Thermal Properties of Calcium Carbonate Powder Reinforced Vinyl Ester Composites: Pilot Study

Harry Ku,[1,2] Francisco Cardona,[1,2] Mustapha Jamal Eddine[1,2]

[1]Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland 4350, Australia
[2]Centre of Excellence in Engineered Fibre Composites, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

Correspondence to: H. Ku (E-mail: ku@usq.edu.au)

ABSTRACT: The viscoelastic properties of vinyl ester (VE) composites filled with calcium carbonate (CC) ($CaCO_3$) powder have been evaluated using the dynamic mechanical analysis (DMA) technique. It was found that irrespective of the percentage by weight of $CaCO_3$ powder, the VE composites postcured in an oven up to 60°C have higher glass transition temperatures (T_g) and storage modulus than their counterparts cured at ambient conditions. However, the loss moduli were lower for composites postcured in an oven than their ambient cured counterparts. It was also found that the crosslinking density of the composites slightly increased with particulate ($CaCO_3$) loading and composites postcured in an oven have higher crosslinking density than their counterparts cured at ambient conditions. These results confirmed an increase in stiffness for composites with postcuring treatment. Micrographs by SEM were obtained and confirmed a close inter phase adhesion of the CC filler with the VE resin matrix in the composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The popularity of the composite materials is expected to grow exponentially since composite materials still offer numerous new possible applications. Composites materials have several advantages over traditional metal and alloy-based structures. As compared to these traditional structures, composites encompass superior strength-to-weight ratios, lower maintenance requirements and greater corrosion resistance. Moreover, composites exhibit a higher strength to weight ratio than steel or aluminum and can be engineered to provide a wide range of tensile, flexural, fracture, and impact strength properties. For example, a composite's strength per unit density is roughly two times that of aluminium and four times that of steel. However, while composites offer significant potential for application in civil engineering structures, their acceptance into this industry continues to be discouraging due to their expensive manufacturing cost relative to the traditional building materials. Furthermore, composites are difficult to repair since most composites use thermoset matrices that cannot be reshaped.[1]

Nevertheless, with increased demand and applications for composites, pressure is being placed on developing less expensive composites with superior or comparable material properties. To make the composite more cost effective, cheap fillers are being used. Additionally, cost can be reduced further by improving the manufacturing techniques. The Centre for Excellence in Engineered Fiber Composites (CEEFC) at the USQ seeks to facilitate the development and introduction of lightweight composite materials into engineering commercial applications. Although there are many different types of resin in use in the composite industry, the majority of structural parts are made with three main types, namely polyester, vinyl ester (VE), and epoxy. The mechanical properties of polyester resins are inferior when compared with epoxy resins, which are very expensive. Vinyl ester resins are the compromised of the two types of resins. VE resins are similar in their molecular structure to polyesters, but differ primarily in the location of their reactive sites, these being positioned only at the ends of the molecular chains. As the whole length of the molecular chain is available to absorb shock loadings this makes VE resins tougher and more resilient than polyesters.[2]

The VE molecule also features fewer ester groups. These ester groups are susceptible to water degradation by hydrolysis, which means that VEs exhibit better resistance to water and many
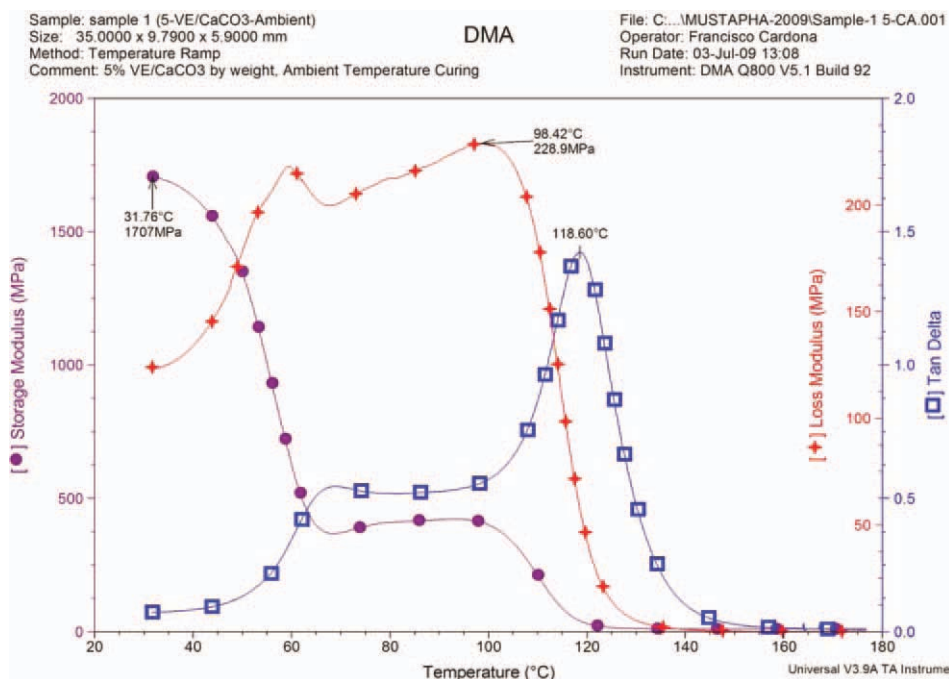
Figure 1. DMA results of vinyl ester reinforced with 5% by weight of calcium carbonate powder cured in ambient conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other chemicals than their polyester counterparts, and are frequently found in applications such as pipelines and chemical storage tanks. The material is therefore sometimes used as a barrier or 'skin' coat for a polyester laminate that is to be immersed in water, such as in a boat hull. The cured molecular structure of the VE tends to be tougher than polyester, although to really achieve these properties the resin usually needs to post-cured at elevated temperatures.[2] This is why the specimens were postcured in oven at elevated temperatures in three stages.

The main industrial use of calcium carbonate (CC) is in the construction industry, either as a building material in its own right e.g., marble or limestone aggregate for road building or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln. CC is also widely used as filler in plastics.[3,4] CC is referred as precipitated calcium carbonate (PCC) in industry.[5]

Ground CC is widely used in thermoset applications. It is a key extender in fiberglass reinforced polyester applications such as sheet molding compound (SMC) and bulk molding compound (BMC) where it functions as a cost-effective extender with no adverse effects on processing or final physical properties. It is used for viscosity control, to limit shrinkage and as a coefficient of thermal expansion.[6]

Not much literature about CC filled VE composites could be found. Even when it did, it was about the chemical properties of CC filled vinyl ester composite. Only, Yusriah et al. made composites from VE reinforced woven glass fiber with two types of particulate fillers. The fillers used were CC and phenolic hollow microspheres (PHMS) and the extend of work was limited. As researchers, the authors would therefore like to study the thermal properties of CC

filled VE resin, with a view to reducing the cost of the composites, but at the same time maintaining their properties.

THE MATERIALS AND COMPOSITE SAMPLES

The CC powder used was manufactured by LabServ and supplied by Biolab, Australia. Its purity is 99% (assay 99.0%). The VE resin used is Hetron 922 PAW in winter. The VE is dissolved in 50% by weight in styrene monomer. It is based on the reaction between methacrylic acid and diglycidylether of bishphenol A. The VE resin catalyst ratio used in the experiment was 98% resin by volume and 2% catalyst by volume.[7] The catalyst used was MEKP (Butanox LA from AKZO NOVEL).

The reinforcement was CC powder ($CaCO_3$) and they were made 5 to 15% by weight in the cured VE composite, VE/GP (X%), where X is the percentage by weight of the filler. As the raw materials of the composites are liquid and powder, the specimens of $60 \times 4 \times 10$ mm^3 were cast to shape. The resin is a colorless liquid and is first mixed with the colorless accelerator. After that the CC powder was added to the mixture and they were then mixed to give the uncured composite.

After initial 24 h curing, half of the test pieces were removed from the mold and their thermal properties were measured using dynamic mechanical analysis (DMA) technique. The other half of the samples were in an oven. The postcuring temperatures and times in the oven were:

- 16 h at 40°C
- 16 h at 50°C
- 8 h at 60°C

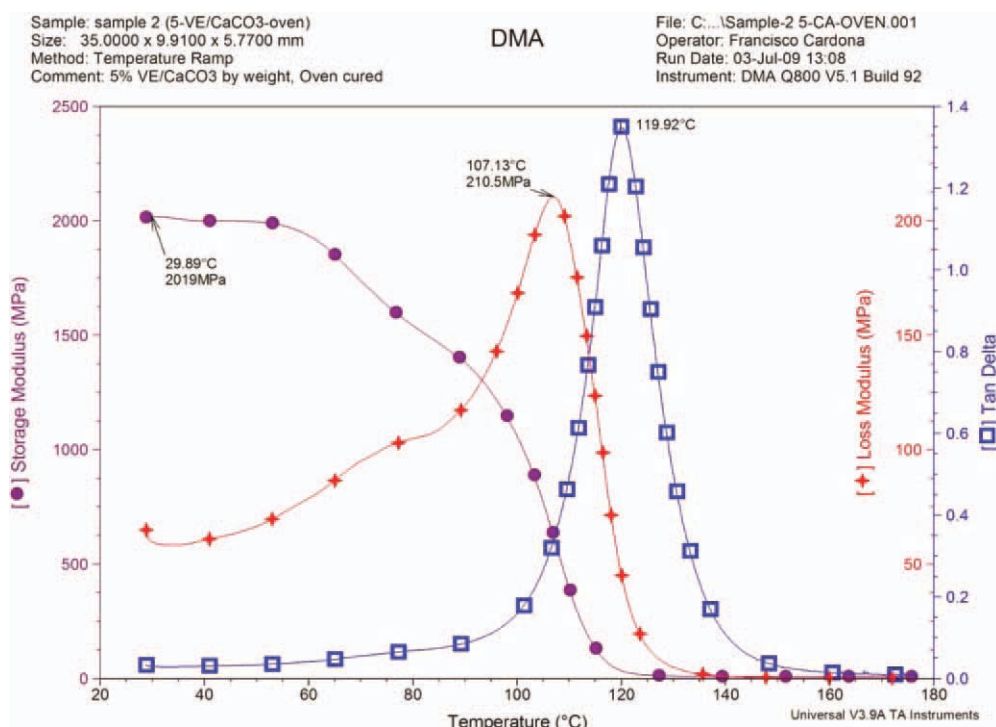The thermal properties of the specimens were then measured.

Figure 2. DMA results of vinylester reinforced with 5% by weight of calcium carbonate powder cured an oven. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Mechanical Analysis

In this work a Q800 DMA Model from TA Instruments was used. A dual cantilever probe with a frequency of 1 Hz, a displacement of 15 microns and a heating rate of 3°C/min were applied. The analysis was conducted from 20 to 180°C. UNIVERSAL ANALYSIS 2000 software was used to carry out the calculations. From these experiments, graphs of tangent delta loss and storage modulus were produced.

RESULTS AND DISCUSSIONS

Figures 1 and 2 illustrate the DMA results of VE samples reinforced with 5% by weight of CC powder cured in ambient conditions, and in ambient conditions plus postcured in an oven, respectively. These figures show that the glass transition temperatures for samples cured in ambient conditions and in ambient conditions plus postcured in an oven are 118.60 and 119.92°C, respectively. From the figures, the maximum storage and loss moduli of them are 1707 and 228.9 MPa, respectively for the ambient cured specimen and 2019 and 210 MPa, respectively for the ambient plus postcured specimen.

The glass transition temperature for the ambient plus oven postcured specimen is slightly higher than that of its counterpart. This means that, the ambient plus oven postcured specimen will change from hard and brittle to soft and pliable at a temperature higher than that of the ambient cured specimen, i.e., higher stiffness. The storage modulus of the specimen postcured in an oven was 2019 MPa and that of cured in ambient conditions was 1707. This shows that the postcured sample is able to store more energy than its counterpart, i.e., higher stiffness.

Furthermore, the loss modulus of the postcured sample is lower than that of its counterpart. Low loss moduli yields stiff material, therefore postcured sample is stiffer than ambient cured sample. In conclusion, the glass transition temperature, storage modulus, and loss modulus support the fact that postcured sample is stiffer than its counterpart because of higher degree of curing.

From Figures 1 and 2, it is worth noting that the results for both specimens have similar trends in both storage modulus and glass transition curves. This indicates that post curing do not change the viscoelastic properties of the composite significantly. Ku et al. studied the thermal properties of epoxy composites filled with 5 wt % of glass powder and phenolic composites filled with 5 wt % of SLG (ceramic hollow spheres), respectively and discovered the same behaviors for the materials studied.[7,8]

Table I summarizes all the results obtained from the DMA measurements. It can be found that for both the ambient cured and postcured samples, composites with higher particulate loadings had higher glass transition temperatures. The values for the glass transition temperature for all the samples were found to be around 120°C. The stiffness of the samples can be argued to increase with increasing wt % of CC powder. In addition, the glass transition temperatures of composites postcured in an oven were higher than their rivals. This means that the postcured samples were stiffer than their counterparts.

It was also observed that the maximum storage modulus increased with increasing filler content for samples cured in an oven as shown in Table I. This is logical as it follows the simple "rules of mixture." However, the maximum storage modulus of samples cured in ambient conditions did not have a trend and

Table I. DMA Results for All the Samples with Different Curing Method and Filler Percentages

Curing method	CaCO$_3$ (wt %)	Glass transition temperature (°C)	Maximum storage modulus (MPa)	Maximum loss modulus (MPa)	Crosslink density (mol/cm^3)
Ambient	5%	118.6	1707	228.9	2.512 × 10^{-3}
Ambient	10%	118.81	1570	177.3	2.263 × 10^{-3}
Ambient	15%	119.55	1580	179.0	2.967 × 10^{-3}
Ambient plus oven	5%	119.92	2019	210.5	2.231 × 10^{-3}
Ambient plus oven	10%	120.94	2105	187.7	2.408 × 10^{-3}
Ambient plus oven	15%	121.3	2257	223.9	2.670 × 10^{-3}

this may be because of the aggregation of the CC powder in the polymer matrix. However, the glass transition temperature of both types of composites increased with particulate loading as depicted in Table I. It was also found that the crosslinking density of samples cured in an oven had the same trend and behavior of the maximum storage modulus and glass transition temperature. The crosslinking density had been estimated using the following equation: $G'' = \Phi v R T$[9] in which G'' is the storage modulus at $T_g + 40$°C; Φ is the front factor and is unity in this case; R is the gas constant and v is the crosslink density. The crosslink density has been calculated from the rubber elasticity theory as: $d = E/3RT$, where E is the elastic modulus as measured by the storage modulus value at a temperature of $T_g + 50$°C, and because this E value is measured well above the T_g value of the resin then the effect of the filler present in the composite on the actual value of the modulus is negligible. This is due to the fact that at a temperature well above the T_g of the resin of the composites, the interaction and stress transfer between the matrix and the filler and/or reinforcement is minimum due to the high molecular mobility of the resin. The results indicated that the crosslink density of the VE/CaCO$_3$ composites samples cured in an oven increased with increasing CaCO$_3$ powder content. This is in line with the behavior of their maximum storage modulus and glass transition temperature. This indicates that samples cured in an oven are stiffer than their counterparts cured under ambient conditions. This is due to the higher particulate loading and crosslink density of the VE/CaCO$_3$ composites cured in the oven in comparison with the samples cured at room temperature. However, the crosslink density of the VE/CaCO$_3$ composites cured at ambient conditions did not have a clear trend and this may be due to the fact of being cured at room temperature without any additional postcuring treatment. Further studies will be required to fully clarify this thermal-related effect on the viscoelastic properties of the composites.

Scanning electron microscopy (SEM) was also employed to analyze the failure modes of the specimens and it was found that the fractured surfaces examined were correlated with the fracture toughness.[10] Figure 3 shows that the CaCO$_3$ particles were well distributed in the VE matrix but different sizes of CaCO$_3$ aggregated particles also appeared in a composite sample with 25 wt % of filler. The mixture of the filler and the polymer matrix was not good enough so the fracture toughness of the composites were lower than that of the neat resin. Figure 4 illustrates the SEM image of neat epoxy resin postcured for a total

of 40 h at 40, 50, and 60°C, respectively at a magnification of 200 times. Faint striations followed by a 'turbulent flow' can be found in the fractured surface of the neat resin. This shows that plastic deformation had taken place in the resin. The second SEM image (Figure 5) was for 35 wt % of CaCO$_3$ filled composite, which had the highest fracture toughness value except the neat resin. It can be found that the patches of CaCO$_3$ powder served as second phase to strengthen the composite.[10] The filler mixed with the resin better at lower wt % of filler and there was only one phase in the system but there were voids and was weaker as depicted in Figure 6 (25 wt % of CaCO$_3$ powder), which had the lowest fracture toughness value.

Yusriah et al. made composites from VE reinforced woven glass fiber with two types of particulate fillers. The fillers used were CC and phenolic hollow microspheres (PHMS), which were varied from 1, 3, and 5 wt %. "The loss tangent, tan δ peak (glass transition temperature) for neat VE resin was high when compared with the tan δ peaks for woven-fabric-glass fiber-reinforced composites and both CC- and PHMS-filled VE and woven glass fiber composites." However, the tan δ peaks or glass transition temperatures for all composites were more or less the same. "The addition of glass fiber and particulate fillers had reduced the glass transition temperature, T_g of the composite
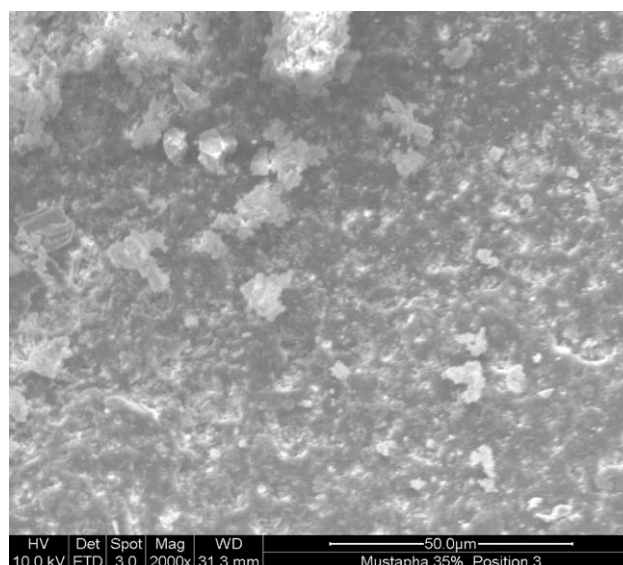
Figure 3. Different sizes of CaCO$_3$ aggregated particles in vinyl ester composite with 25 wt % of filler, 2000×.
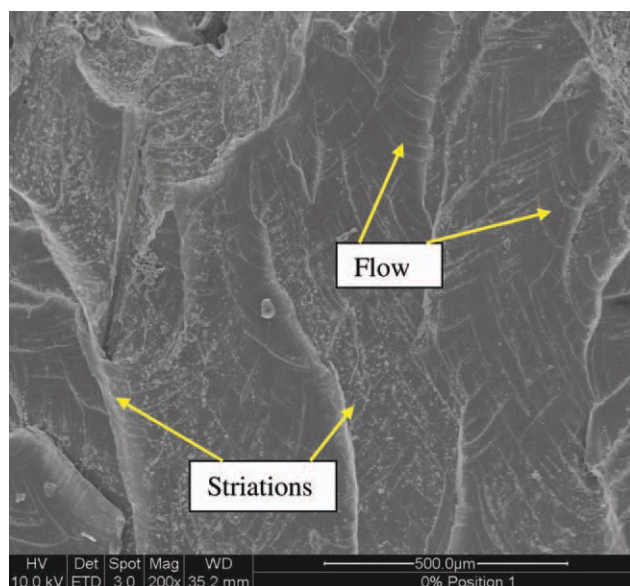
Figure 4. The fractured surface of neat vinyl ester resin, illustrating striations followed by a turbulent flow pattern of the fractured zone, 200×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

systems. This was believed to attribute to the increase in free volume of the composites, which was influenced by the increase in the void contents of the CC and PHMS filled VE composites."[11] The results of this study were the same as the glass transition temperatures of the CaCO$_3$ powder composites were more or less the same as depicted in Table I.

Yusriah et al. also found that "the storage modulus value had increased with the incorporation of the fillers into the woven
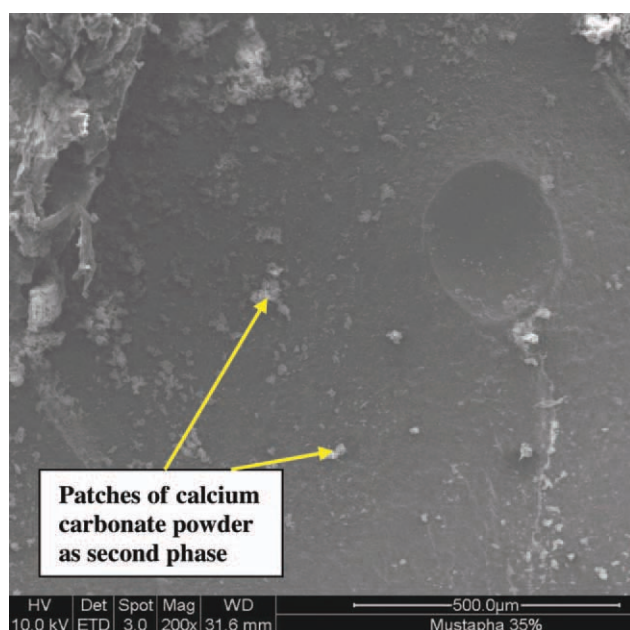

Figure 5. The fractured surface of 35 wt % calcium carbonate powder filled vinyl ester composite, 200×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. The fractured surface of 25 wt % calcium carbonate powder filled vinyl ester composite, 200×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

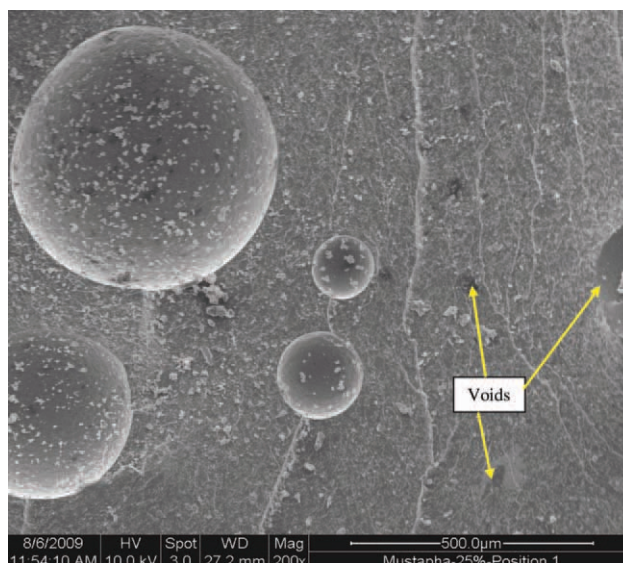fabric glass fiber composite system. This was due to the reinforcement imparted by the particulate fillers that allowed greater stress transfer at the matrix–fillers interface. The storage modulus value for composites filled with 5 wt % CC fillers is higher than that of the PHMS filled composites of the same fillers content. This is because CC fillers are more rigid and stiffer than the PHMS fillers."[11] All these matched the storage modulus and loss modulus results of this study aforementioned.

Zuo et al. prepared composites by blending wheat gluten (WG) as matrix, CC as filler, and glycerol as plasticizer. The mixture was then molded by compression molding at 120°C to crosslink the WG matrix. Glycerol was added as plasticizer to depress glass transition temperature and reduce intermolecular forces. Morphology observation showed that the CaCO$_3$ particles were finely dispersed in matrix. They claimed that the addition of up to 10 wt % CaCO$_3$ into the composites caused the Young's modulus and tensile strength of the samples to increase markedly. They also found that "introduction CaCO$_3$ particle in the samples cause a gradual improvement of the strain-hardening behavior, and introduce additional physical crosslinking sites in the matrix. The results demonstrated that incorporation of CaCO$_3$ particles was a straightforward way to prepare WG composites with improved strength."[12] The results of fracture toughness of CaCO$_3$ powder filled VE composites studied by the authors were not in line with this as the matrix of the polymer was different.[11] However, it can be argued that if tensile properties of the composites were sought after, the results might be the same with the results of Zuo et al.

Li et al. also made composites of poly(propylene carbonate) (PPC) reinforced with CC particles, using the same techniques of Zuo et al. as described above. They found that "tensile strength, stiffness, and ductility of the composites increased with increasing contents of CC particles. This improvement in the tensile properties was attributed to good interfacial adhesion

between the fillers and matrix."[13] These tensile property results were in line with those found by Zuo et al. They also found that the addition of "CC particles into PPC resulted in a slight improvement in its thermooxidative stability."[13]

CONCLUSIONS

The viscoelastic properties of CC/VE composites were investigated and established. This study evaluated the relationship between the glass transition temperature, storage modulus, and loss modulus, of the composites, versus the percentage loading of the filler. It was observed that the glass transition temperature (T_g) of the composites cured in an oven (up to 60°C) was higher than that of its counterpart cured only at ambient temperature. This result was observed at all loads of CC filler (from 5 to 15 wt %) investigated in this work. That is to say the stiffness of samples cured in an oven was higher than their ambient cured counterparts. The results of this study matched those of other studies made by Ku et al.[7,8] and Yusriah et al.[11]

REFERENCES

1. Barbero, E. J. Introduction to Composite Materials Design, 2nd ed.; CRC Press: Boca Raton, **1998.**

2. Agarwal, B. D.; Broutman, L. J.; Chandrasshekhara, K. Analysis and Performance of Fiber Composites, 3rd ed.; Wiley: NJ, **2006.**

3. Solvay Chemicals, Precipitated Calcium Carbonate, http://www.solvaychemicals.com/EN/products/pcc/default.aspx. viewed on 17 May **2011.**

4. Reade Advanced Materials, Calcium Carbonate http://www.guidechem.com/com-reade/pro-show304825.html. viewed on 17 May 2011.

5. Askeland, D. R. The Science and Engineering of Materials, 3rd ed.; Stanley Thornes: **1998.**

6. Huber, Thermoset Composites, undated, http://www.hubermaterials.com/products/calcium-carbonate/thermosets.aspx viewed on 17 May **2011.**

7. Ku, H.; Cardona, F.; Ball, J.; Jacobsen, W.; Trada, M. *J. Compos. Mater.* **2008,** *42,* 2083.

8. Ku, H.; Cardona, F.; Wong, P.; Huang, J.; Fung, H. *J. Reinf. Plast. Compos.,* to appear.

9. Ishida, H.; Allen, D. *J. Polym. Sci.: B, Polym. Phys.* **1996,** *34,* 1019.

10. Ku, H.; Jamal Eddine, M.; Trada, M. *J. Eng. Mater. Technol.* **2011,** submitted.

11. Yusriah, L.; Mariatti, M.; Abu Bakar, A. *J. Vinyl Addit. Technol.* **2010,** *16,* 98.

12. Zuo, M.; Lai, Z. Z.; Song, Y. H.; Zheng, Q. *Chin. Chem. Lett.* **2008,** *19,* 992.

13. Li, X. H.; Tjong, S. C.; Meng, Y. Z.; Zhu, Q. *J. Polym. Sci. B: Polym. Phys.* **2003,** *41,* 1806.