

Processing and Characterization Techniques for a Mica Filled Polymer Composite

Sarah Whipkey, Chance Roman, and Kevin Seay

Virginia Polytechnic Institute and State University, Department of Materials Science and Engineering, Blacksburg, VA 24061

Abstract

Mica particulates (filler) were combined with polymethyl methacrylate (matrix) to form a polymer matrix ceramic composite (PMCC). Mica concentrations in the range of 10-80 wt% mica with particulate sizes in the range of 53-212 μm were used. Dynamic mechanical analysis was used to conduct stress/strain tests on these composites in order to observe the resulting elastic moduli with varying mica particulate size and concentration. The elastic moduli showed an overall increase with increasing mica concentration in all but one tested particulate size, which exhibited a peak modulus at 60 wt% mica filler. Statistical analysis showed that both the mica concentration and mica particulate sizes were significant to the resulting elastic moduli, as well as the interaction between these two factors. Optical microscopy was used to observe the interface between the polymer matrix and mica particulates in order to determine the degree to which the two materials bonded to each other. It was observed that the PMMA and mica showed good bonding, meaning the formed materials were successfully combined into a cohesive composite.

Keywords: Polymer matrix ceramic composites (PMCC), muscovite mica, polymethyl methacrylate (PMMA), dynamic mechanical analysis (DMA).

1. Introduction

1.1 Background

Composite materials are an important sector of materials science, as the combination of constituents in a composite allows for a range of properties that would never be achievable from the individual components.¹ Polymers are often combined with a filler material, such as a ceramic, to increase their strength and hardness, and reduce the effect of temperature on their behavior.²

When designing a composite material, many factors must be considered in order to achieve the desired properties. Considering a polymer matrix ceramic composite, the ceramic filler shape used can significantly alter a material's properties.^[1] Filler shapes can include geometries such as spheres, blocks, flakes and fibers.¹ Filler geometries with high area-to-volume aspect ratios tend to have better mechanical properties, as the greater surface area allows for more stress transfer between the composite components.¹ One such filler material that has a relatively high aspect ratio is muscovite mica $[2\text{Al}_2\text{K}_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4]$.³ Another critical factor of composite design involves the interfacial adhesion between the ceramic and the polymer binder.¹ This interface

is typically described as the weakest point in a composite system, and therefore must be carefully considered during its design.¹ The orientation of the composite filler material is also critical in determining the composite properties.¹

1.2 Mica-polymer Composites

Mica is used as a reinforcing filler in many polymeric composites because of its functional, morphological, and surface characteristics.⁴ Mica readily breaks down into smaller thin flakes with very high area-to-volume ratios, which can be used as reinforcement in composites if properly aligned.¹ Mica powder is commonly used as reinforcement for polymer composites in products such as paints, coatings and cements to reduce sagging, shrinkage, cracking, and UV susceptibility.¹ In general, mica is characterized as being highly crystalline, having smooth surfaces between sheet layers, and being an inert material.¹

The addition of mica to a polymer can result in significant improvements to the material properties such as raise the heat distortion temperature, increase tensile and flexural strengths, reduce isotropic shrinkage and permeability, enhance the dielectric and thermal properties, and improve surface properties.⁴ Mica has been previously studied in

combination with a wide variety of plastic thermosets and elastomers such as polypropylene, polyethylene, polycarbonate, Nylon 6, Nylon 66, polyester, and styrene.⁴

Mica-polymer composites are often favored due to the composite's improved strength with the addition of the mica.¹ The mica filler tends to immobilize the polymer chains, effectively preventing the polymer chains from slipping past each other, resulting in the increased strength.¹ Due to mica flakes being an inert material, there is typically no chemical bonding between mica and polymer chains, consequently the surface adhesion between the mica and the polymer is usually poor.¹ As a result, this surface adhesion must be carefully considered when designing a mica-polymer composite. In order to help improve the surface adhesion, sometimes coupling agents, which act as a binder between the polymer matrix and filler, are used in polymer composites.¹ Coupling agents that could be considered with mica to form a composite include silanes, zirconates, titanates, and stearic acid.¹ Mica-polymer composites can be formed in a variety of ways, including hot compaction, extrusion, and pultrusion.⁴⁻⁶

1.3 Previous Mica-polymer Composite Research

Polypropylene is a commonly used polymer for polymer-mica composites, and various experiments have been conducted on this composite system.^{2,7,8} Mica has been shown to be a low-cost way of improving polypropylene performance by improving chemical resistance, dimensional stability, and reducing gas diffusivity, and has been applied to a wide range of uses, including automotive parts, fan blades, dashboard panels, floor and grill panels, and ignition system parts.^{2,9}

Previous studies on mica-filled polypropylene showed an optimized mica concentration of 20 wt% to minimize crack propagation and increase flexural and impact strengths in the polymer composite.^{2,7} The mixing parameters that have been reported to effect the mica-polypropylene system include mixing concentration, method of mica addition to the polymer, and initial particle size.⁸ Corresponding to the potential breakdown of this composite system, it has also been reported that mechanical degradation is likely to occur first by the gradual weakening of larger mica flakes to form smaller flakes, and the most rapid degradation will take place when the mica is incorporated into the molten polymer resin.^[8] Another related composite system has been tested with mica-filled polyester, in which the flexural strength and elastic modulus was found to increase with increasing mica concentration while the tensile strength decreased.¹⁰

One mica-polymer combination where previous research was not found was the use of polymethyl methacrylate (PMMA) [(C5O2H8)n] as the matrix. This polymer is a synthetic resin produced from the polymerization of methyl methacrylate.¹¹ A transparent and rigid plastic, PMMA

is often used as a substitute for glass in products such as shatterproof windows, skylights, illuminated signs, and aircraft canopies.¹¹ PMMA is typically a low cost polymer material that can be easily handled and processed, however, the polymer is also typically weak and brittle under an applied stress.¹¹ The introduction of mica as filler into the PMMA matrix could possibly improve specific properties of the composite and open the door for new applications.

1.4 Direction of Work

The primary goal of this project is to design a repeatable ceramic-reinforced polymer composite with predictable properties in order to demonstrate the effects of added ceramic filler into a polymer matrix. Muscovite mica was chosen as a filler material with PMMA to form a polymer matrix ceramic composite (PMCC). Dynamic mechanical analysis (DMA) was used to measure the elastic modulus and tensile strength of the composite system as the wt% and particulate size of the filler material varied. Optical microscopy was also performed to determine the degree of bonding between the matrix and the filler in the fabricated composites. The various experimental stages are described succinctly in the section that follows.

2. Experimental Procedure

2.1 Dry Ball Milling of Mica Flakes

The mica material was received in flakes from the supplier in the approximate particle size range of 3-7 mm. The subsequent particle size reduction was done by dry ball milling in which 100 grams of mica were placed in an alumina milling jar with alumina milling media and placed in the roll mill machine. The roll mill was set to 50% the maximum rotational speed and run for approximately 24 hours.

2.2 Particle Size Distribution of Mica Flakes

After ball milling, the mica particulates were sieved according to AFS standard 1105-03-S to obtain specific particle size ranges. The sieved particles were separated into twelve flake sizes in the range of greater than 3 mm to less than 53 μm .

2.3 Uniaxial Pressing of Samples

Using a standard laboratory analytical scale, mica percentages were weighed and mixed with PMMA. Samples of concentrations of 10-80 wt% mica were made using five mica particulate sizes in the range of <53 μm to 212 μm , and a reference sample of 100% PMMA was also created.

The samples were pressed using a Buehler TechPress II[®] with an iso-octane Buehler release agent applied to all surfaces interacting with the material to ensure easy release of the sample after pressing. The press was programmed with a 7

minute preheat phase to 165°C. Samples were then heated to 177°C, followed by an 11 minute cooling cycle, held at a constant pressure of 3700 psi. The polymer in the pressed sample had a hard consistency and a colorless-transparent appearance which made further sample preparations (e.g., cutting and polishing) and visual observations of the imbedded mica easier.

2.4 Dynamic Mechanical Analysis (DMA)

The pressed samples were cut using a low speed cutting saw (Buehler Isomet®1000) into rectangular samples approximately 37 mm long, 2 mm wide and 0.5 mm thick. Three samples of each pressed composite were tested in a TA Instruments Q800 DMA system under ambient conditions. Stress/strain tests were conducted using an 8 mm dual cantilever clamp to hold the samples. Run conditions were a preload force of 0.001 N, a force ramp rate of 2 N/m³, and an upper force limit of 18 N. The tests were run until the sample fractured or the force reached the maximum possible by the DMA system (18N).

2.5 Optical Microscopy of Component Interface

Two PMCC samples with 10 wt% mica filler were mounted into an epoxy using metal clips to ensure the samples maintained a flat surface against the bottom of the mounting cup. These samples were placed under vacuum at 93 kPa with a cup of epoxy liquid mounting media mix, in order to remove as much air from the epoxy as possible. After evacuation, the epoxy was poured into the cup with the samples, brought to atmospheric pressure, and allowed to cure overnight. The encapsulated samples were ground and polished using a Buehler Ecomet 3[®] polishing unit with 400 and 600 grit sandpaper for 3 minutes. Further polishing was completed using 12.5, 5, and 1 μm alumina polishing media and water mixture for 5, 10, and 30 minutes respectively on a Buehler TexMet[®] pad. Optical microscopy was then used to observe the interface between the mica particulates and PMMA, as well as the orientation of the mica particulates in the polymer matrix.

3. Results & Discussion

3.1 Dynamic Mechanical Analysis

Shown in Figure 1 is a representative stress/strain data plot for the tested samples using the TA Instruments Universal Analysis software. The figure shows one PMMA sample with no mica filler (dashed line) and one sample with a 10 wt% filler mica of 53-75 μm size (solid line). The elastic moduli were determined for the tested samples from the linear sections of the stress/strain plots. Each sample condition was replicated three times, and the average elastic moduli values for each replication condition are shown below in Figure 2. As the mica filler concentration increased in the samples, it became more difficult to produce viable composites, as

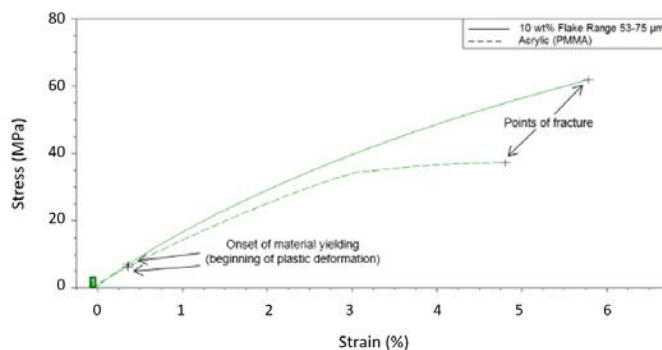


Figure 1: Stress-Strain graphs for one PMMA sample and one composite sample with a 10 wt% of 53-75 μm mica filler.

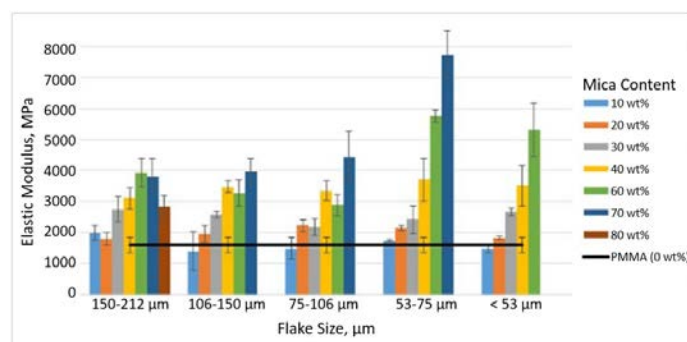


Figure 2: Average elastic moduli (ordered by decreasing mica particulate size and by increasing mica concentration).

the samples crumbled immediately after pressing. Due to this effect, only four of the five mica particulate sizes were pressed for the 70 wt% mica filler samples and one of the five particulate sizes was pressed for the 80 wt% mica filler samples.

Figure 2 shows the average elastic modulus for each sample concentration tested, sorted by the mica particulate sizes. It is noted that there is an overall increasing trend in elastic moduli with increasing mica filler concentration. The largest mica particulate size samples (150-212 μm) showed that a maximum elastic modulus was reached at 60 wt% mica filler, with a decrease in modulus to the 70 and then 80 wt% mica filler samples. The next two smallest mica filler particulate size ranges (106-150 μm and 75-106 μm) showed a slight decrease in modulus from 40 to 60 wt% mica filler, followed by another increase in modulus with the 70 wt% mica filler samples. The increase in elastic modulus was expected to a point, where a peak modulus was anticipated before a decrease in modulus, like the behavior observed in the largest flake size samples. The overall increase seen in the other four flake sizes was not expected.

Compared to the pure PMMA samples tested (shown by the black horizontal line in Figure 2), the 10 wt% mica filler samples demonstrated elastic moduli similar to that of PMMA, while the increasing mica concentration samples showed a steady increase from the elastic modulus of the PMMA samples with increasing mica concentration.

A two-way analysis of variance was conducted for the experimental elastic moduli with mica concentration and particulate size as two independent variables. It was determined that both concentration and flake size were significant to the experimental results, as well as the interaction between the two. When observing the elastic moduli results across varying flake sizes, a relationship is not as clear as the overall trend of increasing elastic modulus with increasing concentration. The statistical interaction between the flake size and concentration most likely contributes to the lack of a clear trend with varying flake size.

3.2 Optical Microscopy

Optical microscopy was conducted on mounted samples to observe both the mica particulate orientation and mica-polymer matrix adhesion. Figure 3 shows the orientation of the mica flakes for the 10 wt% mica filler sample with 150-212 μm particulate size range. The figure shows that the mica flakes seem to have developed a degree of orientation in the transverse direction to the uniaxial press during the composite formation. This orientation also means that the samples were tested mechanically in the transverse direction to the force applied.

After the orientation of the mica was observed, the adhesion of the mica to the PMMA was investigated at various magnifications. This observation was done by looking at a fractured sample with a larger mica flake size than the five tested flake size ranges in order to facilitate observations. The fractured sample in Figure 4 shows component adhesion with no delamination between the mica and polymer, demonstrating that the PMMA and mica successfully bonded together to form a cohesive composite.

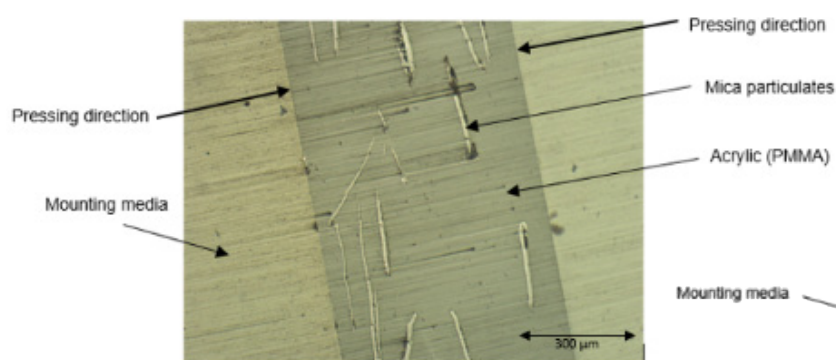


Figure 3: Orientation of mica particulates for 10 wt% mica filler samples with 150-212 μm particulate size range.

4. Conclusion

When polymethyl methacrylate is reinforced with mica filler, the overall elastic modulus increases with increasing mica filler concentration. Both the mica concentration and particulate size were shown to be statistically significant to the resulting elastic modulus, as well as the interaction between the two. It is unclear as to why there was not a peak modulus observed followed by a decrease with increasing mica concentration, which was expected due to the matrix eventually becoming more mica filler than PMMA. This effect was observed in previous literature, however, the experiment showed that only one of the mica flake sizes behaved in this way, while the others showed an overall increasing elastic modulus with increasing mica concentration.^{2,7,8,10}

Optical microscopy on the fractured composite surface showed that a significant bond formed between the PMMA and mica particulates and that there was no need to utilize a coupling agent to develop the bonding. The lack of separation between the polymer matrix and the mica particulates in the fractured composite showed that mica has a strong binding affinity with PMMA. This allowed for a truly cohesive composite to be formed rather than particulates present within another material as two separate entities. Overall PMMA and mica are able to be combined into a repeatable composite that can be used to demonstrate the behavior of polymer matrix composites.

5. Future Work

In order to continue this experiment towards the development of a repeatable composite system, further testing would be needed to characterize the properties of the composite from this work. Further mechanical testing would be useful, such as the mechanical properties of the composite system in tension, since only bending was observed in this experiment. Other orientations of the applied test force are possible to be tested as well, e.g. parallel and oblique. Thermomechanical

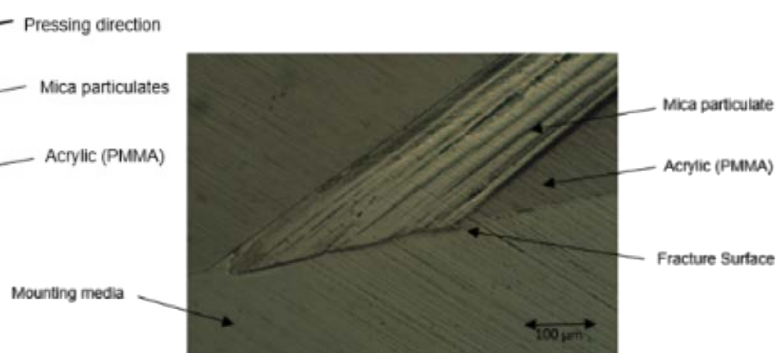


Figure 4: Fractured adhesion surface of the PMMA and mica filler particulate for 10 wt% mica sample with 150-212 μm particulate size range.

testing could also be done to observe how the composite behaves under varying temperature conditions, as only ambient temperatures were tested in this study due to time restrictions. The electrical properties of the composite could also be analyzed, as both mica and PMMA are insulating materials, and the possibility exists for the composite to be a successful insulator. With a range of these properties tested and recorded, a system could be developed for the two components in which certain properties could be optimized for specific polymer/composite applications in the future.

Acknowledgements

This project was conducted as part of a senior design project with the guidance of Dr. Carlos Suchicital and Dr. Thomas Staley. Further thanks goes to Mr. Hesham Elmkharram and the graduate teaching assistants at Virginia Tech for their laboratory support and to the Materials Science and Engineering Department at Virginia Tech for their support for this project.

References

1. Mallick, P.K. *Fiber-Reinforced Composites*, Marcel Dekker, Inc.: New York, **1993**.
2. Vu-Khanh, T.; Sanschagrín, B.; Fisa, B. *Polymer Composites*. 1985, 6, 249-260.
3. Norton, F. H. *Elements of Ceramics*, 2nd ed.; Addison-Wesley Publishing Company: Massachusetts, 1974.
4. Verbeek, J.; Christopher, M.; Thomas, S.; et al. *Mica-Reinforced Polymer Composites*. In *Polymer Composites*; Ed.; Wiley-VCH: Germany, 2012; Vol. 1; pp 673-714.
5. Michler, G.H.; Balta-Calleja, F.J. *High Stiffness and High Impact Strength Polymer Composites by Hot Compaction of Oriented Fibers and Tapes*. In *Mechanical Properties of Polymers based on Nanostructure and Morphology*; Ed.; Taylor and Francis Group: Florida, 2005; pp 683-722.
6. Bader, M.G. *Reinforced Thermoplastics*. In *Handbook of Composites: Fabrication of Composites*; Ed.; Elsevier Science Publishing Company, Inc.: New York, 1983; Vol. 4; p 177-218.
7. Xavier, S.F.; Sharma, Y.N. *Polymer Composites* **1986**, 7, 42-49.
8. Fisa, B.; Sanschagrín, N.; Favis, B. *Polymer Composites* **1984**, 5, 264-276.
9. Mica Composite. <http://www.micaworld.in/micacomposite.html> (accessed April 27, 2014).
10. Sreekanth, M.S.; Bambole, V.A; Mhaske, S.T.; Mahanwar, P.A. *Journal of Mineral and Materials Characterization and Engineering* **2009**, 8, 271-282.
11. Encyclopedia Britannica Online. Polymethyl methacrylate (PMMA). <http://www.britannica.com/EBchecked/topic/1551203/polymethyl-methacrylate-PMMA>. (accessed May 4, 2015).

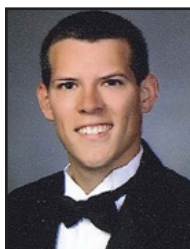
About the Authors



Sarah Whipkey graduated with a Bachelor of Science from the Department of Materials Science and Engineering at Virginia Tech in May 2015. She has been accepted into the graduate program at Alfred University for ceramic engineering beginning Fall 2015.



Chance Roman graduated with a Bachelor of Science from the Department of Materials Science and Engineering at Virginia Tech in May 2015. He has accepted a position with Freeport McMoran: Copper & Gold in Bagdad, Arizona.



Kevin Seay graduated with a Bachelor of Science from the Department of Materials Science and Engineering at Virginia Tech in May 2015. He will be working for Kratos Defense and Security Solutions Inc. at Dahlgren Naval Base in Virginia.