basalt/PHMS 0%	15.7	16.7	350	37.2
VE/basalt/PHMS 5%	15.8	16.2	330	53.4
VE/carbon/PHMS 0%	5.0	5.4	350	29.5
VE/carbon/PHMS 5%	6.9	7.0	330	48.2

prevented crack growth via crack blunting, thus enhancing the toughness of the matrix.[21]

Coefficient of thermal expansion. Coefficient of thermal expansion (CTE) is an important parameter used to define the dimensional stability of a material in response to temperature changes. CTE values are crucial in designing parts to prevent the mismatch of materials during heat exposure. According to Mottram et al.,[22] the thermal expansion behavior of any fiber-reinforced polymer composite can be influenced by many factors, such as the type of resin used, fiber-wetting characteristics, volume fraction of constituents, residual thermal stress state, moisture absorption, thermal history, and relative modulus of the constituents, as well as fabrication parameters. The dilatometric tests are carried out at the temperature range of 25–165°C to obtain information on the dimensional stability of the composites under temperature before reaching glass transition temperature (T_g) and points beyond T_g.

Based on the CTE values listed in Table 3, the neat vinyl ester decreased when woven fibers were incorporated into the resin. Reduction in CTE values of the composites can be attributed to the wide gap of difference in the expansion behaviors of the fibers and the vinyl ester matrix. The decrease in CTE values of the composites is expected because glass, basalt, and carbon fibers are known to have low CTE values (refer to Table 1) compared to the vinyl ester matrix owing to the rigidity of these fibers; hence, drastically decreasing the CTE values of the woven fabric-reinforced vinyl ester composites.[23] The incorporation of carbon fiber into the vinyl ester resin showed a pronounced effect where it reduced the CTE of the vinyl ester resin by 92% when the CTE for neat vinyl ester reduced from 71.85 ppm/°C to 7.05 ppm/°C below the glass transition temperature. A further decrease in CTE values of all woven fabric-reinforced vinyl ester composites was observed upon the inclusion of PHMS fillers into the composites. This is believed to be caused by the fact that particulate PHMS fillers had occupied most of the free volumes in the composites, thus restricting the polymer molecular chains movements in the matrix when the composites were subjected to heat.

Thermogravimetric analysis. TGA experimental results for woven fabric-reinforced vinyl ester composites and woven fabric-reinforced vinyl ester composites filled with PHMS fillers are summarized in Table 3 and Figure 3. The data presented in Table 3 are the TGA analysis of the initial degradation temperature of weight loss for the all the composites obtained at a heating rate of 10°C/min. The initial degradation temperature was measured by the temperature at 5% degradation. The initial degradation temperature of vinyl ester was found to increase with the presence of the woven fiber reinforcement in the matrix than with the neat vinyl ester. This is attributed to the good thermal stability of the fibers. According to Vanaja et al.,[24] the thermal stability of a composite is governed by the matrix, as well as the individual reinforcement constituents of the composite. The reinforcing material, especially fibers, is generally known to be quite thermally stable and temperature-resistant,[25] and is often used in applications at elevated temperatures. It is noted that the dramatic improvement in thermal stability of the vinyl ester composites was contributed by the glass fibers. Meanwhile, the vinyl ester reinforced with woven carbon fiber was found to be low in thermal stability owing to the fact that carbon fiber is thermally less stable by nature.[25] On the other hand, the lower thermal stability of the basalt fiber-reinforced vinyl ester composites is related to the tendency of the basalt fiber to undergo a gradual crystallization during exposures to high temperature, which never occurs in glass fiber.[6,26] The gradual crystallization occurred because of the difference in crystallization temperatures of various structural components in basalt fiber, namely, plagioclase, magnetite, and pyroxene, which varied in the range of 720°C–1010°C.[27] In addition, Cerny et al.[6] and Glogar et al.[28] reported that there are changes observed in the shape of basalt fibers when exposed to heat, where the originally circular

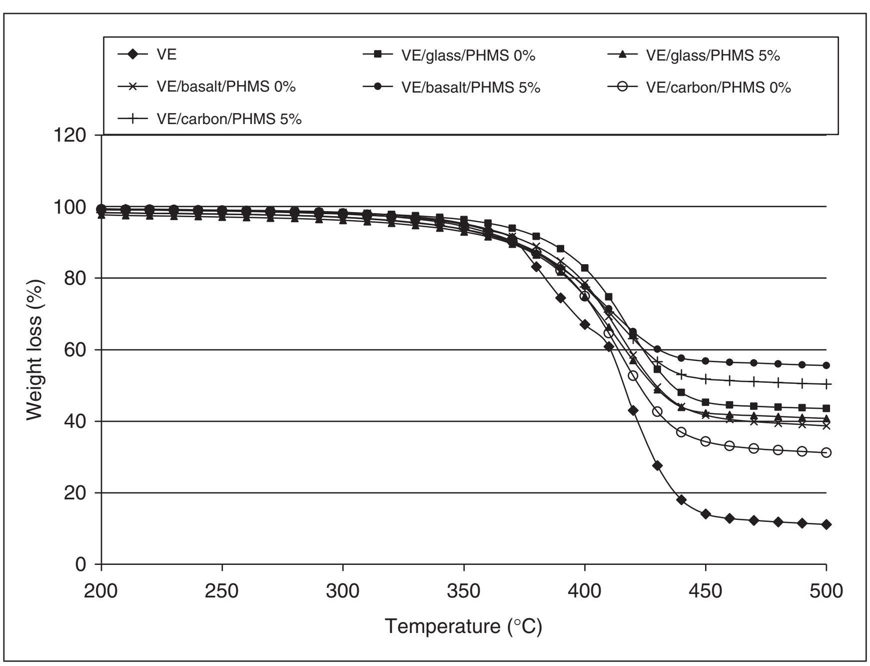

Figure 3. Thermogravimetric analysis of neat vinyl ester, woven fabric reinforced vinyl ester composites, and PHMS-filled woven fabric reinforced vinyl ester composites.

shape of the basalt fiber was found to be plastically distorted. These authors suggested that the change in the shape of the fiber was due to the basalt fibers being highly susceptible to softening at high temperature, which influenced their thermal stability.

The thermal degradation behavior of composites filled with PHMS fillers for glass, basalt, and carbon-reinforced vinyl ester composites were similar when a significant drop of degradation temperature was observed compared to that of the unfilled woven-reinforced vinyl ester composites. The decrease in thermal stability of the PHMS -filled composites was believed to be due to the tendency of the PHMS fillers to act as an ablative material when exposed to extreme heat (www.phenoset.com). This is due to the inevitable nature of phenol formaldehyde resin, the main component of PHMS fillers, to decompose at high temperatures.[29]

During the exposure of the PHMS-filled composites to the high thermal environment, the PHMS fillers absorbed the heat by increasing their internal temperature, which resulted in changes in the chemical and physical structures of the PHMS fillers. The absorbed heat was then dissipated from the structure via a mass loss. This char ablation process is a mechanism to protect critical structures from intense heat via loss of mass. The degradation reaction that occurred during the whole ablation process produce chars, which developed in the temperature range of 250–600°C. The chars with porous structures act as the thermal barrier to prevent heat diffusion, at the same time reducing further oxygen diffusion to eliminate undesirable exothermic degradation reaction of the matrix.[30] Judging from the residue values of all PHMS-filled composites as listed in Table 3, the significant increase in the residue of the composites at 600°C can be related to the mass amount of char yields during the decomposition of the PHMS fillers.

Conclusions

The present study examined the specific flexural properties, specific impact strength, and thermal properties of the vinyl ester composites reinforced with woven glass, basalt, and carbon fibers. The effects of the inclusion of PHMS fillers into the composites were also analyzed. The observations of this study are as follows:

1. The flexural and impact properties of the woven fabric-reinforced vinyl ester composites are mostly dominated by the inherent properties of the constituent fiber itself, whereas the inclusion of the PHMS fillers has contributed to enhanced plastic deformation of the vinyl ester matrix.
2. The woven fibers have served as stress bearers when the composites were subjected to load. Several toughening mechanisms of the fibers and PHMS fillers, such as step structures, fiber, and PHMS debonding/fractures, were observed via SEM micrographs.
3. The thermal stability of the woven fabric-reinforced vinyl ester composites was governed mainly by the thermal properties of the fibers used. A decrease in thermal stability was found with the inclusion of PHMS fillers into the composites owing to the tendency of the PHMS fillers to undergo ablation process when subjected to intense heat.

Acknowledgements

The Authors are grateful to Universiti Sains Malaysia for awarding them a research grant (USM-RU-PGRS; grant no. 8032031), which made this study possible. The authors also wish to express their thanks to Kamenny Vek, Russia for providing the Basalt fabric.

References

1. Ahmed KS and Vijayarangan S. Tensile, flexural and interlaminar shear properties of woven jute and jute-glass fabric reinforced polyester composites. *J Mater Process Technol* 2008; 207: 330–335.
2. Chowdhury FH, Hosur MV and Jeelani S. Investigations on the thermal and flexural properties of plain weave carbon/epoxy-nanoclay composites by hand-layup technique. *J Mater Sci* 2007; 42: 2690–2700.
3. Ratna D. Toughened FRP composites reinforced with glass and carbon fiber. *Composites: Part A* 2008; 39: 462–469.
4. Liu Q, Shaw MT and Parnas RS. Investigation of basalt fiber composite mechanical properties for applications in transportation. *Polym Compos* 2006; 27: 41–48.
5. Adanur S and Onal L. Factors affecting the mechanical properties of laminated glass-graphite epoxy hybrid composites. *J Ind Text* 2001; 31: 123–133.
6. Cerny M, Glogar P and Sucharda Z. Mechanical properties of basalt fiber reinforced composites prepared by partial pyrolysis of a polymer precursor. *J Compos Mater* 2009; 43: 1109–1120.
7. Chandradass J, Kumar MR and Velmurugan R. Effect of clay dispersion on mechanical, thermal and vibration properties of glass fiber- reinforced vinyl ester composites. *J Reinf Plast Compos* 2008; 27: 1585–1601.
8. Papa E, Corigliano A and Rizzi E. Mechanical behaviour of a syntactic foam/glass fibre composite sandwich: Experimental results. *Struct Eng Mech* 2001; 12(2): 169–188.
9. Palumbo M and Tempesti E. Fiber-reinforced syntactic foams as a new lightweight structural three-phase composite. *Appl Compos Mater* 2001; 8: 343–359.
10. Shivakumar KN, Swaminathan G and Sharpe M. Carbon/vinyl ester composites for enhanced performance in marine applications. *J Reinf Plast Compos* 2006; 25: 1101–1116.

11. Mingchao W, Zuoguang Z, Yubin L, Min L and Zhijie S. Chemical durability and mechanical properties of alkali-proof basalt fiber and its reinforced epoxy composites. *J Reinf Plast Compos* 2008; 27: 393–407.
12. Cecen V, Sarikanat M, Yildiz H and Tavman IH. Comparison of mechanical properties of epoxy composites reinforced with stitched glass and carbon fabrics: Characterization of mechanical anisotropy in composites and investigation on the interaction between fiber and epoxy matrix. *Polym Compos* 2008; 29: 840–853.
13. Wouterson EM, Boey FYC, Hu X and Wong SC. Specific properties and fracture toughness foam: Effect of foam microstructures. *Compos Sci Technol* 2005; 65: 1840–1850.
14. Wouterson EM, Boey FYC, Hu X and Wong SC. Effect of fiber reinforcement on the tensile, fracture, and thermal properties of syntactic foam. *Polym* 2007; 48: 3183–3191.
15. Deak T and Czigany T. Chemical composition and mechanical properties of basalt and glass fibers: A comparison. *Text Res J* 2009; 79: 645–651.
16. Palumbo M, Donzella G, Tempesti E and Ferruti P. On the compressive elasticity of epoxy resins filled with hollow glass microspheres. *J Appl Polym Sci* 1996; 60: 47–53.
17. Siriwaredena S, Ismail H, Ishiaku US and Perera MCS. Mechanical and morphological properties of white rice husk ash filled polypropylene/ethylene-propylene-diene terpolymer thermoplastic elastomer composites. *J Appl Polym Sci* 2002; 85: 438–453.
18. Ambrogi V, Cosco S, Carfagna C, Cicala G, Oliveri L and Recca A. Comparison of the effect of epoxy microspheres on the thermomechanical and rheological properties of an epoxy resin system. *Polym Eng Sci* 2006; 46: 1739–1747.
19. Maharsia RR and Jero HD. Enhancing tensile strength and toughness in syntactic foams through nanoclay reinforcement. *Mater Sci Eng, A* 2007; 454–455: 416–422.
20. Lee J and Yee AF. Inorganic particle toughening I: Micro-mechanical deformations in the fracture of glass bead filled epoxies. *Polym* 2001; 42: 577–588.
21. Pritchard G and Yang Q. Microscopy of impact damage in particulate-filled glass-epoxy laminates. *J Mater Sci* 1994; 29: 5047–5053.
22. Mottram JT, Geary B and Taylor R. Thermal expansion of phenolic resin and phenolic-fibre composites. *J Mater Sci* 1992; 27: 5015–5026.
23. Nakagaito AN and Yano H. The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on microfibrillated cellulose. *Cellulose* 2008; 15: 555–559.
24. Vanaja A and Rao RMVGK. Fibre fraction effects on thermal degradation behaviour of GFRP, CFRP and hybrid composites. *J Reinf Plast Compos* 2002; 21: 1389–1398.
25. Cao S, Woo Z and Wang X. Tensile properties of CFRP and Hybrid FRP composites at elevated temperatures. *J Compos Mater* 2009; 43: 315–330.
26. Militky J, Kovacic V and Bajzik V. Mechanical properties of basalt filaments. *Fibres Text East Eur* 2007; 15: 64–65.
27. Saravanan D. Spinning the rocks – basalt fibres. *IE (I) Journal-TX* 2006; 86: 39–45.
28. Glogar P, Sucharda Z, Eerny M, Puchegger S and Peterlik H. Microstructures and mechanical properties of heat resistant composites reinforced with basalt fibers. *Ceram-Silik* 2007; 51(4): 190–197.
29. Haiyun J, Jigang W, Zhichao D and Fan L. Study on the microstructure evolution of phenol-formaldehyde resin modified by ceramic additive. *Front Mater Sci Chin* 2007; 1(1): 35–39.
30. Torre L, Kenny JM, Boghetich G and Maffezzoli A. Degradation behaviour of a composite material for thermal protection systems. Part III char characterization. *J Mater Sci* 2000; 35: 4563–4566.