

Effect of Talc/MMA *In Situ* Polymerization on Mechanical Properties of PVC-Matrix Composites

X. L. XIE,¹ B. G. LI,² Z. R. PAN,² R. K. Y. LI,³ S. C. TJONG³

¹ Department of Chemistry, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China

² State Key Laboratory of Polymerization Reaction Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

³ Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China

Received 3 June 2000; accepted 19 June 2000

ABSTRACT: In this study, polymethyl methacrylate (PMMA)-coated talc was produced by the *in situ* polymerization of methyl methacrylate on the talc surface. The polymerization reaction was performed by both batch and semicontinuous emulsion processes. The polymerization kinetics, particle size and distribution, grafting efficiency, and coated-talc morphology were systematically investigated. It was found that the talc particles have no effect on the polymerization of PMMA. The PMMA produced was found to cover the talc surface well. However, only a small amount can be grafted onto the talc. The size distribution of talc particles treated by semicontinuous emulsion polymerization is more uniform than by batch polymerization. The treated talc was subsequently used as filler in a poly(vinyl chloride) (PVC) matrix, and mechanical properties of the PMMA-coated-talc/PVC composites were studied. Morphological structure of PVC-matrix composites revealed that the PMMA coating on talc improved the dispersion of talc in the PVC matrix and enhanced the interfacial adhesion between the talc and PVC. The mechanical properties of the composites, especially the impact strength, were found to be improved. There appears to be a critical covering thickness of PMMA on the talc surface for optimum toughening. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2105–2112, 2001

Key words: PVC-matrix composite; talc; surface modification; *in situ* polymerization

INTRODUCTION

Particle-reinforced polymer composites (PRPC) have been widely applied in the automobile, household, biomedical, and electrical industries.

However, the inorganic fillers usually have high surface energy because of their hydrophilic ionic nature. The hydrophobic polymer does not wet or interact with the fillers because of their differences in surface energy.^{1–3} To increase the applicability of PRPC, many studies have been conducted to try to improve the compatibility between the fillers and the polymer matrix to optimize the mechanical and other physical properties. Therefore, improving the interfacial adhesion between the inorganic particles and the poly-

Correspondence to: X. L. Xie.

Contract grant sponsors: National Postdoctoral Foundation of China and the Foundation of Huazhong University of Science and Technology.

Journal of Applied Polymer Science, Vol. 80, 2105–2112 (2001)
© 2001 John Wiley & Sons, Inc.

mer matrix by modifying the filler surface becomes inevitable in toughening a polymer matrix.^{4–11} The traditional method of treating filler surface by low-molecular coupling agents or surfactants has been found to be reasonably effective.^{12–14} However, low molecular weight compounds have a tendency to migrate out from the interface to the surface of PRPC. As a consequence, there is degradation in the mechanical and physical properties of PRPC. Also, an undesirable surface appearance caused by surface scorching or bulging will result. To enhance the toughness of PRPC, an elastomeric interlayer such as butadiene acrylonitrile copolymer has been coated on the fillers before being incorporated into the polymer matrix like epoxy resins.^{15–17} However, nonhomogeneous filler distribution greatly reduces the toughening efficiency. Another method for surface modification is by plasma treatment which enables a structural change in the interface so as to increase the compatibility between the fillers and the polymer matrix. In a study of linear low density polyethylene (LLDPE) filled by plasma-treated CaCO₃, it was noted that the plasma could first remove all residuals on the filler and then create a new coating on them, leading to an increase in tensile strength and toughness of polymer-matrix composites.¹⁸ However, there are some limitations for engineering application. Therefore, there is a demand for new technologies of filler surface treatment. At present, some new approaches, such as sol-gel processing, *in situ* intercalative polymerization and *in situ* polymerization, have been proposed for particulate surface treatment to produce high-performance PRPC. The sol-gel processing^{19–26} involves acid or base catalyzed hydrolysis of the metal alkoxides (such as silicon alkoxides), followed by polycondensation of the hydrolyzed intermediates such as tetraethoxysilane. This method provides a good means for the preparation of inorganic metal oxides from organic metal alkoxides. The formation of a crosslinking network of organic metal oxides makes it difficult to process, which prevents the widespread application of this method. *In situ* intercalative polymerization^{27–31} is a good method for production of polymer/clay composites or nanocomposites such as PA6/montmorillonite hybrid. It was reported that ω -amino acid can intercalate with the *n*-montmorillonite layer, making the montmorillonite swollen. However, this method is limited to the preparation of high-performance clay-filled polymer composites. Recently, another new fabrica-

tion method called “*in situ* polymerization” has been proposed.^{32–34} *In situ* polymerization is a method in which inorganic particles are first dispersed into suitable monomers and this mixture is then polymerized using a technique similar to bulk polymerization. The monomer layer of polymer coated on the particles reduces particle surface energy as well as promotes dispersion of the particles and interfacial adhesion, leading to enhanced mechanical properties, toughness, and processibility of the resulting PRPC.

In this study, the *in situ* polymerization of methyl methacrylate (MMA) on the surface of the micron-sized talc was performed by using the batch and semicontinuous emulsion processes. The treated talc was subsequently used to fill poly(vinyl chloride) (PVC). It is expected that the PMMA covered on the surface of talc can improve the mechanical properties of the resulting PVC-matrix composites.

EXPERIMENTAL

Materials

Talc powders (1250, 2500 mesh) were purchased from Sichun Serpentine Mineral Factory in China. MMA monomer was purified by distillation under reduced pressure before use. All of the water used was deionized. PVC was donated by Qilu Petrochemical Engineering Company in China.

Polymerization Procedures

The polymerizations were performed by a batch and a semicontinuous process, respectively, in a 1000-mL glass reactor (stirring rate 200 rpm). For the batch polymerization, the ingredients [deionized water, sodium dodecyl sulfonate (SDS) as emulsifier, MMA as monomer and talc] were added to the reactor vessel, heated, and stirred continuously, until the reaction temperature was reached. Then an aqueous solution of ammonium persulfate (APS) as initiator (preheated to the reaction temperature) was added to start the polymerization reaction.

For the semicontinuous polymerization, the doubly distilled water, APS, SDS, and the talc powder were poured into the reactor vessel and heated under constant stirring. Once the reaction temperature was reached, the aqueous solution of initiator was added. After 10 min, a continuous

dosage of the monomer was added under monomer-starved conditions.

The particle-size distribution of the untreated and treated talc was determined by using a LS-230 particle-size tester (Coulter Co., USA) before emulsion breaking. The products were dried at 45°C under vacuum after emulsion breaking and centrifugation. The conversion was determined by the following equation:

Conversion (%)

$$= \frac{\text{precipitate (g)} - \text{talc (g)}}{\text{monomer used (g)}} \times 100\%$$

Percentage of Grafting of Polymer

The polymerization products were extracted with acetone for 24 h in a Soxhlet apparatus to remove the ungrafted polymer and dried to a constant weight under vacuum. The percentage of grafting onto the surface of talc was calculated by the following equation:

Percentage of grafting (%)

$$= \frac{\text{Polymer grafted (g)}}{\text{Talc used (g)}} \times 100\%$$

Fourier transform infrared (FTIR) spectroscopy was applied to characterize the changes in the chemical structure of talc after *in situ* polymerization. Thin film specimens were pressed with KBr powder.

Preparation of PMMA-Coated-Talc-Filled PVC Composites

The PVC matrix used in this investigation has the following composition: 100 parts PVC, three parts heat stabilizer (XP-301), 1 part process aid (ACR-401), 0.6 parts paraffin wax (intermediate lubricant), and 0.5 part stearic acid. PMMA-coated talc and untreated talc were mixed with the PVC matrix mixture in a high-speed mixer. The talc weight fraction (W_p) was kept at 20% for all the composites. The composite mixtures were plasticized by a two-roll mill at 180°C for 10 min. Composite plates with dimensions of 200 × 80 × 3.2 mm³ were compression molded at 180°C for 8 min, with a 5-min preheating period. Care was taken at this stage to ensure precise timing so as to eliminate any differences that might arise as a result of the samples having different thermal histories. These plates were cut into dog-bone-

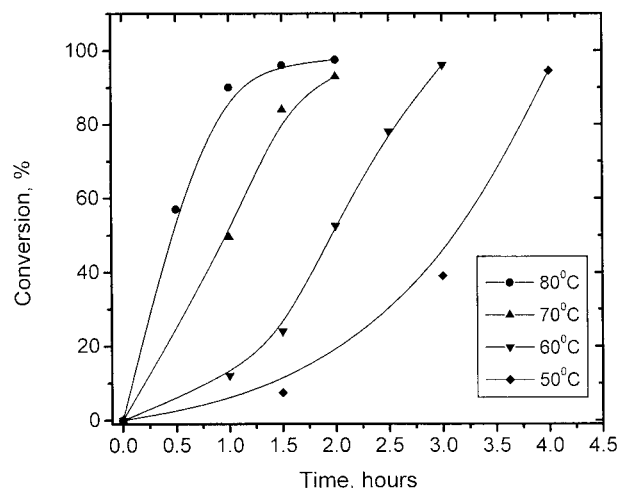


Figure 1 Reaction kinetics curves of batch *in situ* emulsion polymerization of MMA/talc at different temperatures.

shaped tensile bars. Notched izod impact specimens were also prepared from the plates.

Mechanical Properties

The tensile behavior was determined by using an Instron tester (model 4206, Instron Co., USA) at room temperature under a cross-head speed of 1 mm/min. Izod impact specimens with dimensions of 65 × 13 × 3.2 mm³ were cut from the plaques, and were tested by a CEAST pendulum impact tester. A blunt notch with a notch tip radius of 0.25 mm was introduced to the impact specimens with a CEAST notch opener.

Morphology Observations

The morphologies of the fracture surfaces were observed by using a scanning electron microscope (model S-300). The specimens were fractured after immersion in liquid nitrogen. All fractured surfaces were coated with a thin layer of gold before scanning electron microscopy (SEM) examination.

RESULTS AND DISCUSSION

Reaction Kinetics of *In Situ* Emulsion Polymerization

Figure 1 shows the reaction kinetics of batch *in situ* emulsion polymerization at different temperatures. The average size of talc was 1250 mesh, and the weight ratio of talc and MMA was 1:1.

Table I Effect of Water/MMA Ratio on the Polymerization Conversion of MMA

Water/MMA	10	15	20	50
Conversion (%)	97.5	98	96.7	97

Note: talc/MMA 1 : 1; APS 1%; SDS 0.5%; 70°C, 4 h.

The results indicated that the temperature significantly affected the polymerization rate. The higher the temperature, the earlier the autoacceleration occurred and the shorter the time to achieve equilibrium conversion. For the different temperatures used in this investigation, the last conversions all approached 100%. From these results, it can be concluded that the talc does not inhibit the polymerization of MMA. The results are proved by X-ray photoelectron spectroscopic analysis of talc.³⁵

At the same polymerization conditions, the ratio of water and MMA does not affect the conversion of MMA (see Table I). However, for the sake of cost consideration and the dispersion of talc in the polymerization system, it is necessary to select the proper ratio of water and MMA. Table II shows the influence of the initiator content to the *in situ* emulsion polymerization. It can be seen that 1% APS can already efficiently initiate the polymerization of MMA.

Particle Size and Distribution

The particle sizes of untreated talc and PMMA-coated talc are listed in Table III. As expected, the particle size of the PMMA-coated talc is bigger than that of the pure talc, which also increases with increasing the ratio of MMA and talc during polymerization. These results indicate that the PMMA polymer indeed covered the surface of talc. The particle distribution index of talc and PMMA-coated talc are shown in Table IV. It can be seen that the particle distribution of PMMA-coated talc produced by semicontinuous *in situ* polymerization is more uniform than that by batch *in situ* polymerization. The finer the talc is,

Table II Effect of Initiator Content on the Polymerization Conversion of MMA

APS (%)	1	2	4
Conversion (%)	97.5	98	98.5

Note: talc/MMA 1 : 1; water/MMA 10 : 1; SDS 0.5%; 70°C, 4 h.

Table III The Particle Size of Talc and PMMA-Coated Talc (μm)

Talc/MMA	Talc	8	4	2	1
Batch process	13.56	13.80	42.03	70.67	104.7
Semicontinuous process (1250 mesh)	13.56	20.10	19.35	20.42	20.67
Semicontinuous process (2500 mesh)	6.12	10.35	10.43	10.56	10.50

Note: APS 1%; SDS 0.5%; 70°C, 4 h and 80°C, 1 h.

the more uniform is the particle-size distribution. This may be because, in the semicontinuous process, the monomer is in a starved condition, and the semicontinuous polymerization avoids the formation of new PMMA particles. Moreover, the polymerized PMMA easily covers the surface of small talc particles. It leads to the uniform size distribution of particles.

FTIR Spectra and Grafting Effect of PMMA

Figure 2 shows the FTIR spectra of the untreated talc and the PMMA-coated talc before and after extraction with acetone for 24 h. It can be seen that there is an absorption peak located at about 1730 cm^{-1} in the extracted PMMA-coated talc. The peak is associated with the stretching vibration of the carbonyl groups of PMMA. The other peaks of PMMA are weak because of the strong bond vibrations in the talc.

To assess the grafting of PMMA onto the talc surface, the percentage of grafting was determined. The results are summarized in Table V. As shown in Table V, the percentage of grafting onto talc is very low. It indicates that PMMA is

Table IV The Particle Size Distribution Index of Talc and PMMA-Coated Talc

Talc/MMA	Talc	8	4	2	1
Batch process	21	5.5	82	48	50
Semicontinuous process (1250 mesh)	21	—	11	12	11
Semicontinuous process (2500 mesh)	24	4.8	5.2	4	3.8

Note: APS 1%; SDS 0.5%; 70°C, 4 h and 80°C, 1 h.

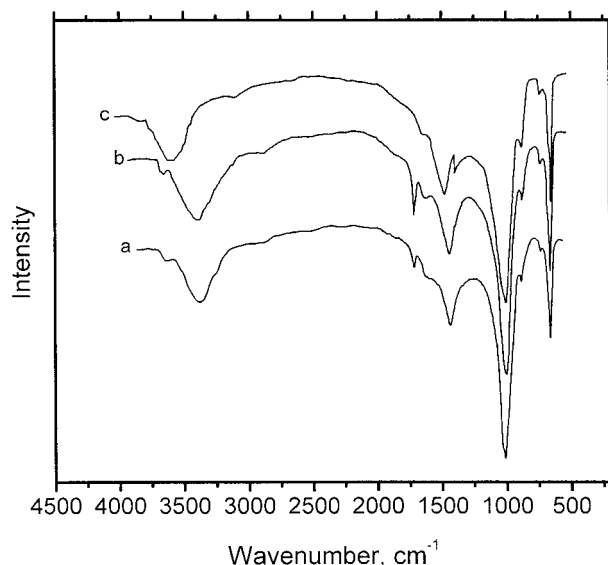


Figure 2 FTIR spectra of (a) PMMA-coated talc after extraction with acetone for 24 h; (b) PMMA-coated talc before extraction; and (c) untreated talc.

mainly covered on the talc surface by physical interaction, and there are only a few PMMA macromolecules that can intercalate and be absorbed into the talc.

Morphology

Figure 3 shows the SEM fractographs of the PVC-matrix composites (talc content: 20 wt % of talc). It can be seen that the edges and corners of the untreated talc in the composite are very smooth [Fig. 3(a)]. For the PMMA-coated-talc particles, they are uniformly distributed in the PVC matrix, and their surface is very rough. When the PMMA-coated-talc particles are produced by semicontinuous polymerization of MMA, the interface between talc and matrix is more adhesive. Moreover, it can be seen that the finer the talc is, the better the interface between talc and PVC matrix

Table V The Percentage of PMMA Grafting onto Talc Surface

Talc/MMA	8	6	4	2
Batch process	0.3	0.7	0.8	0.4
Semicontinuous process (1250 mesh)	0.4	0.9	1.2	1.0
Semicontinuous process (2500 mesh)	0.5	1.2	1.6	1.7

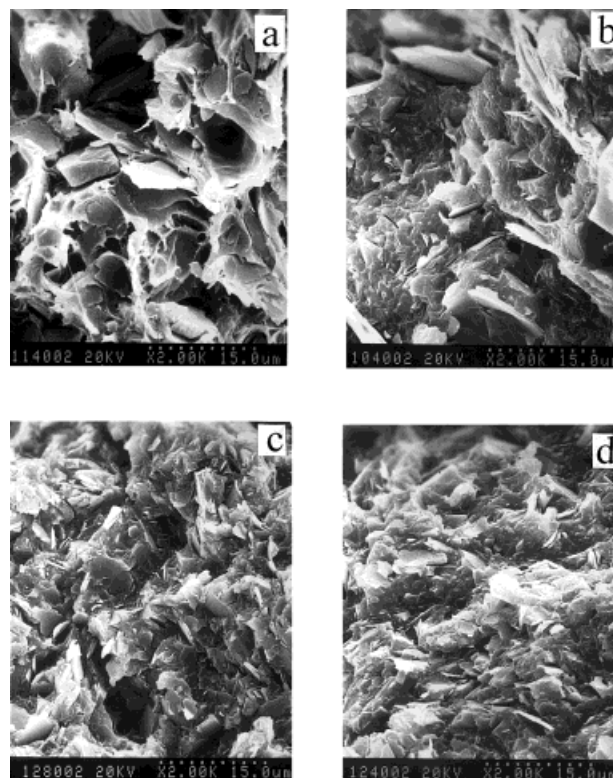


Figure 3 SEM fractographs of PMMA-coated-talc/PVC-matrix composites containing 20 wt % of talc. (a) untreated talc; (b) $w_{\text{PMMA}}/w_{\text{talc}} = 1/4$, 1250 mesh, batch process; (c) $w_{\text{PMMA}}/w_{\text{talc}} = 1/4$, 1250 mesh, semicontinuous process; (d) $w_{\text{PMMA}}/w_{\text{talc}} = 1/4$, 2500 mesh, semicontinuous process.

is. These results indicate that the PMMA covered on the surface of talc enhances the interaction between the talc and PVC, and improves the adhesion and morphological structure of PVC-matrix composites.

Mechanical Properties

The variation of Young's modulus and tensile strength for the PMMA-coated-talc/PVC composites (with 20 wt % filler content) are plotted against coating thickness in Figures 4 and 5, respectively. Apparently, the Young's modulus and tensile strength of the composites were enhanced because of the PMMA surface coating on the talc. They increased with increasing the PMMA coating thickness. Comparing the two polymerization processes, the modulus and tensile strength improvement, when the PMMA coating was produced by semicontinuous *in situ* polymerization, are higher than by the batch process. Moreover,

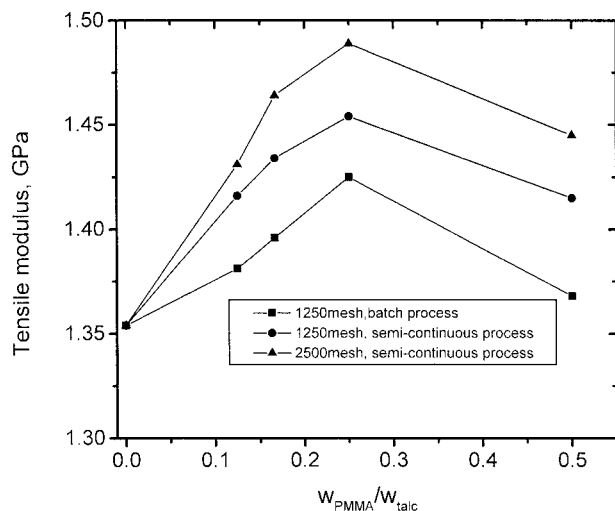


Figure 4 Variation of Young's modulus with the PMMA coating thickness for PMMA-coated-talc/PVC composites.

the modulus and tensile strength of the composites are higher when the talc fillers are finer. With further increase of the PMMA coating thickness, however, both modulus and tensile strength started to decrease. In other words, there is a critical PMMA coating thickness for tensile properties of the composites.

The poor mechanical properties of untreated-talc/PVC composites are due to the poor interfacial bonding between PVC and talc. It is well known that PVC and PMMA are completely mis-

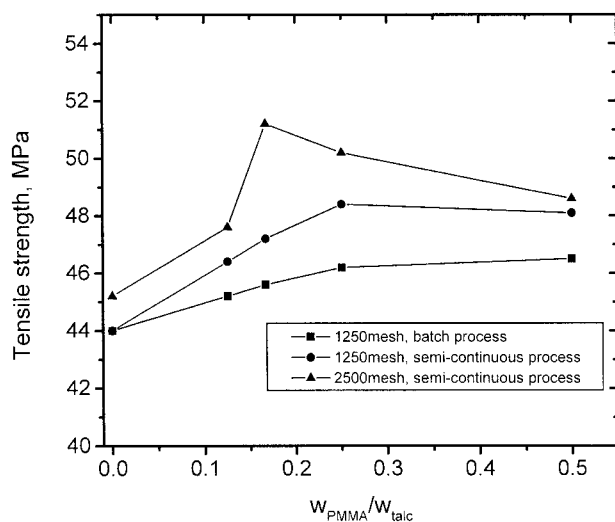


Figure 5 Variation of tensile strength with the PMMA coating thickness for PMMA-coated-talc/PVC composites.

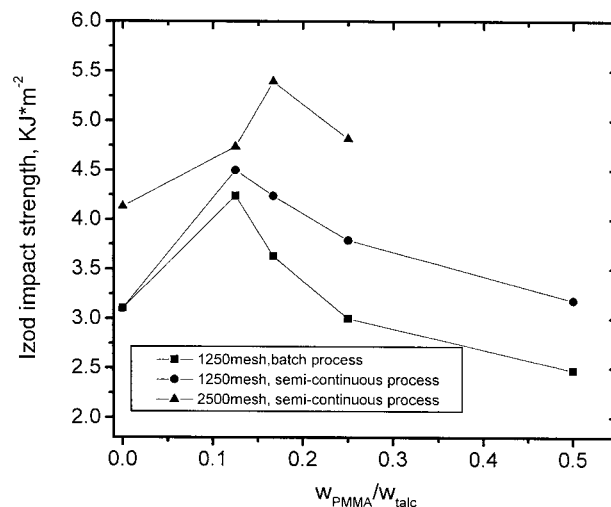


Figure 6 Variation of impact strength with the PMMA coating thickness for PMMA-coated-talc/PVC composites.

cible. When the surface of talc is covered by *in situ* polymerized PMMA, the PMMA enhances the interaction between the talc and PVC, and improves the interfacial adhesion. This leads to increasing Young's modulus and tensile strength of the PMMA-coated-talc/PVC composites. However, when the PMMA coating thickness is higher than the critical value, the mechanical properties of the composites decrease because of the low modulus and tensile strength of PMMA. Moreover, as discussed above, a more uniform particle size distribution was found for the talc treated by semicontinuous *in situ* polymerization than that by batch *in situ* polymerization. Also, the finer the talc is, the more uniform the particle size distribution is. These factors led to the conclusion that the semicontinuous *in situ* polymerization modification, together with a small talc particle size, are more favorable to improve the modulus and tensile strength of PMMA-coated-talc/PVC composites.

The variation of impact strength of PMMA-coated-talc/PVC composites with the PMMA coating thickness is shown in Figure 6. From the impact experiment, it was found that the impact strength of pure PVC is 3.2 kJm^{-2} . The impact strengths of PMMA-coated-talc/PVC composites are 3.37 and 4.05 kJm^{-2} , when filled with 1250- and 2500-mesh talc particles, respectively. It indicates that the talc with 2500 mesh size provides an obvious toughening to PVC matrix, but the talc with 1250 mesh has almost no significant effect. A definite size effect on impact toughening can

therefore be concluded. Liang and Li³⁶ found an obvious toughening effect with 3000-mesh glass bead-filled polypropylene. When the glass bead is treated by a silane coupling agent, the impact strength of the glass-bead/PP composite increases. In the present study, the impact strength of the PVC composites filled by 20 wt % of talc was improved when the talc was coated by PMMA. Their impact toughening behavior is the same as their tensile reinforcement, as discussed above, and there is an optimum and critical covering thickness of PMMA on the talc surface. Moreover, semicontinuous *in situ* polymerization modification and reduction of the particle size of talc are more efficient to enhance the impact strength of PMMA-coated-talc/PVC composite. The results can be explained by the following.

As discussed above, the *in situ* polymerized PMMA covering the talc surface improves the interfacial adhesion between talc and PVC matrix. The improved interfacial adhesion is favorable to transmit impact force and to absorb fracture energy. However, particles of the talc treated by semicontinuous *in situ* polymerization are finer and more uniform than those by the batch process. The finer the talc is, the finer and more uniform the modified talc is. Obviously, reducing the size of filler is helpful for improving the toughness of composites. According to adhesive theory,³⁷ there is a critical adhesive thickness to get an optimum adhesive strength. Our research results are in accordance with adhesive theory. So the excess PMMA on the surface of talc will reduce the impact strength of the PMMA-coated-talc/PVC composites by further increasing the covering thickness of PMMA.

CONCLUSION

MMA was *in situ* polymerized on the surface of talc by batch and semicontinuous emulsion processes, respectively. The treated talc was filled into PVC. The results showed that talc has no influence on the polymerization of PMMA. The PMMA thus produced was found to cover the talc surface, with very little grafted onto the talc surface. The size distribution of talc treated by semicontinuous emulsion polymerization is more uniform than that by batch polymerization. Morphological structure study of PVC-matrix composites revealed that the PMMA covered on the surface of talc improves the dispersion of talc in the PVC matrix and enhances the interfacial adhesion be-

tween the talc and PVC matrix. The mechanical properties of the composites, especially the impact strength, are improved. There is a critical covering thickness of PMMA. Further increase in the PMMA coating thickness adversely affected the mechanical properties of the composites.

REFERENCES

1. Boluk, M. Y.; Schreiber, H. P. *Polym Compos* 1986, 7, 295.
2. Candau, F. in *Polymerization in Organized Media*; Paleos, C., Ed.; Gordon and Breach: Reading, PA, 1992, p. 215.
3. Ruckenstein, E.; Park, J. S. *Polymer* 1992, 33, 405.
4. Li, R. K. Y.; Lu, S. N.; Choy, C. L. *J Thermoplast Compos Mater* 1995, 8, 304.
5. Li, Q.; Zheng, W. G.; Qi, Z. N.; Zhu, X. G.; Choy, C. L. *Sci Sinica B* 1993, 36, 18.
6. Li, Q.; Zheng, W. G.; Qi, Z. N.; *Sci Sinica B* 1992, 3, 236.
7. Lu, S. N.; Zhu, X. G.; Qi, Z. N.; Xu, H. *J Mater Sci Lett* 1995, 14, 1458.
8. Mascia, L. *Thermoplastics: Materials Engineering*; Applied Science Publishers: London, 1982.
9. Xue, G.; Dong, J.; Gu, X.; Qian, Y.; Sheng, W.; Wang, G. H. *J Adhes Sci Technol* 1994, 8, 971.
10. Zhu, X. G.; Choy, C. L.; Wu, X. Z.; Deng, X. H.; Qi, Z. N. *Proceedings of the International Symposium on Polymer Alloys and Composites*, Hong Kong, 1992.
11. Zheng, W. G.; Qi, Z. N.; Shi, L. H. *Chin Sci Bull* 1992, 37, 904.
12. Lu, S. N.; Yan, L.; Zhu, X. G.; Qi, Z. N. *J Mater Sci* 1992, 27, 4633.
13. Qu, Y. C.; Yu, Z. Z. *Polym Int* 1995, 37, 113.
14. Sekutowaski, D. *Plast Eng* 1987, Aug., 43.
15. Amdouni, N.; Sautereau, H.; Gerard, J. F.; Fernagut, F.; Coulon, G.; Lefebvre, J. M. *J Mater Sci* 1990, 25, 1435.
16. Amdouni, N.; Sautereau, H.; Gerard, J. F. *J Appl Polym Sci* 1992, 46, 1723.
17. Wu, D. C.; Tang, N.; Gu, D. Z. *Int Polym Proc* 1990, 1, 47.
18. Wu, G. C. *Polym J* 1982, 14, 571.
19. Ellsworth, M. W.; Novak, B. M. *J Am Chem Soc* 1991, 113, 2756.
20. Fitzgerald, J. J.; Landry, C. J. T.; Pochan, J. M. *Macromolecules* 1992, 25, 3715.
21. Haraguchi, K.; Usami, Y.; Yamamura, K.; Matsumoto, S. *Polymer* 1998, 39, 6243.
22. Huang, H. H.; Orlor, B.; Wikes, G. L. *Polym Bull* 1985, 14, 557.
23. Landry, C. J. T.; Coltrain, B. K.; Wesson, J. A.; Zumbulyadis, N.; Lippert, J. L. *Polymer* 1992, 33, 1496.

24. Mark, J. E. *J Appl Polym Sci* 1992, 50, 273.
25. Sur, G. S.; Mark, J. E. *Eur Polym J* 1985, 21, 1051.
26. Wen, J.; Mark, J. E. *J Appl Polym Sci* 1995, 58, 1135.
27. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1174.
28. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
29. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
30. Kyu, T.; Zhou, Z. L.; Zhu, G. C.; Tajuddin, Y.; Qutubuddin, S. *J Polym Sci* 1996, 34, 1761.
31. Kyu, T.; Zhou, Z. L.; Zhu, G. C.; Tajuddin, Y.; Qutubuddin, S. *J Polym Sci* 1996, 34, 1769.
32. Ou, Y. C.; Yang, F.; Chen, J. *J Appl Polym Sci* 1997, 6, 2317.
33. Ou, Y. C.; Yang, F.; Yu, Z. Z. *J Polym Sci* 1998, 36, 789.
34. Xie, X. L.; Li, B. G.; Pan, Z. R. *J Mater Sci Eng* 1999, 17, 63.
35. Gao, J. F. Graduation Thesis of Zhejiang University, Hangzhou, China, 1997.
36. Liang, J. Z.; Li, R. K. Y. *Polymer* 1999, 40, 3191.
37. Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.