# Improvement in Impact Property of Continuous Glass Mat Reinforced Polypropylene Composites

**XIAODONG ZHOU, GANCE DAI, QUNFANG LIN**

Polymer Processing Laboratory, East China University of Science and Technology, Shanghai, 200237, People's Republic of China

*Received 19 March 2001; accepted 5 July 2001*

**ABSTRACT:** The toughened polypropylene (PP) was obtained by the blending of PP with ethylene-propylene diene monomer (EPDM). The impact property of continuous glass mat-reinforced polypropylene was adjusted through three ways: different toughness PPs and their blends were used as matrices, the functionalized polypropylene was added into the matrix to control the interfacial adhesion; the ductile interlayer was introduced at the fiber/matrix interphase by the grafting and crosslinking of rubber chains on fiber surface. The effect of PP toughness, interfacial adhesion, and ductile interlayer on the mechanical properties of composite systems was studied. The impact toughness of GMT increased with increasing the matrix toughness, whereas the flexural strength and modulus decreased. The good interfacial adhesion resulted in the low impact toughness. However, GMT composite with high strength, modulus, and impact toughness could be obtained by the introduction of a ductile interlayer at fiber/matrix interphase. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2680–2688, 2002

**Key words:** poly(propylene); toughness; ductile; interfaces; thermoplastics, composites

## INTRODUCTION

Glass mat-reinforced polypropylene composites (GMT–PP) have been succeeded in automotive application because of their excellent properties and short processing time. Resistance to impact loading is of major concern in GMT for many engineering applications. Impact properties of composites depend on the architecture and property of reinforcement, the property of the matrix, the matrix/reinforcement adhesion, etc. The deformation and fracture in a neat resin and those in its fiber composite are obviously quite different. For fiber-reinforced composites, they can absorb the fracture energy by means of fiber breakage, matrix deformation and crack, interfacial debonding, fiber pull-out, material interlaminar separation, etc.[1–7] Generally, an improvement of the interfacial adhesion will result in an increase in the shear strength at an expense of the impact strength.[8,9] To eliminate this conflict, polymer interlayers that can absorb impact energy and can form physical and/or chemical bonds with the matrix were coated onto the fibers.[10–13] The mechanisms of rubber toughening in combination with fiber reinforcement in PP matrix were investigated by Jang et al. They believed that the delamination was the dominant failure mode in PP matrix composites subjected to low-velocity impact.[14,15] The fracture behavior of GMT–PP has been studied to a lesser extent.[5,16] In this article, the effect of matrix toughness, interfacial adhesion, and ductile interlayer on the impact tough-

*Correspondence to:* X. Zhou.

Contract grant sponsors: the National "863" Hi-Tech Projects Agency and Shanghai Ministry of Education.

Journal of Applied Polymer Science, Vol. 83, 2680–2688 (2002)

DOI 10.1002/app.10245

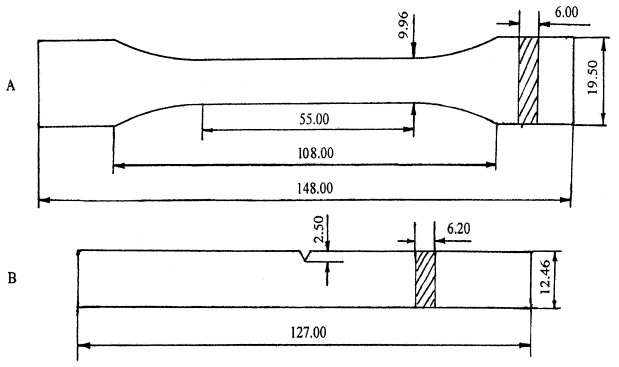



**Figure 1** Shape and dimension of injection specimens: (A) tensile specimen; (B) impact specimen.

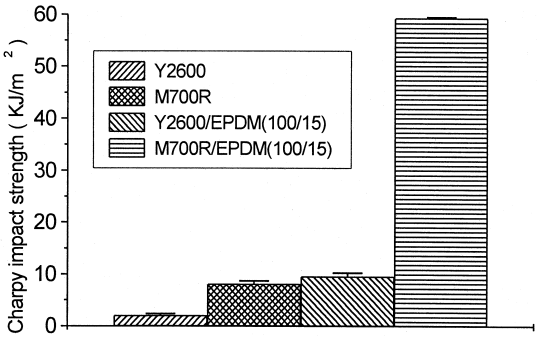



**Figure 2** Notch charpy impact strength of polypropylene and their blends.

ness of continuous glass mat reinforced polypropylene was investigated.

## EXPERIMENTAL

### Materials

Polypropylene (types Y1200, Y2600, and M700R) was purchased from the Plastics of Shanghai Petrochemical Complex (China). Coupling agent A-174 was supplied by Shanghai Yaohua Glass Company (China). *cis*-Polybutadiene rubber (CPBR) was supplied by Shanghai Rubbers Company (China). Ethylene-propylene diene monomer (EPDM) was generously supplied by DSM (The Netherlands). Benzoyl perxide (BPO) and all the solvents were chemically pure grade and were used without further purification. Polypropylene grafted maleic anhydride (PP-*g*-MAH) was prepared in our laboratory. Random continuous glass mat came from Nanjing Fiberglass Research & Design Institute (China).

### Blend of PP with EPDM

EPDM was plasticated in a SK-1600B plastic mixing mill (China) and cut into pellets. Then the blends of PP and EPDM in different weight proportions were carried out in a GE2.8.30-41 twin-screw extruder (Luxembourg) at a screw speed of 160 rev/min.

### Mechanical Testing of PP and Their Blends

PP and their blends were injection molded with a TTI-80 plastic injection machine (China) in accordance with China Standard for Test Methods GB1043-79. The shape and dimension of specimens were shown in Figure 1. Then the tensile property was measured on a LJ-10000N tensile machine (China) with a crosshead speed of 5 mm/min, and notched charpy impact strength was tested with a WPM-charpy impact tester (Germany).

### Introduction of Rubber Molecular Chain

The glass mats treated with sizing agent that contains an A-174 coupling agent were immersed in a BPO solution of acetone. After being vacuum dried, the mats were immersed in the solutions of different rubbers in xylene again. Then the mats were places in a vacuum oven, and the temperature was raised to 110°C in an atmosphere of nitrogen, under which conditions the rubbers reacted with coupling agent for 1 h.

### Preparation of Glass Mat-Reinforced PP (GMT–PP) Sheets

The matrix resin was rolled out in films about 1 mm thickness. Three resin films and two mats, precut to 280 × 280 $mm^2$, were sandwiched in a

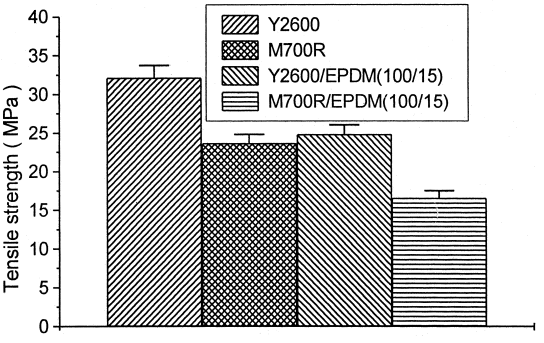



**Figure 3** Tensile strength of polypropylene and their blends.

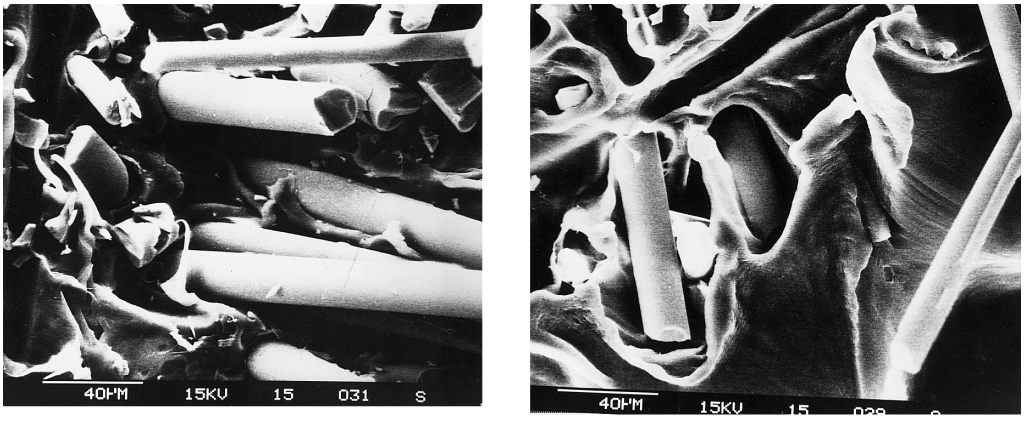



**Figure 4** SEM micrograph of impact specimen of GMT with the Y2600 matrix.

mold. Then the mold was placed in a molding press, pressure was raised to 0.9 MPa at a temperature of 210°C and maintained for 4 min. After rapid cooled to room temperature, the GMT–PP sheet was obtained.

### Mechanical Testing of GMT–PP Sheets

The notched Izod specimens were cut from the sheets and tested according to ASTM D256, the sample dimension was 63.5 × 12.75 × 3.5 $mm^3$ with a notch of 2.5 mm in depth. The flexural test was performed in accordance with ASTM D790. The charpy impact specimen of the dimension 55 × 6 × 3.5$mm^3$ was tested on the WPM-charpy impact tester at room temperature. Additionally, the different impact specimens were treated in a low-temperature oven for 4 h and quickly transferred to the impact tester. Then the low-temperature impact strength was tested. At least five specimens were tested for each sample. Dynamic mechanical tests were performed by a DMA2980 dynamic mechanical analyzer (American) at a speed of 1°/min with a forced constant amplitude-fixed frequency of 10 Hz, the specimen dimension was 63.5 × 12.75 × 3.5$mm^3$.

## RESULT AND DISCUSSION

### Effect of Matrix Toughening on the Impact Property of GMT–PP

#### *Toughening of PP*

Figure 2 showed the impact strength of PP matrix and their blends with EPDM.

M700R is the copolymer of propylene and ethylene, where the existence of a few ethylenic segments results in a less regular structure. So it has lower crystallinity and higher toughness than the homopolymer Y2600. After PP blended

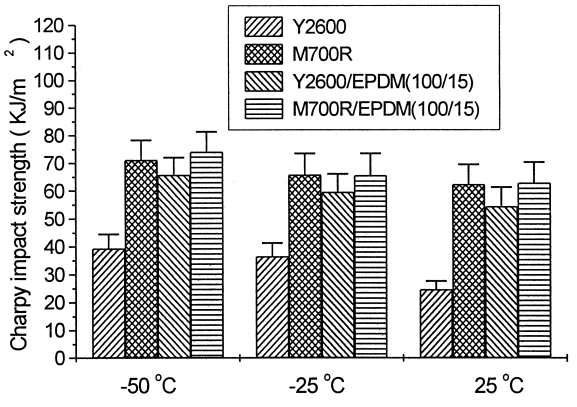



**Figure 5** Charpy strength of GMT–PP with various matrices at different temperatures.

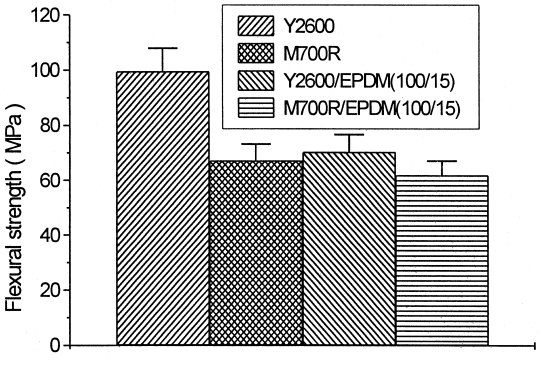



**Figure 6** Effect of the matrix on the flexural property of GMT–PP.

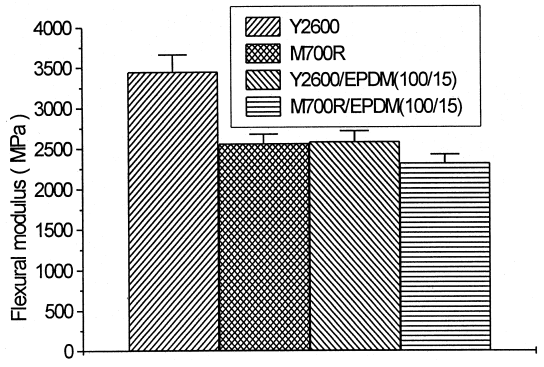



**Figure 7** Effect of the matrix on the flexural modulus of GTM–PP.

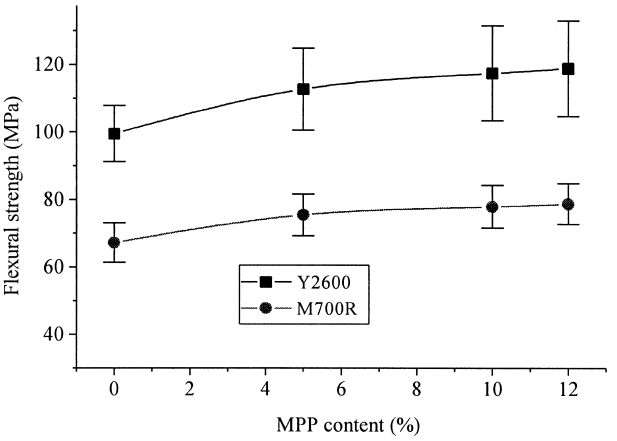



**Figure 9** Effect of PP-*g*-MAH content on the flexural stength of GMT–PP.

with EPDM, EPDM particles served as stress concentrators to initiate a multiplicity of small crazes around the particles, thus absorbing impact energy and diverting the ultimate catastrophic crack. The branching of crazes also help stop crazes from growing catastrophically.[17] Hence, the impact strength of blends at room and low temperature was significantly improved.

The tensile strength of injection specimens of PP and their blends was shown in Figure 3. After PP blending with EPDM, their tensile strength decreased.

### *Effect of Matrix Toughness on the Impact Resistance of GMT–PP*

The different GMT–PP sheets (fiber content 25.6%) were obtained by various PP and their blends compounding with the same continuous glass fiber mat.

Similar to other fiber composites, GMT–PP can absorb impact energy by means of fiber breakage, matrix deformation and crack, interfacial debonding, fiber pull-out, etc.[1–7] It is approved by the fractographs of impact specimen of GMT with Y2600 matrix (as can be seen in Fig. 4). Generally, the continuous fiber mat composites show more impact resistance than the discontinuous fiber composites. Figure 5 demonstrated that the impact strength of GMT with different PP matrices increased with increasing the matrix toughness and decreasing test temperature in the temperature range of 25 to −50°C.

For the brittle materials, the impact energy absorbing was restricted by the limited deforma-

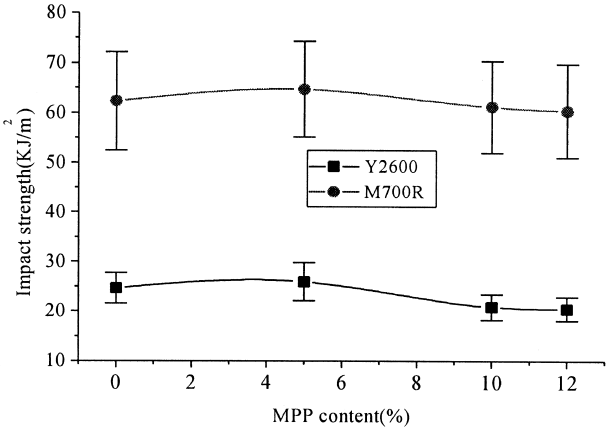



**Figure 8** Effect of PP-*g*-MAH content on the impact strength of GMT–PP.

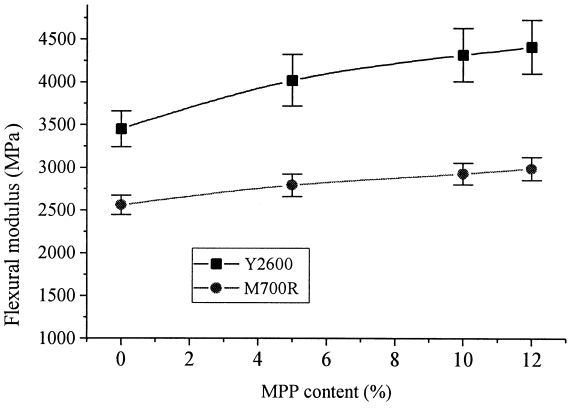



**Figure 10** Effect of PP-*g*-MAH content on the flexural modulus of GMT–PP.

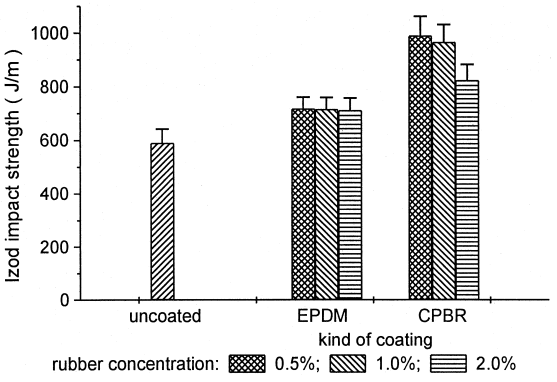



**Figure 11** Effect of rubber coating on the Izod impact strength of GMT–PP.

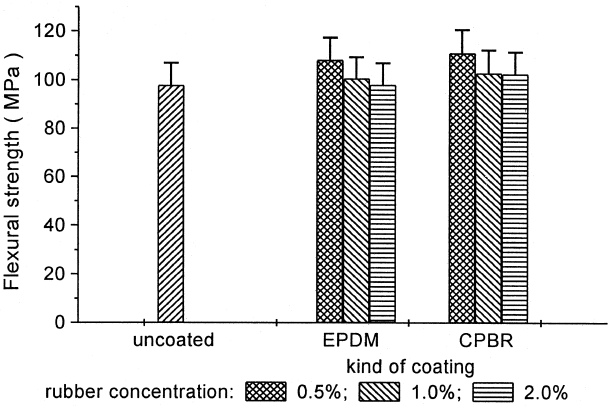



**Figure 12** Effect of rubber coating on the flexural strength of GMT–PP.

tion capability of the material, whereas the ductile materials showed large deformation and corresponding energy absorption. In the case of GMT–PP sheets, the contribution of matrix deformation to the total absorbed energy was not to be ignored. The rubber toughening of the brittle matrix (Y2600) significantly improved the impact resistance of fiber composites. Figure 5 showed the charpy strength could be increased from 24.6 to 54.5 kJ/m$^2$. However, toughening a ductile matrix (M700R) did not result in a meaningful improvement in impact property. Figures 6 and 7 showed the different extent of decrease in flexural strength and modulus with the increase in matrix toughness.

At low temperature, the absorbing energy of GMT by matrix deformation and crack decreased. However, interfacial shear strength increased at such low temperature.[18] Therefore, interfacial debonding could absorb more energy. Moreover, the compressive stresses generated by the shrinkage of matrix resin increased with temperature decreasing. Accordingly, the energy dissipation of frictional fiber pull-out would be enhanced. Because the rise in energy absorption of interfacial debonding and frictional pull-out was higher than the decrease in energy absorption of matrix deformation and crack, the impact strength of GMT improved at low temperature.

To obtain good impregnation and adhesion between fiber and matrix, the better melting fluidity of matrix is required during the melt impregnation process and the compression molding of GMT. Poor flow of the matrix results in a number of void and flaw, and the mechanical properties decreases accordingly.

## Effect of Fiber–Matrix Adhesion on the Impact Resistance of GMT–PP

When the interfacial adhesion is poor, the advancing crack can propagate by debonding at the fiber/matrix interphase, thus dissipating the impact energy and enhancing the impact resistance. When the interfacial adhesion is good, debonding becomes more difficult and the advancing crack propagates through the fibers, resulting in low impact properties.[8,9] So it is necessary for obtaining GMT–PP with excellent comprehensive mechanical properties to design a proper interfacial adhesion. After maleated polypropylene (PP-*g*-MAH) was added to the PP matrix, the chemical and polar interactions of PP matrix-maleated PP-fiber improve the interfacial adhesion between the fiber and the matrix.[19] Figures 8–10 showed the impact strength,

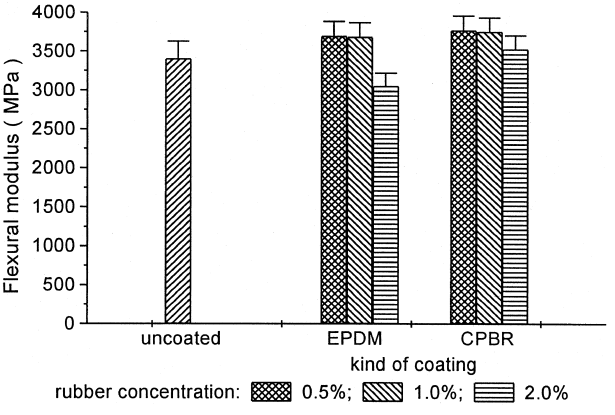


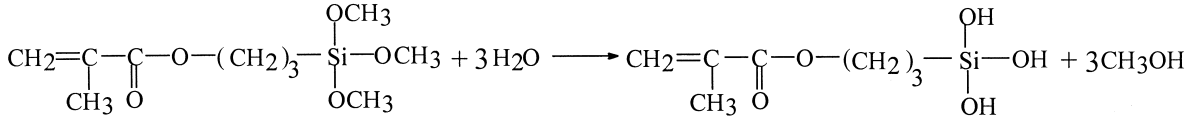

**Figure 13** Effect of rubber coating on the flexural modulus of GMT–PP.

flexural strength, and modulus of GMT sheets (fiber content 25.6%) in which PP-*g*-MAH was added. In the case of the Y2600/glass mat system, when the interfacial bonding strength tended to a certain value, the system cannot further absorb impact energy by means of interface debonding, fiber pull-out, and friction between the fiber and the matrix. This leads to the decrease in impact resistance of the system. In the case of the M700R/glass mat system, the impact resistance of the system does not decrease significantly when its interfacial adhesion was good.

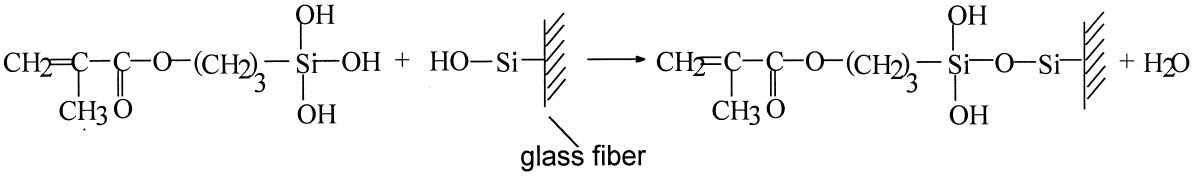
### Effect of Ductile Interlayer on Impact Property of GMT–PP

The continuous glass mat before and after the grafting rubber was compounded with the same matrix (Y1200+1%carbon black) under the same conditions. The impact strength, flexural strength, and modulus of the produced GMT–PP sheets (fiber content 27.3%) were shown in Figure 11–13.

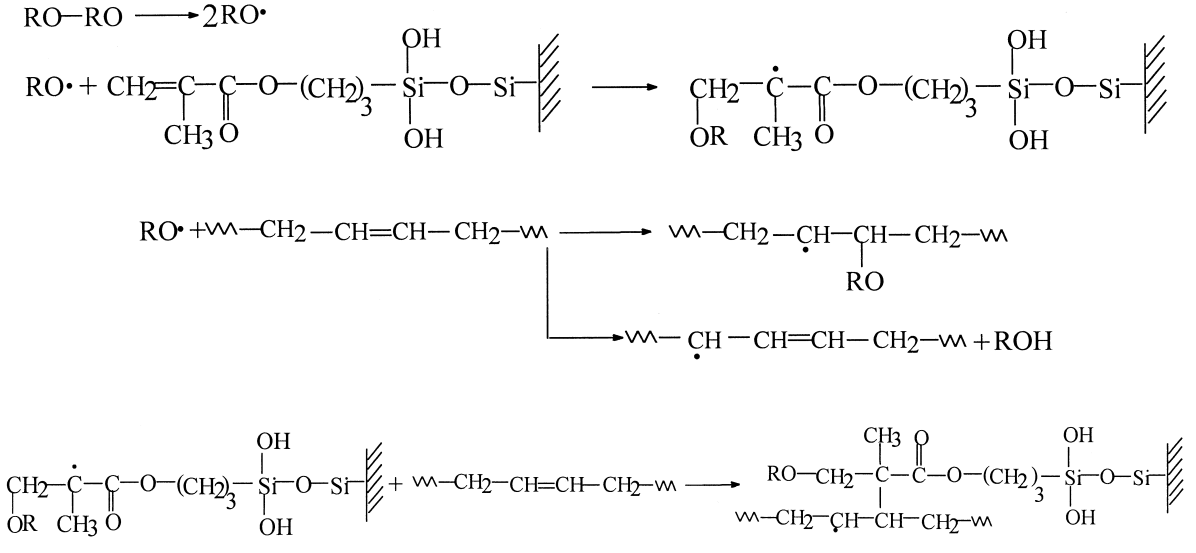
The proposed reaction pattern can be schematically represented as follows: coupling agent A-174 hydrolyzes to Si—OH:[20]

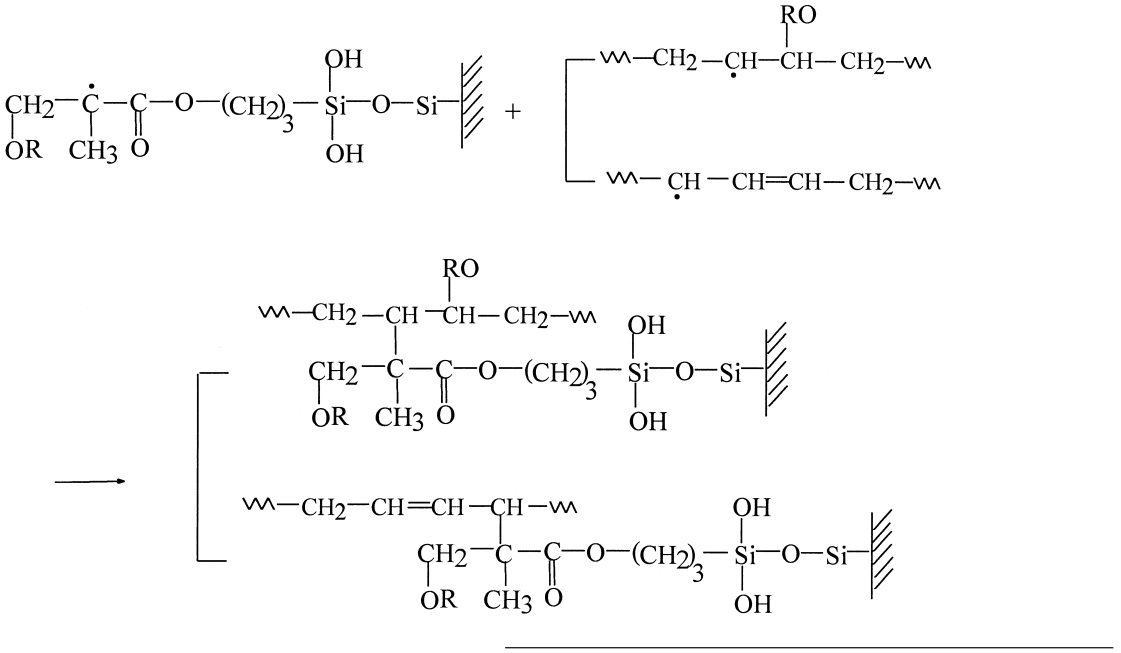


Then the produced Si—OH condenses with the Si—OH at glass fiber surface:




Some rubber chains graft with the coupling agent on the fiber surface under BPO initiating, which leads to the chemical bonding between rubber chains and fibers:





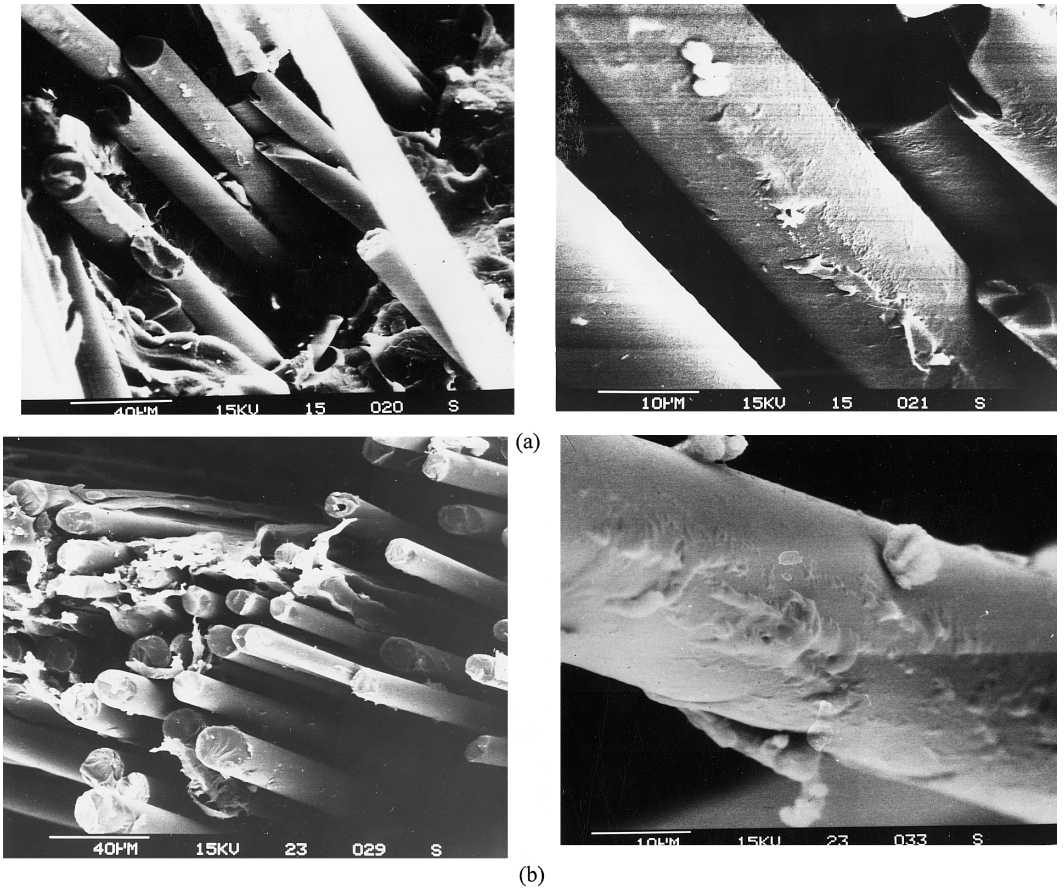



**Figure 14** SEM micrograph of the impact specimen of GMT–PP introducing the ductile interlayer (Y1200 matrix) (a) coated with 0.5% CPBR solution; (b) coated with 2% CPBR solution.

The fracture of GMT–PP exhibits more complicattion after introducing the ductile interlayer at the fiber/matrix interphase.[21,22] Figure 14 showed the fractographs of impact specimen of GMT–PP introducing the CPBR ductile interlayer. A number of fiber pull-outs were observed in both of the two systems coated with rubber solutions of different concentrations. Some resin adhered on the fiber surface when the fiber was coated with 0.5% CPBR solution, whereas the failure of the ductile interlayers was observed in the system coated with 2% CPBR solution.

The ductile interlayer having large deformability encourages relatively bigger matrix deformation, which results in the increase in shear bands. When cracks extend to the interface of the matrix/interlayer, the interlayer can prevent crack propagation by its further deformation. It can also dissipate energy by the matrix/interlayer debonding or absorb energy by the craze initiation. When the crack reaches the interface of interlayer/fiber, the impact energy can be dissipated by the interlayer/fiber debonding. In addition, the energy absorption due to fiber pull-out is higher than that of the composite system without a ductile interlayer because of stronger frictional force. After introducing a ductile interlayer at the fiber/matrix interphase, a significant impact improvement can be noticed in Figure 11; the Izod impact strength of GMT with CPBR interlayer is reached 989.2 J/m when the GMT without a ductile interlayer only has 589.6 J/m Izod impact strength.

After the glass mat was treated with CPBR and EPDM solution, the rubber chains were grafted onto the fiber surface or crosslinked around the fibers. The thickness of the coatings relates to the concentration of the rubber solutions. When the treated mats were compounded with the PP matrix, a better compatibility between rubber and PP results in their chain entanglement, which leads to the improvement in the interfacial adhesion of the composite. When the load is applied to the composites, the local stress concentration will decrease the load-bearing capability of the composites. However, the interlayer is very desirable to reduce the local stress concentration and transfer the stress to the fibers. At the same time, it can relieve the thermal stress due to the difference in thermal properties of the PP and the fiber.[23–25] Thus, the flexural modulus and strength of the composites were also improved.

With a further increase in CPBR concentration, the energy absorption of the interphase de-

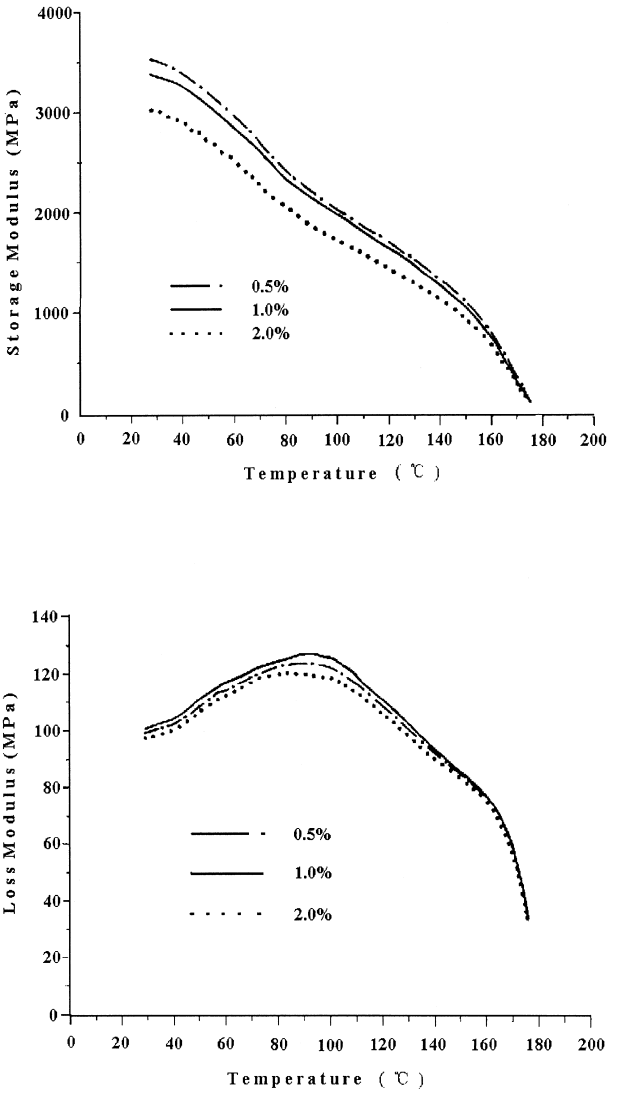



**Figure 15** Effect of rubber concentration on dynamic mechanical property of GMT–PP.

formation and the interfacial debonding decreases because the strength and modulus of the ductile interlayer are much lower than that of the matrix. At the same time, the energy dissipation due to the plastic deformation of ductile interlayer and matrix in the vicinity of fiber decreases during the process of fiber pull-out. The impact resistance and flexural property decrease accordingly. The dynamic mechanical spectrum of the composite system with a CPBR interlayer was shown in Figure 15. At the initial stage, the storage modulus of the system decreases with increasing the concentration of CPBR, and the loss modulus has no significant change.

The compatibility of EPDM and PP is similar to that of CPBR. However, the strength and mod-

ulus of EPDM and the EPDM/fiber bond are lower than that of CPBR, which contains more double bonds. The energy absorption of the CPBR interlayer deformation is higher. So the composite with the CPBR interlayer has higher impact and flexural properties.

## CONCLUSIONS

The toughened PP system having high impact toughness was obtained by means of blending with EPDM. The impact toughness of the GMT–PP sheet increases with increasing the matrix toughness. However, the ductile matrices and their toughened systems usually have low flexural and tensile properties, which would sacrifice such properties of GMT–PP materials.

A proper bond between the fiber and the matrix can be designed. When cracks reach the interphase, the weak interfacial adhesion promotes interfacial debonding and subsequent frictional fiber pull-out, which give rise to the total composite fracture toughness. However, the weak interfacial adhesion results in the lower tensile and flexural properties.

After a proper ductile interlayer was introduced into the composite, a significant impact improvement could be obtained without the decrease in flexural strength and modulus. With the rise in the ductile interlayer thickness, both the impact resistance and flexural strength and modulus decreased.

This research was supported by the National "863" Hi-Tech Projects Agency and Shanghai Ministry of Education.

## REFERENCES

1. Yeung, P.; Broutman, L. J. Polym Eng Sci 1978, 18, 62.
2. Cooper, G. A.; Kelly, A. J Mech Solids 1967, 15, 279.
3. Beaumont, P. W. R. J Adhesions 1974, 6, 107.
4. Feies-Kozma, Z. S.; Karger-Kocsis, J. J Reinforced Plastics Compos 1994, 13, 822.
5. Ericson, M.; Berglund, L. Compos Sci Technol 1992, 43, 269.
6. Jang-Ky, K.; Sehvoom, L.; Yiu-Wing, M. J Mater Sci 1994, 29, 554.
7. Karger-Kocsis, J.; Czigany, T. J Mater Sci 1993, 28, 2438.
8. Agarwal, B. D.; Broutman, L. J. Analysis and Performance of Fiber Composites; John Wiley & Sons: New York, 1980, p. 33.
9. Subramanian, R. V.; Crasto, A. S. Polym Compos 1986, 7, 201.
10. Bell, J. P.; Chang, J.; Rhee, H. W.; Joseph, R. Polym Compos 1987, 8, 46.
11. Chang, J.; Bell, J. P.; Shkolnik, S. J Appl Polym Sci 1987, 34, 2105.
12. Dagli, G.; Sung, N. H.; Pro ACS Polym Mater Sci Eng 1987, 56, 410.
13. Benatar, A.; Gutowski, T. G. Polym Compos 1986, 7, 84.
14. Jang, B. Z.; Liu, C .W.; Wang, C. Z.; Skih, W. K. J Thermoplastic Compos Mater 1988, 1, 242.
15. Jang, B. Z. In Polypropylene: Structure, Blends and Composites, Vol. 3, Composites; Karger-Kocsis, J., Ed.; Chapman and Hall: London, 1995, p. 316.
16. Karger-Kocsis, J. In Polypropylene: Structure, Blends and Composites, Vol.3: Composites; Karger-Kocsis, J., Ed.; Chapman and Hall: London, 1995, p.142.
17. Manson, J. A.; Sperling, L. J. Polymer Blends and Composites; Plenum Press: New York, 1976, p. 104.
18. Pegoretti, A.; Fidanza, M.; Migliaesi, C.; Di Benedetto, A. T. Composites Part A 1998, 29, 283.
19. Zhou, X. D.; Dai, G. C.; Guo, W. J.; Lin, Q. F. J Appl Polym Sci 2000, 76, 1359.
20. Plueddemann, E. P. In Interphases in Polymer, Ceramic, and Metal Matrix Composites; Hatsuo, I., Ed.; Elsevier, New York, 1988, p. 17.
21. Broutman, L. J.; Agarwal, B. D. Polym Eng Sci 1974, 14, 581.
22. Kardos, J. L. Polym Preprint, 1983, 24, 185.
23. Di Benedetto, A. T.; Nicolais, L. Interphases in Composites; Applied Science Publishers: London, 1978, p. 153, chap. 8.
24. Termonia Y. J Mater Sci 1990, 25, 103.
25. Rhee, H. W.; Bell, J.. P. Polym Compos 1991, 12, 213.