



MECHANICAL AND THERMAL PROPERTIES OF MICRO- AND NANO-SILICA-FILLED PMMA MICRO INJECTION MOLDINGS

Yuka Kobayashi*¹, Yew Wei Leong¹, Makoto Sarata¹, Hiroyuki Hamada¹, Kazushi Yamada¹, Masaya Kotaki¹, Kohji Yoshinaga², Hiroyuki Karakawa², Hiroshi Ito³, Kunihiro Kazama³ and Takeshi Kikutani³

¹ Division of Advanced Fibro Science, Kyoto Institute of Technology, Kyoto, Japan

² Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Kitakyusyu, Japan

³ Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan

*Presenting Author E-mail Address: m6651009@edu.kit.ac.jp

Keywords: *grafted surface, thin-wall micromolding, polymer-grafted silica particle, dispersibility, mechanical property, thermal property*

Abstract

Micro- and nano-scale silica particles filled poly (methyl methacrylate) (PMMA) composites were prepared using high shear compounding and thin-wall micromolding. Mechanical performances of the composites were elucidated through tensile tests and internal structures of fractured surfaces were obtained from microscopic observations. The incorporation of silica particle has raised the tensile modulus of all specimens irrespective of processing conditions. Distribution of micro-fillers in the molded specimens was preferential towards the end side than the gate and center sides. Nano-filler particles were dispersed uniformly in most parts of the specimen while boundary separations between filler and matrix could be observed at the skin layer in micro silica filled PMMA. Thermo gravimetric analysis (TGA) data suggested anisotropic distribution of micro-silica particles in the specimens. The degradation temperature of the composites increased especially at regions with high concentration of micro-silica particles. The glass transition temperatures (T_g) of filled micro-silica specimens were higher than neat PMMA and nano-silica specimen.

1 Introduction

In composite materials, the bulk mechanical properties are not only dependent on the individual properties of the matrix or reinforcement alone, but also on the extent of interfacial interaction between these components. For this reason, the consideration of interfacial properties cannot be avoided especially when a reinforcing effect from the fibers or fillers is desired.

Incorporation of surface treatments on reinforcements is common to enhance their interfacial bonding with the matrix resin. These treatments are usually performed prior to processing and fabrication of the final product. Upon surface treatment, physical and chemical structure of the reinforcements could change, which subsequently affects the reinforcement-matrix interaction. The effects of treatment could often be assessed through mechanical testing, thermal characteristics and evaluation of the orientation and distribution of the reinforcements. Hence, the aim of this work is to establish a relationship between initial surface treatment and final product properties through interfacial characterization and a series of mechanical testing.

Recently, the usage of nano-sized fillers as reinforcements for various polymer systems has been rampant[1-4]. One of the most frequently used

nano-reinforcements is silica, as it is relatively cheap and easily available. In this study, poly (methyl methacrylate) (PMMA) grafted micro and nano silica particle was incorporated into PMMA resin, which was later molded using thin-wall micro injection molding technology. The detailed methodology and advantages of this method can be found elsewhere [5, 6]. The dispersion of the filler was evaluated and later correlated to the filler-matrix interaction and mechanical properties of the moldings.

Micro and nano silica particle filled poly (methyl methacrylate) (PMMA) composites were prepared using high shear compounding and thin-walled micro injection molding. PMMA-grafted silica fillers were also used to evaluate their effectiveness towards enhancing the dispersion and mechanical properties. Dynamic and static mechanical performance of the composites was elucidated while internal structures of fractured surfaces were obtained from microscopic observations. The resistance of the composites to thermal degradation was also evaluated.

2 Materials and Sample Preparation Methods

2-1 Materials

The micro (C300; Wako Pure Chemical Industries Ltd.) and nano-sized silica (Sphericaslurry 120; Catalysts & Chemicals Industries Co. Ltd.) were obtained commercially. In order to modify the surface of the fillers, the polymer grafting method was employed. Three types of silica i.e. micro-sized untreated, micro-sized PMMA-grafted and nano-sized PMMA-grafted silica were incorporated into the PMMA matrix. Figure 1 shows microphotographs of silica particles. The specifications of the silica treatments are described in Table 1.

2-2 Sample Preparation Methods

The treated silica fillers were dried for 6 hours at 80 °C and compounded with PMMA resin by using a mixer (Labo Plastomill, 100C100; Toyoseikiseisakusho Ltd.) set at a temperature of 200 °C. Mixer rotation was set at a speed of 50 rpm for 5 minutes. The filler content was fixed at 10 wt% in all specimens. Injection molding was conducted by using a compact electric injection molding machine (ELJECT AU3E; Nissei Plastic Industrial Co. Ltd.). Cylinder temperature was varied at 240 and 260 °C

while injection speeds of 120 and 150 mm/s were used. Mold temperature was maintained at 70 °C. This injection system is composed of a screw barrel for plastication and a plunger injection system. The diameter of the screw in the plastication unit is 14 mm while the injection plunger is 8 mm in diameter. This enables a small and precise amount of material to be injected for each cycle used. Two types of

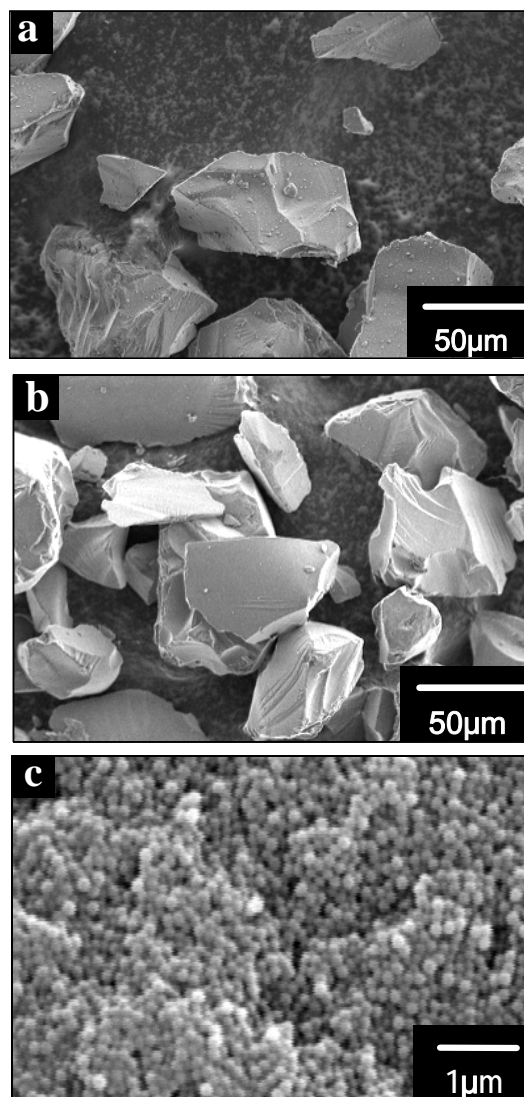


Fig. 1. SEM micrographs: (a) untreated micro-silica, (b) treated micro silica, and (c) treated nano-silica

Table 1. Molecular weight of grafted PMMA on silica surface

	Neat PMMA	Untreated silica	Treated silica 1	Treated silica 2	Treated silica 1	Treated silica 2
Molecular Weight (Mn)	0	0	9500	13000	5300	25000
Silica Particle Diameter (μm)	20-80	20-80	20-80	20-80	0.12	0.12

specimens were molded; one was rectangular ($36 \times 5.5 \times 0.3$ mm), and another was dumbbell shaped (in accordance with ISO37-4).

Tensile tests were performed by using a compact tensile testing machine (Minimat; Rheometric Scientific Inc.). The gauge length was 12.0 mm while test speed was 1.0 mm/min. At least 3 specimens were used for each specimen configuration. Furthermore, the relative standard deviation of each configuration was ensured to be less than 45%.

Thermo gravimetric analyses (TGA) were performed using a TA Instrument TGA2950 on samples taken at various flow lengths of the molding to evaluate the degradation temperature as well as the dispersion of the filler. Specimens were heated from 30 to 700 °C in air. Dynamic mechanical analyses (DMA) were performed using a TA Instrument DMA 2980. Rectangular samples were analyzed at a temperature range of 25 to 180 °C under tensile mode. Furthermore, dumbbell shaped samples were analyzed at isothermal conditions (30 °C), at a constant force of 15N, for 120 min. After DMA, dumbbell shaped samples were tested under similar conditions of normal tensile tests.

Samples were notched and fractured under cryogenic conditions at regions adjacent to the gate, at the middle of the specimen, and at regions near the end of the specimen flow length. The fracture surface was observed by using the Scanning Electron Microscope (SEM) (JSM-5200: JEOL Ltd.) and optical microscope (PME3: Olympus Co.).

Table 2. Relation between: (a) tensile modulus, (b) tensile strength, and (c) strain at brake and micro-silica/PMMA injection molded composites.

(a) Tensile modulus (GPa)					
Molding Condition		Neat	Untreated	Treated	Treated
Cylinder	Injection	PMMA	micro	micro	micro
Temperature (°C)	Speed (mm/s)		silica	silica 1	silica 2
240	120	2.19	2.25	2.29	2.66
240	150	1.87	2.11	2.22	2.64
260	150	1.94	2.14	2.17	2.54

(b) Tensile Strength (MPa)					
Molding Condition		Neat	Untreated	Treated	Treated
Cylinder	Injection	PMMA	micro	micro	micro
Temperature (°C)	Speed (mm/s)		silica	silica 1	silica 2
240	120	72.5	67.4	69.2	71.9
240	150	69.1	66.5	65.9	71.9
260	150	76.1	65.5	63.7	70.8

(c) Strain at break (%)					
Molding Condition		Neat	Untreated	Treated	Treated
Cylinder	Injection	PMMA	micro	micro	micro
Temperature (°C)	Speed (mm/s)		silica	silica 1	silica 2
240	120	9.3	4.7	4.5	4.8
240	150	8.8	4.9	4.4	4.8
260	150	11.7	4.5	4.2	5.2

3 Results & Discussion

3-1 Mechanical properties of filled micro-silica

The results from tensile tests of micro-silica specimens are shown in Table 2. Each value indicates a mean value. Due to the high rigidity of the silica fillers, the tensile modulus of the composites was superior to that of the neat PMMA.

An increase in tensile strength is observed in samples incorporated with treated micro-silica as opposed to the non-treated one. However, the strength of the composites is lower than that of neat PMMA, which indicates that the silica is a non-reinforcing filler due to its isotropic particle shape. Hence, in this case, the filler treatment had not only acted as a filler-matrix interaction enhancer; but also as an effective dispersion agent.

The significantly lower strain at break of the composite is testament to their brittleness as compared to neat PMMA. Almost all micro-silica specimens broke near the end position (Figure 2).

3-2 Mechanical properties of filled nano-silica

Table 3 shows results of tensile tests of nano-silica specimens. The tensile modulus of the composites also improved as compared to the neat PMMA. Specimens incorporated with nano-silica particles grafted with higher molecular weight (M_w) PMMA exhibited the lowest tensile strength as compared to other nano-silica specimens and neat

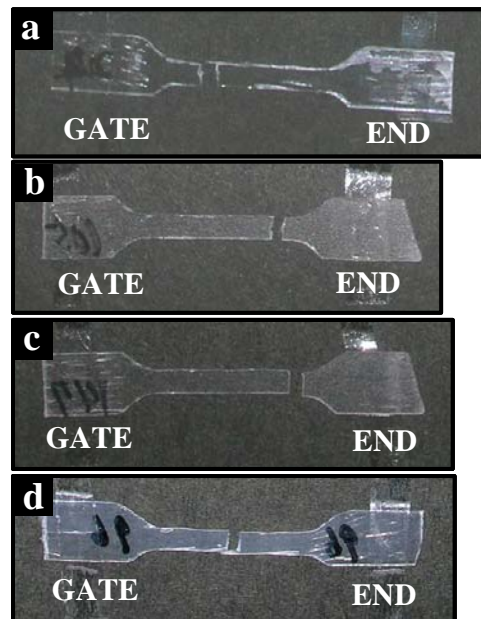


Fig. 2. Photos of after tensile tests specimens: (a) PMMA, (b) untreated micro silica filled PMMA, (c) treated micro silica filled PMMA, (d) nano silica filled PMMA.

PMMA. It should also be noted that the tensile moduli of the nano-silica composites were lower than that of micro-silica specimens. This is due to the lower nano-silica content in the composites, which can be attributed to filler loss during processing.

Specimens molded at 240 °C, exhibited slightly higher tensile strength when low M_w PMMA was grafted onto the silica surface while the opposite is true when the specimens were molded at 260 °C.

The dispersion of the nano-fillers was more heterogeneous, even with the presence of filler treatment, as compared to the micro-silica composites. However, in some cases, large

Table 3. Relation between: (a) tensile modulus, (b) tensile strength, and (c) strain at brake and nano-silica/PMMA injection molded composites.

(a) Tensile modulus (GPa)				
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2
Cylinder Temperature (°C)	Injection Speed (mm/s)			
240	120	2.19	2.55	2.40
240	150	1.87	2.47	2.38
260	150	1.94	2.48	2.49

(b) Tensile Strength (MPa)				
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2
Cylinder Temperature (°C)	Injection Speed (mm/s)			
240	120	72.5	65.8	56.3
240	150	69.1	61.5	52.9
260	150	76.1	55.1	60.3

(c) Strain at break (%)				
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2
Cylinder Temperature (°C)	Injection Speed (mm/s)			
240	120	9.3	6.6	5.6
240	150	8.8	6.1	5.3
260	150	11.7	5.5	6.0

agglomerates have formed throughout the nano-silica composites, as can be seen in Figure 3. These agglomerated regions act as effective stress concentration points, which will further reduce the load bearing properties of the composites, as evidently depicted in Table 3.

A slight decrease in strain at break was also evident when the nano-silica composites were molded at 240 °C while the overall deformability of the composites as well as neat PMMA resin appeared to have improved when the barrel temperature was increased to 260 °C.

3-3 Microscopic Observation

As previously shown in Figure 3, the distribution of the micro-silica fillers seemed to be extremely heterogeneous, whereby a high concentration of fillers were found at the end of flow length while filler concentrations near the gate were low. On the other hand, the dispersion of the nano-silica particles had greatly improved although some aggregations were observed at the flow end. It is believed that the size and shape of the silica particles could significantly influence their interaction with the polymer matrix, which would later produce different dispersive states.

These results are coherent with findings in Figure 4, which shows high magnification scanning electron micrographs at the fracture surfaces of tensile tested specimens. The skin-core regions are evident in all the specimens, although these regions are more distinctly recognizable in neat PMMA and nano-silica composite specimens. In these specimens, the skin is represented by a highly plastically

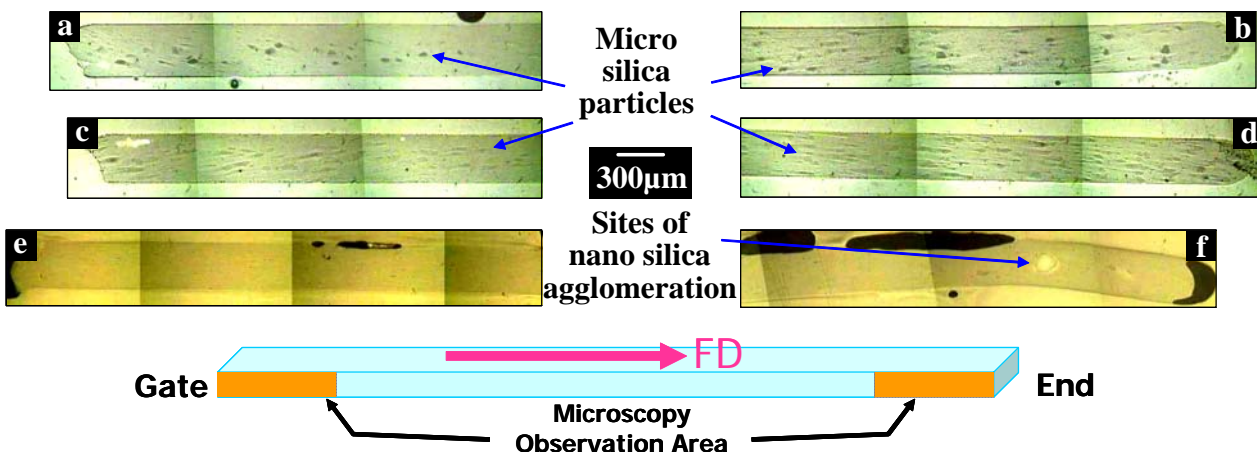


Fig. 3. Optical microscope images at various positions of the specimens filled with (a) untreated micro silica gate position; (b) untreated micro silica end position; (c) treated micro silica gate position; (d) treated micro silica end position; (e) treated nano silica gate position; and (f) treated nano silica end position.

MECHANICAL AND THERMAL PROPERTIES OF MICRO- AND NANO-SILICA-FILLED PMMA MICRO INJECTION MOLDINGS

deformed region, which sandwiches a flatter region that will be the core. The core region in nano-silica specimens exhibits very minimal fibrillation, which indicates brittleness. Meanwhile, morphological examination of the micro-silica composite specimens revealed that the skin and core regions are vaguely distinguishable, especially in specimens containing treated micro-silica. This is a very strong indication that very minimal plastic deformation has occurred in these specimens while it is also important to note that fracture occurs at regions with very high filler content (and low in polymer content), hence the polymeric fibrils can be scarce. In addition, a higher degree of boundary separation between the micro-silica particles and the PMMA matrix was observed, especially at the skin region which was highly plastically deformed. In the case of treated

micro-silica filled composites, less boundary separation was observed due to better filler-matrix interaction.

Figure 5 indicates the state of filler-matrix interfacial properties in all composite specimens. From these pictures, it is learned that the treatment of fillers can also improve, to a certain extent, the filler-matrix interaction. This is especially evident in micro-silica systems where there were very few cavities present at the interfacial regions between the filler and matrix, which strongly suggests good filler matrix interaction.

3-4 Thermal properties

The filler distribution at various flow lengths with reference to the gate can be elucidated from the

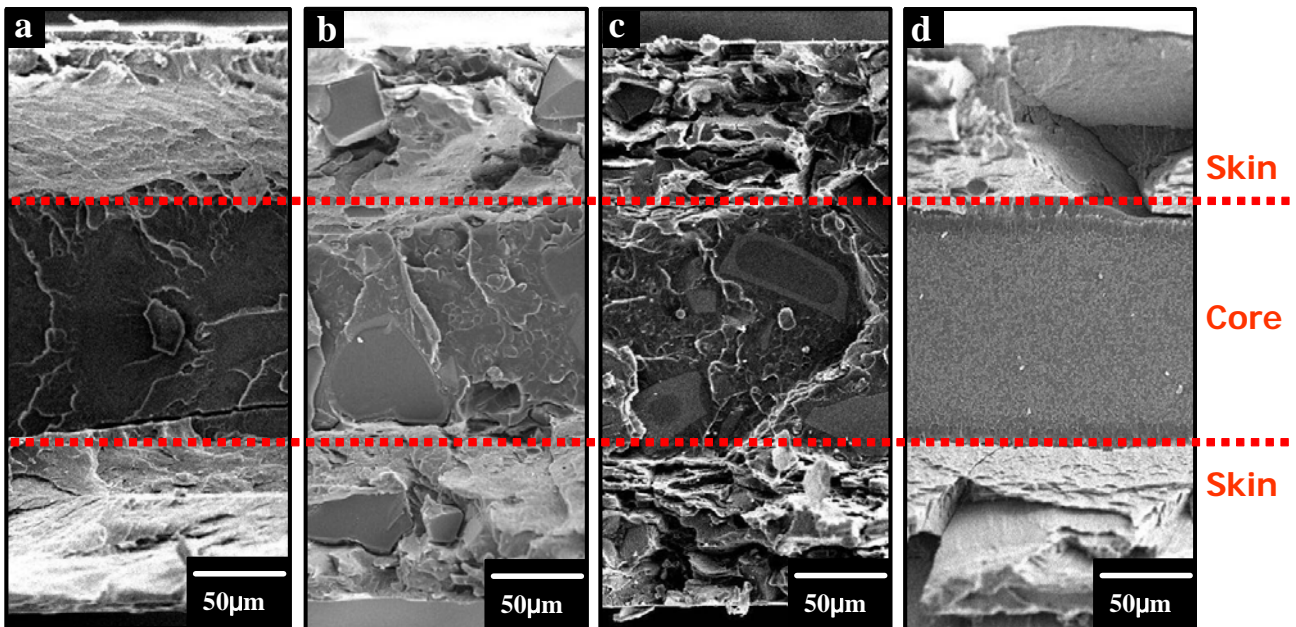


Fig. 4. SEM micrographs: (a) PMMA, (b) untreated micro silica filled PMMA, (c) treated micro silica filled PMMA, (d) treated nano silica filled PMMA.

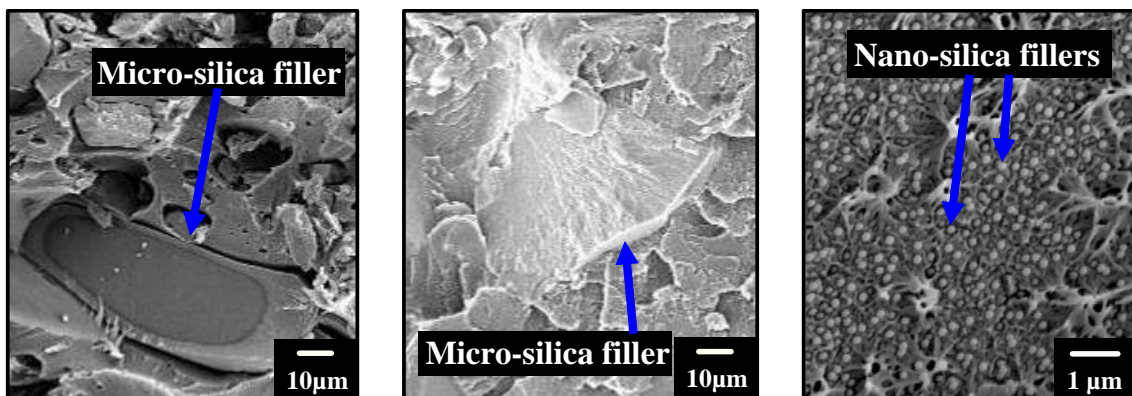


Fig. 5. SEM micrographs of (a) boundary separation of micro-silica, (b) good filler-matrix interaction of micro-silica, (c) good dispersion of nano-silica.

TGA results shown in Figure 6. The heterogeneous distribution of the micro-silica fillers, as was detected in Figure 3, could be confirmed here. This highly anisotropic distribution indicates that there is stronger interaction between the micro-sized fillers and the PMMA resin, hence they are bound to follow the flow of the resin and accumulate towards the end of the flow length. A more homogeneous distribution of fillers, however, can be observed in nano-silica specimens, although the filler content is below the expected level irrespective of flow length. It is believed that the large surface area of the filler coupled with its almost spherical shape allows the resin to flow past the filler particles without much resistance, thus aggregation of the nano-particles towards the end of the flow length is avoided.

The degradation temperature of the composites at various flow lengths could also be elucidated from the TGA results as shown in Figure 7. It is apparent that the degradation temperature increases with flow length in micro-silica composites while the degradation of nano-silica composites is almost independent of flow length. From this observation, it is believed that the degradation temperature of the composite is directly correlated to the filler content at the respective flow lengths. It is also interesting to note that the untreated micro silica specimens are more susceptible to degradation than both treated micro silica specimens and treated nano silica specimens, indicating stronger interaction between treated fillers and the resin.

The $\tan \delta$ peaks, obtained from dynamic mechanical analyses, indicate the glass transition temperatures (T_g) of the specimens (Figure 8). Obvious shifts of the T_g towards higher temperatures with reference to neat PMMA can be observed in specimens incorporated with micro-silica. On the contrary, the $\tan \delta$ peak of nano-silica specimens has not only shifted towards a lower temperature but also are broader, which is a strong indication that the nano-particles are behaving like a plasticizer to the resin. A possible explanation for this occurrence could be the relatively spherical nature of nano-silica, which not only creates less friction between particles but also less resistance towards molecular motion of the resin. The rougher and more irregular surface of the micro-silica particles creates more resistance due to a higher degree of mechanical interlocking between the filler and matrix.

3-5 Controlled force analysis by DMA

Figure 9 shows results of DMA at controlled force mode. The overall strain recorded for untreated

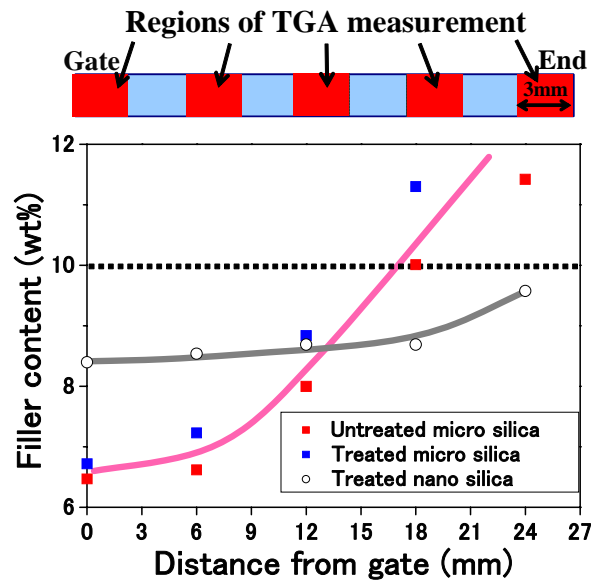


Fig. 6. Dispersion of silica particles at various distances from gate.

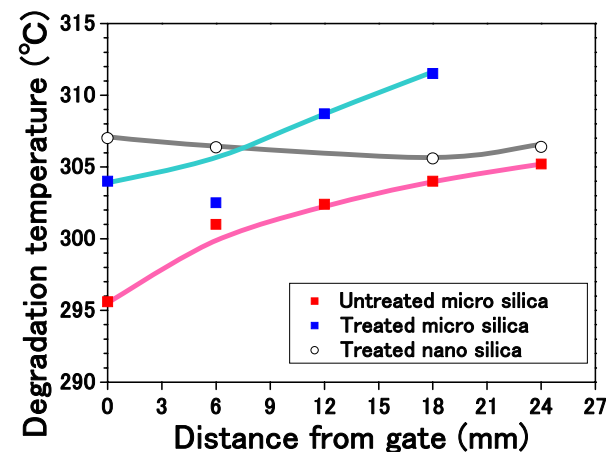


Fig. 7. Degradation temperature of composites at various flow lengths from the gate.

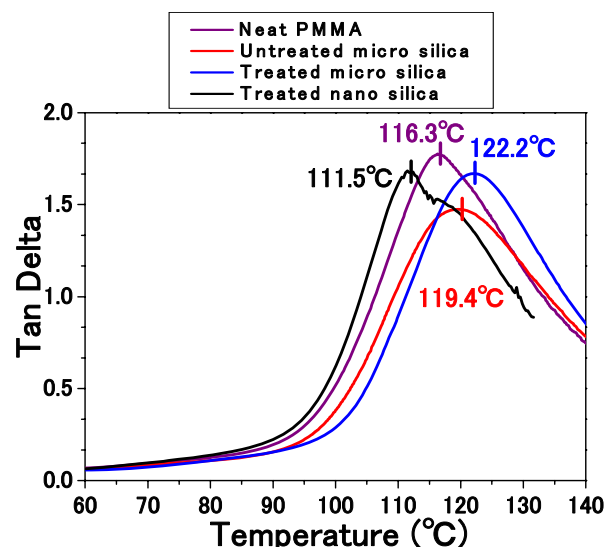


Fig. 8. Tan delta peaks of composites incorporated with fillers of different size and treatment.

MECHANICAL AND THERMAL PROPERTIES OF MICRO- AND NANO-SILICA-FILLED PMMA MICRO INJECTION MOLDINGS

micro silica specimens were lower than the other specimens. The initial increments in strain for nano silica composites were the greatest.

The tensile tests results are shown in Tables 4 and 5. They can become of comparing with Table 2, 3. The tensile modulus increased in all specimens. In particular, increment was the biggest in neat PMMA specimen. The tensile strength improved in almost all specimens. The strain at break had varied quite significantly according to the type of silica used. The strength values of neat PMMA and nano silica specimens severely deteriorated. The incorporation of high molecular weight PMMA grafted silica significantly enhanced the tensile properties of PMMA.

4 Conclusions

The influences of filler surface treatment, particle

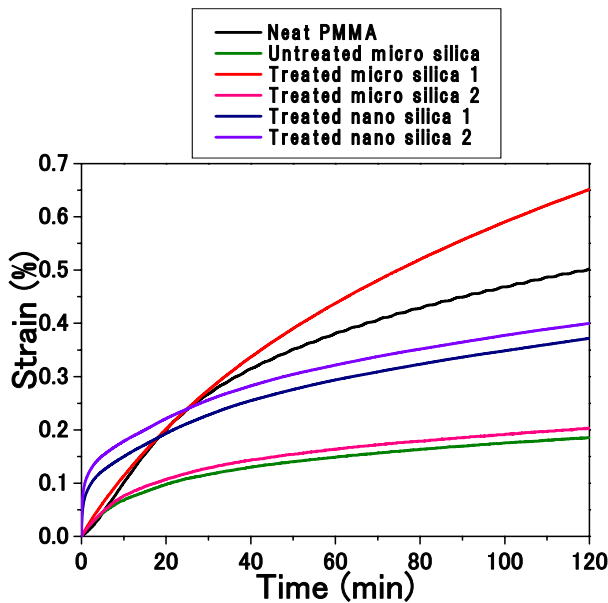


Fig. 9. Strain-Time curves of composites incorporated with fillers of different size and treatment.

Table 4. Relation between: (a) tensile modulus, (b) tensile strength, and (c) strain at brake and micro-silica/PMMA injection molded composites after DMA.

(a) Tensile modulus (GPa)					
Molding Condition		Neat PMMA	Untreated micro silica	Treated micro silica 1	Treated micro silica 2
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120				
240	150	2.46	2.69	2.69	2.95
260	150				

(b) Tensile Strength (MPa)					
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2	
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120		65.3		
240	150	72.0			
260	150			59.5	

(c) Strain at break (%)					
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2	
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120		3.8		
240	150	4.7			
260	150			3.5	

size, and injection molding conditions on the mechanical properties of silica-filled PMMA composites were estimated. The particle size presents the biggest effect on the mechanical properties since it affects the distribution as well as dispersion of the fillers in the matrix. Distinct morphological differences could also be observed when different silica sizes were incorporated, especially the state of plastic deformation at the skin and core regions of the moldings. Filler treatment contributed minimally towards mechanical property enhancement, although there were evidences pointing towards improvements in filler dispersion as well as filler-matrix interaction.

The effects of filler surface treatment and particle size on the dynamic mechanical and thermal properties of silica-filled PMMA composites were evaluated. The particle size and shape exerted the largest influence on the filler dispersion, whereby the nano-silica particles were better dispersed due to its spherical particle shape. Due to this geometrical factor, the nano-silica has also acted as a mild plasticizer, which effectively lowered the T_g of PMMA. However, this does not indicate weak interaction between the filler and matrix, since the degradation temperature of the composite was relatively high. Composites incorporated with treated micro-silica displayed higher T_g and better resistance to degradation, although the dispersion of filler was heterogeneous due to the irregular particle shape.

From DMA controlled force mode, effect of Mw of PMMA grafting on interfacial properties between Table 5. Relation between: (a) tensile modulus, (b) tensile strength, and (c) strain at brake and nano-silica/PMMA injection molded composites after DMA.

(a) Tensile modulus (GPa)					
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2	
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120		2.87		
240	150	2.46			
260	150			2.87	

(b) Tensile Strength (MPa)					
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2	
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120		65.3		
240	150	72.0			
260	150			59.5	

(c) Strain at break (%)					
Molding Condition		Neat PMMA	Treated nano silica 1	Treated nano silica 2	
Cylinder	Injection				
Temperature (°C)	Speed (mm/s)				
240	120		3.8		
240	150	4.7			
260	150			3.5	

silica particles and the matrix was better understood.

5 References

- [1] M. Q. Zhang, M. Z. Rong, H. B. Zhang and K. Friedrich. "Mechanical properties of low nano-silica filled high density polyethylene composites". *Polymer Engineering and Science*, Vol. 43, No. 2, pp 490-500, 2003.
- [2] L. Zhang, K. C. Tam, L. H. Gan, C. Y. Yue, Y. C. Larn, X. Hu, "Effect of Nano-Silica Filler on the Rheological and Morphological Properties of Polypropylene/liquid-crystalline Polymer Blends". *J. Applied Polymer Science*, Vol. 87, No.9, pp1484-1492, 2003
- [3] W. H. Ruan, X. B. Huang, X. H. Wang, M. Z. Rong, M. Q. Zhong, "Effect of Drawing Induced Dispersion of Nano-Silica on Performance Improvement of Poly(propylene)-Based Nanocomposites". *Macromolecular Rapid Communications*, Vol. 27, No. 8, pp581-585, 2006
- [4] J. T. Han, K. Cho, *J. Materials Science*, "Nanoparticle-induced enhancement in fracture toughness of highly loaded epoxy composites over a wide temperature range". Vol. 41, No.13, pp4239-4245, 2006
- [5] H. Ito, Y. Yagisawa, T. Saito, T. Yasuhara, T. Kikutani and Y. Yamagiwa, "Fundamental Study on Structure Development of Thin-Wall Injection Molded Products". *Theoretical and Applied Mechanics Japan*, Vol. 54, No. 0, pp263-268, 2005
- [6] H. Ito, K. Kazama, T. Kikutani, K. Okubo, S. Tanaka, "Evaluation of Material Properties and Processability Using The Intelligent Micro-scale Polymer Processing System" *ANTEC 2006 Tech. paper*, Charlotte, North Carolina, USA, pp2511-2515, 2006