

Dynamically Cured Polypropylene/Epoxy Blends

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ABSTRACT: The dynamic vulcanization process, usually used for the preparation of thermoplastic elastomers, was used to prepare polypropylene (PP)/epoxy blends. The blends had crosslinked epoxy resin particles finely dispersed in the PP matrix, and they were called dynamically cured PP/epoxy blends. Maleic anhydride grafted polypropylene (MAH-g-PP) was used as a compatibilizer. The effects of the reactive compatibilization and dynamic cure were studied with rheometry, capillary rheometry, and scanning electron microscopy (SEM). The crystallization behavior and mechanical properties of PP/epoxy, PP/MAH-g-PP/epoxy, and dynamically cured PP/epoxy blends were also investigated. The increase in the torque at equilibrium for the PP/MAH-g-PP/epoxy blends indicated the reaction between maleic anhydride groups of MAH-g-PP and the epoxy resin. The torque at equilibrium of the dynamically cured PP/epoxy blends increased with increasing epoxy resin content. Capillary rheological measurements also showed that the addition of MAH-g-PP or an increasing epoxy resin content increased the viscosity of PP/epoxy blends. SEM

micrographs indicated that the PP/epoxy blends compatibilized with PP/MAH-g-PP had finer domains and more obscure boundaries than the PP/epoxy blends. A shift of the crystallization peak to a higher temperature for all the PP/epoxy blends indicated that uncured and cured epoxy resin particles in the blends could act as effective nucleating agents. The spherulites of pure PP were larger than those of PP in the PP/epoxy, PP/MAH-g-PP/epoxy, and dynamically cured PP/epoxy blends, as measured by polarized optical microscopy. The dynamically cured PP/epoxy blends had better mechanical properties than the PP/epoxy and PP/MAH-g-PP/epoxy blends. With increasing epoxy resin content, the flexural modulus of all the blends increased significantly, and the impact strength and tensile strength increased slightly, whereas the elongation at break decreased dramatically. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1437–1448, 2004

Key words: poly(propylene) (PP); epoxy resin; dynamic cure

INTRODUCTION

Dynamic vulcanization is the process of vulcanizing elastomers during melt mixing with molten thermoplastics, resulting in the production of a new class of materials called thermoplastic vulcanizates.^{1–3} This process was first introduced by Gessler¹ in 1962 and then was developed by Fisher² and Coran and co-workers.^{3–8} at the end of the 1980s. Thermoplastic vulcanizates combine the excellent processing characteristics of thermoplastics with the elastic properties of elastomers. A large number of elastomers and thermoplastics have been blended to produce thermoplastic vulcanizates with dynamic vulcanization, including nitrile rubber (NBR)/poly(vinyl chloride) (PVC),⁴ NBR/polyamide (PA),⁵ polypropylene (PP)/ethylene-propylene–diene rubber (EPDM),⁹ and PA/EPDM.¹⁰ Some thermoplastic vulcanizates have been commercialized with trade names such as Santoprene and Geolast. Many thermoplastic vulcanizates have been attributed to the dynamic vulcanization of elastomers in the molten plastics; however, there are no

publications concerning dynamic vulcanization applied to thermoplastic/thermosetting resin systems.

Epoxy resins constitute a major class of thermosetting resins and are widely used as matrices for fiber-reinforced composites, adhesives, and coatings as well as other engineering materials. However, not all the properties of the materials are beneficial, such as the inherent brittleness. Many high-performance engineering thermoplastics have been used to toughen epoxy resins, such as poly(ether sulfone),^{11,12} poly(ether imide),^{13,14} and poly(ether ether ketone).^{15,16} Recently, many studies have focused on thermoplastics modified with epoxy resins. Venderbosch et al.^{17–19} introduced an epoxy resin as a reactive solvent for the processing of an intractable polymer, such as poly(2,6-dimethyl-1,4-phenylene ether) (PPE). In contrast to the use of miscible polystyrene (PS) as a processing aid, the advantageous thermal and mechanical properties of the PPE phase are recovered.²⁰ The epoxy resin is not only effective as a solvent during processing and impregnation but additionally provides an *in situ* formed structure of the final composite material after curing.^{21–23} Many inventions are related to methods for making curable melt-processed materials composed of mixtures of PPE and PS, particularly high-impact PS, with uncured epoxy resin components, which consist of an epoxy resin and a curing

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agent.^{24–29} The use of multifunctional epoxy resins to increase the melt strength of poly(ethylene terephthalate) (PET) was reported by Japon et al.,³⁰ with the aim of producing PET foams by an extrusion process. Pittman and coworkers^{31,32} recently investigated the addition of crosslinked epoxy resin to thermoplastics to develop PVC/thermosetting resin blends to improve the mechanical properties of PVC. Until now, there have been no publications concerning PP modified with the epoxy resin.

PP has an important place among synthetic polymers because of its growing commercial applications. However, it exhibits lower modulus and stiffness than common engineering plastics. Glass fibers and inorganic fillers are often used to enhance the modulus and stiffness of PP.^{33–36} Dutra et al.²³ reported hybrid composites based on PP, carbon fibers, and epoxy matrices. The aim of this work was to use dynamic vulcanization for the preparation of new types of PP/epoxy blends with the structure of crosslinked epoxy resin particles finely dispersed in the PP matrix. The blends were prepared in the mixing chamber of a Haake rheometer (Germany) through the dynamic curing of an epoxy resin in molten PP. Because the epoxy resin and PP were immiscible, maleic anhydride grafted polypropylene (MAH-g-PP) was used as a compatibilizer. The mechanical properties, rheological properties, and crystallization behavior of dynamically cured PP/epoxy blends were investigated.

EXPERIMENTAL

Raw materials

PP (F401) was produced by Yangzi Petrochemical Co., Ltd. (Nanjing, China) and had a melt-flow index of 1.9 dg/min (230°C, 2.16 kg). Diglycidyl ether of bisphenol A resin (weight-average molecular weight = 4500 g/mol) was supplied by Shanghai Resin Co., Ltd. (Shanghai, China). The curing agent, 2-ethylene-4-methane-imidazole (EMI-2,4), was produced by Shanghai Chemical Agent Co. (Shanghai, China). MAH-g-PP with an MAH content of 1% was prepared by Shanghai Sunny New Technology Development Co., Ltd. (Shanghai, China).

Sample preparation

Before being blended, MAH-g-PP and the epoxy resin were dried at 80°C *in vacuo* for about 8 h. Unless otherwise specified, dynamically cured PP/epoxy blends were prepared in the mixing chamber of a Haake RC90 rheometer at 190°C and 50 rpm. MAH-g-PP and PP were first mixed for 2 min, and then the epoxy resin was added. Two minutes later, the curing agent (EMI-2,4) was added as the mixing continued. The total mixing process lasted about 10 min. The

composition was moved out and compression-molded in a press at 195°C for 10 min and then was cold pressed to produce samples for testing.

Measurements

The tensile properties were measured with an Instron 4465 tester (UK) at a crosshead speed of 20 mm/min according to ASTM D 638. The notched Izod impact strengths were tested with a Ray-Ran universal pendulum impact tester (UK) at an impacting pendulum speed of 3.5 m/s according to ASTM D 256. The flexural properties were measured with an Instron 4465 tester (UK) and a three-point-loading rig, and the central head was loaded onto the specimen at a speed of 1.7 mm/min according to ASTM D 790.

Capillary rheological measurements were performed at 230°C with an Instron capillary rheometer (length/diameter = 40). End effects were neglected, but the Rabinowitsch correction was applied.³⁷

PP/epoxy blend samples were fractured under liquid nitrogen, coated with gold, and observed with a Hitachi S-2150 scanning electron microscope (Japan). The samples of the dynamically cured PP/epoxy blends were etched with dimethyl benzene for 10 min.

The crystallization behavior was analyzed with a PerkinElmer (United States) Paris 1 differential scanning calorimetry (DSC) instrument in a nitrogen atmosphere. For each test, a 2–3-mg sample was first heated to 200°C at 50°C/min and was then maintained at this temperature for 5 min to eliminate any previous thermal history. The specimen was subsequently cooled to 40°C at a cooling rate of 10°C/min and then heated to 200°C at 10°C/min for data collection.

The PP spherulites were studied on thin films with a Leica DMLPI polarized optical microscope with an automatic hot-stage thermal control (Germany). The samples were sandwiched between microscope cover glasses, melted at 200°C for 10 min, and then rapidly cooled to 136°C. The PP spherulites were observed with micrographs taken at certain intervals.

RESULTS AND DISCUSSION

Torque versus time

Torque measurements can be used to give qualitative information concerning the chemical reactivity and the extent of reaction in reactively compatibilized blends.³⁸

Figure 1 shows the relationship between the torque and time for the PP/epoxy (70/30) and PP/MAH-g-PP/epoxy (60/10/30) blends at 190°C. The torque at equilibrium of the PP/MAH-g-PP/epoxy (60/10/30) blend is obviously higher than that of the PP/epoxy (70/30) blend. Shieh, Liao, and Chang³⁹ reported using MAH-g-PP and a multifunctional epoxy resin as

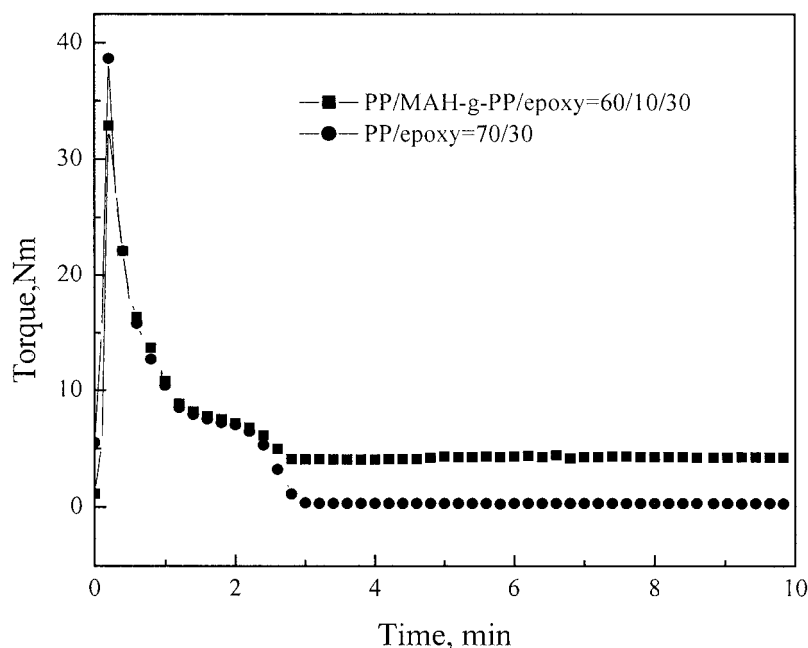


Figure 1 Torque versus time for 70/30 PP/epoxy and 60/10/30 PP/MAH-g-PP/epoxy blends at 190°C.

dual reactive compatibilizers for PP/poly(butylene terephthalate) (PBT) blends. As MAH-g-PP has active maleic anhydride (MAH) groups, the functional groups of MAH-g-PP can react with the hydroxyl or epoxy groups of the epoxy resin. We believe that the reactions between the groups take place in the PP/MAH-g-PP/epoxy blends and lead to the increasing viscosities of PP/PBT/MAH-g-PP blends through the addition of MAH-g-PP; this indicates that reactions

occur between MAH-g-PP and the epoxy resin. The increase in the torque in the PP/MAH-g-PP/epoxy blends should be attributed to the reaction between the functional groups and resultant copolymers.

The effect of the epoxy resin content on the torques of dynamically cured PP/epoxy blends is shown in Figure 2. The addition of the curing agent (EMI-2,4) at the mixing time of 4 min leads to an obvious rise in the torque. This shows that the epoxy resin has been cured

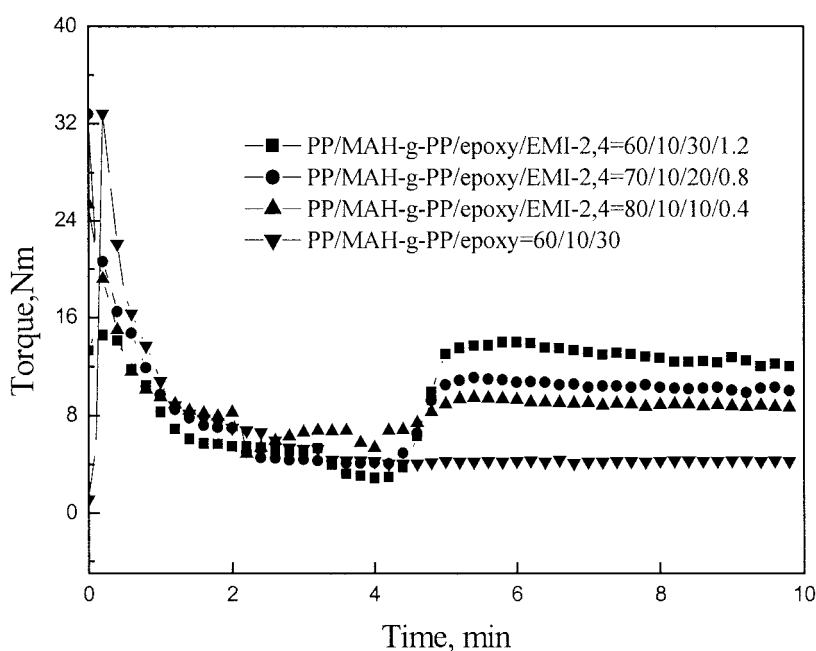
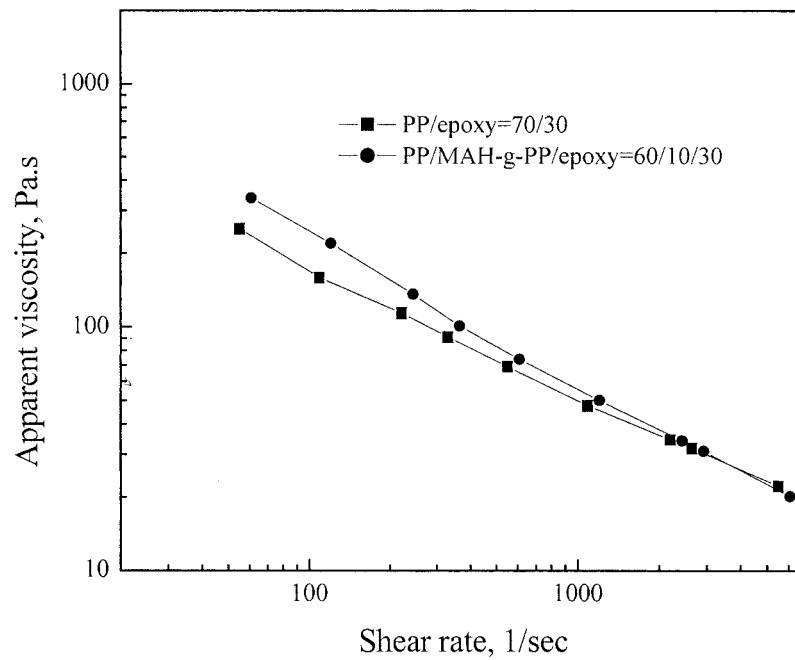
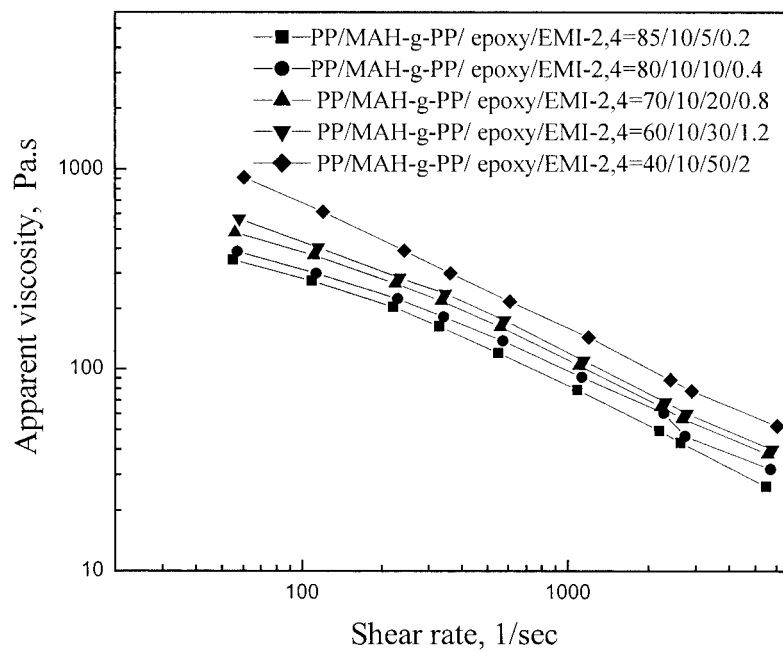


Figure 2 Torque versus time for dynamically cured PP/epoxy blends at 190°C.



(a)



(b)

Figure 3 Apparent viscosity of (a) PP/epoxy and PP/MAH-g-PP/epoxy blends and (b) dynamically cured PP/epoxy blends as a function of the shear rate at 230°C.

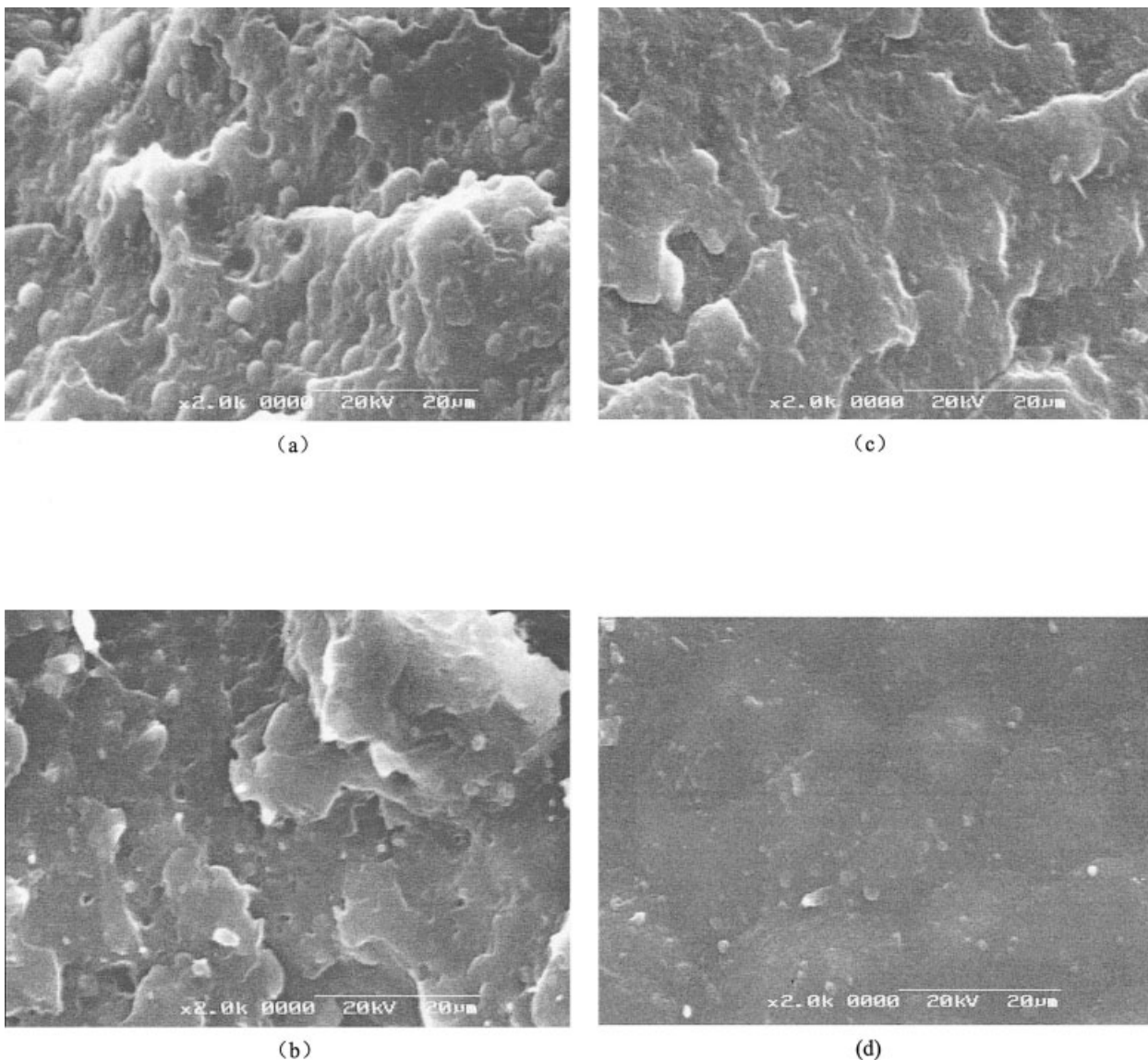


Figure 4 SEM micrographs of PP/epoxy blends: (a) 70/30 PP/epoxy, (b) 60/10/30 PP/MAH-g-PP/epoxy, (c) 60/10/30/1.2 PP/MAH-g-PP/epoxy/EMI-2,4 (dynamically cured, without etching), and (d) 60/10/30/1.2 PP/MAH-g-PP/epoxy/EMI-2,4 (dynamically cured, with etching).

by EMI-2,4 during its mixing with molten PP. The torque at equilibrium of dynamically cured PP/epoxy blends increases with increasing epoxy resin content.

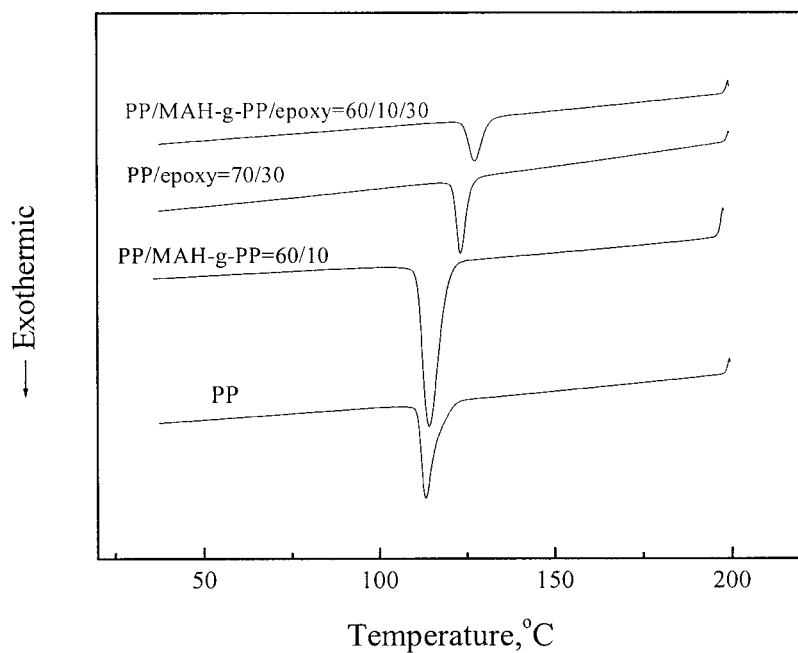
Capillary rheometry

Figure 3 illustrates the apparent viscosity versus the shear rate for the PP/epoxy (70/30), PP/MAH-g-PP/epoxy (60/10/30), and dynamically cured PP/epoxy blends at 230°C. All the molten blends present non-Newtonian fluid and shear-thinning behavior. The viscosity of the PP/MAH-g-PP/epoxy (60/10/30) blend is higher than that of the PP/epoxy (70/30) blend. The apparent viscosity of the dynamically cured PP/epoxy blends increases with increasing ep-

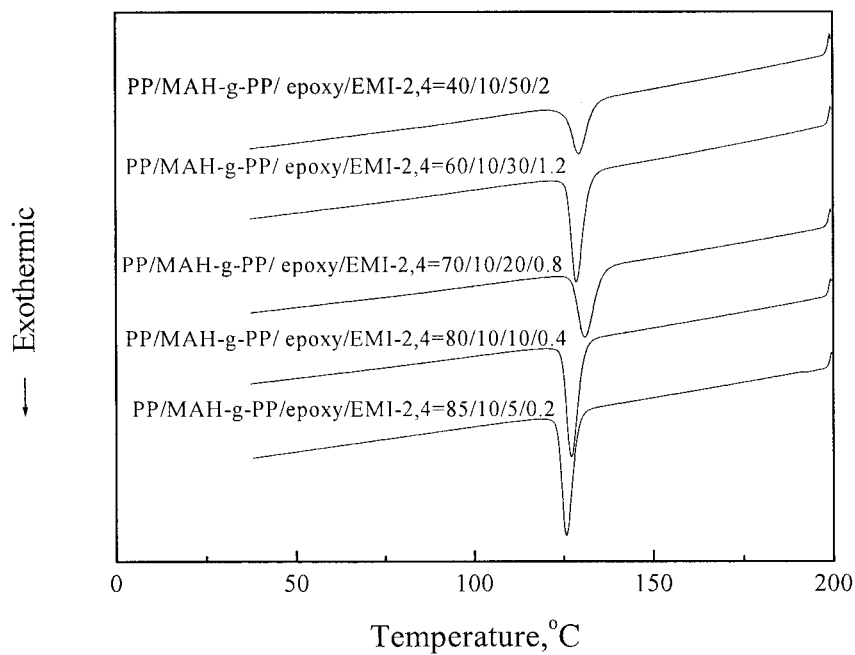
oxy resin content. Chiou and Chang⁴⁰ investigated the reactive compatibilization of polyamide 6/PBT with a multifunctional epoxy resin, and they suggested that a higher viscosity from a better compatibilized blend could be related to the expected higher molecular weight from coupling reactions and the increased interfacial friction of the *in situ* formed copolymers anchored along the interface.

Scanning electron microscopy (SEM) analysis

Figure 4 shows SEM micrographs of the fracture morphology of the PP/epoxy blends. For the PP/epoxy (70/30) blend [Fig. 4(a)], the epoxy resin is dispersed as spherical particles with a diameter of 3–4 μm in the

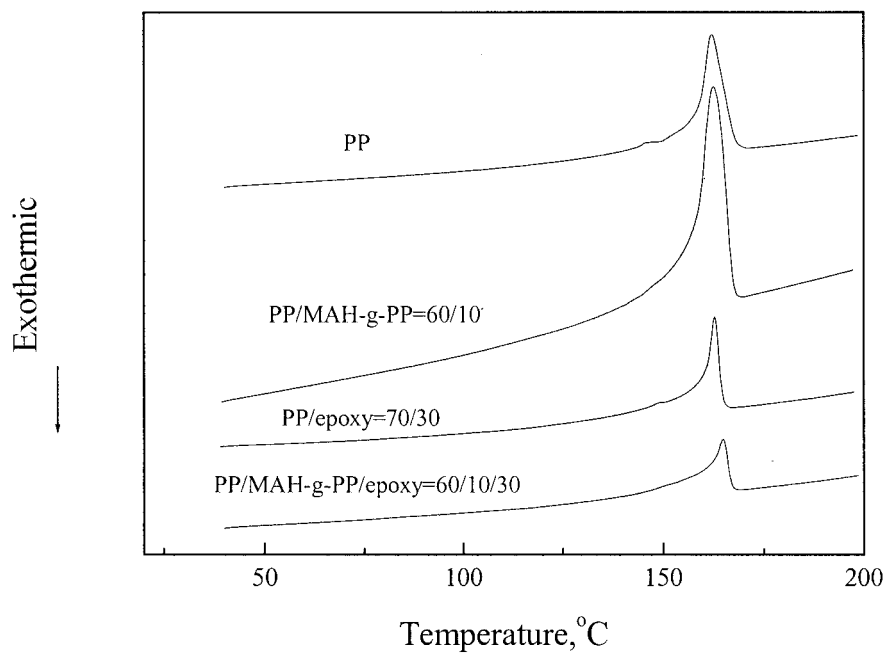


(a)

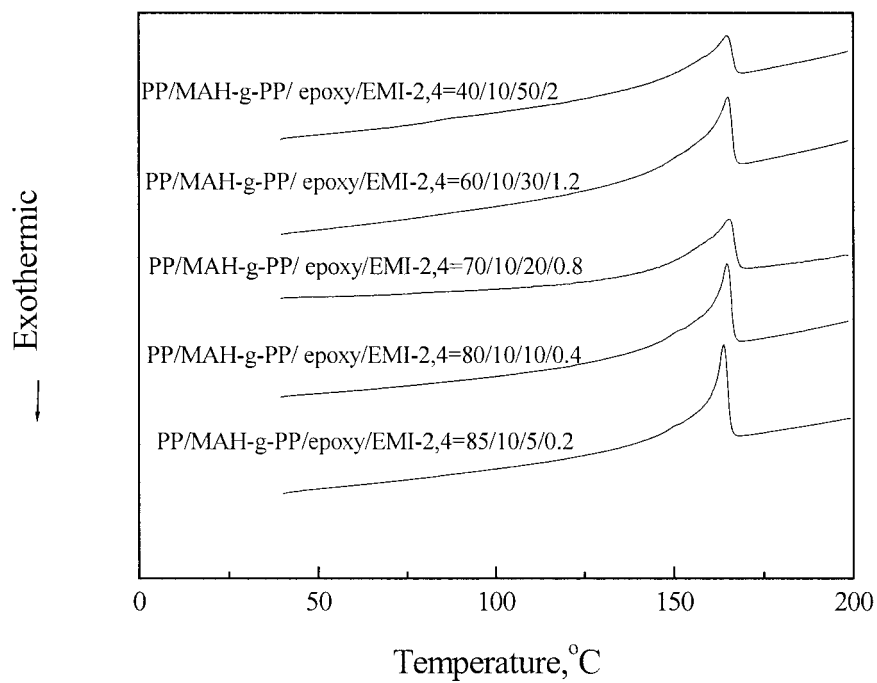


(b)

Figure 5 DSC thermograms at the first cooling of (a) PP, PP/MAH-g-PP, PP/epoxy, and PP/MAH-g-PP/epoxy and (b) dynamically cured PP/epoxy blends.



(a)



(b)

Figure 6 DSC thermograms at the second heating of (a) PP, PP/MAH-g-PP, PP/epoxy, and PP/MAH-g-PP/epoxy and (b) dynamically cured PP/epoxy blends.

TABLE I
DSC Analysis Results for PP and PP/Epoxy Blends

Composition	T_m (°C)	T_c (°C)	X_c (wt %)
PP	162.3	113.1	56.1
60/10 PP/MAH-g-PP	162.6	114.2	56.5
70/30 PP/epoxy	163.5	123.2	53.3
60/10/30 PP/MAH-g-PP/epoxy	164.9	131.3	50.7
85/10/5/0.2 PP/MAH-g-PP/epoxy/ EMI-2,4	163.7	125.8	46.7
80/10/10/0.4 PP/MAH-g-PP/epoxy/ EMI-2,4	164.8	127.3	50.1
70/10/20/0.8 PP/MAH-g-PP/epoxy/ EMI-2,4	165.4	130.0	47.8
60/10/30/1.2 PP/MAH-g-PP/epoxy/ EMI-2,4	165.0	128.6	49.5
40/10/50/2 PP/MAH-g-PP/epoxy/ EMI-2,4	164.8	129.5	39.5

T_m -peak melting temperature; T_c -peak crystallization temperature.

PP matrix, and the boundaries between the dispersed phase and the PP matrix are distinct. For the PP/MAH-g-PP/epoxy (60/10/30) blend [Fig. 4(b)], fine epoxy particles with an average diameter of about 1.0 μm are distributed in the PP matrix through the addition of 10 wt % MAH-g-PP. The boundaries between these epoxy resin particles and the PP matrix are obscure. It can be concluded that MAH-g-PP can improve the compatibility between PP and the epoxy resin. The MAH groups of MAH-g-PP can react with the hydroxyl or epoxy groups of the epoxy resin. The reaction should have taken place in the PP/MAH-g-PP/epoxy blends to form a copolymer to act as a compatibilizer for promoting a fine dispersion of the epoxy resin phase.

Figure 4(c,d) shows the fracture morphology of the dynamically cured PP/epoxy (60/10/30/1.2) blend. The boundaries between the epoxy resin and PP become more obscure, and the cured epoxy resin particles in the blend without etching cannot be seen, and this indicates that the epoxy resin particles have been embedded by the PP matrix. The cured epoxy resin particles in the etched blend can be seen, and the average diameter of the particles is about 0.8 μm . The epoxy resin was cured under high shear in the chamber of a Haake rheometer, and the cured epoxy resin was crushed into particles.

Crystallization and melting behaviors

PP is a highly crystalline polymer that can crystallize rapidly even under quenched conditions. Figures 5 and 6 show the first cooling and second heating DSC scans of PP, PP/MAH-g-PP (60/10), PP/epoxy (70/30), PP/MAH-g-PP/epoxy (60/10/30), and dynamically cured PP/epoxy blends, and Table I gives a

summary of the crystallization and melting data from the DSC thermograms. The crystallinity of the PP component (X_c) in the blends has been calculated with the following equation:

$$X_c(\%) = (\Delta H / \Delta H_0) \times (100/x) \quad (1)$$

where ΔH is the measured heat of crystallization of the blend, ΔH_0 (170 J/g) is the heat of crystallization of 100% crystalline isotactic PP,⁴¹ and x is the mass fraction of PP in the blend.

For PP, PP/MAH-g-PP, and all PP/epoxy blends, only a single crystallization peak can be seen. All the crystallization peak temperatures of the PP/epoxy blends are higher than the crystallization peak of PP (113.1°C). The crystallization peak temperature of PP in the PP/epoxy (70/30) blend is approximately 12°C higher than that of pure PP. The crystallization peak temperature of PP in the dynamically cured PP/epoxy blends is slightly higher than that of PP in the PP/epoxy (70/30) blend. A shift of the crystallization peak to a higher temperature suggests that all uncured and cured epoxy resin particles in the blends can act as effective nucleating agents, accelerating the crystallization of the PP component in the blends. The smaller epoxy resin particles in the dynamically cured PP/epoxy blends are the result of an increase in the number of nucleating agents, and they improve the crystallization peak temperature of PP. Li et al.⁴² reported that polycarbonate (PC) could act as a nucleating agent and accelerate the crystallization of PP in the PP/PC blends. For all PP/epoxy blends, X_c is lower than that of pure PP. X_c in the dynamically cured PP/epoxy blend containing 50 wt % epoxy resin is 39.5% and decreases by 17% compared with that of pure PP. The melting temperature of PP in all the PP/epoxy blends is slightly higher than that of pure PP (162.2°C). A similar result was reported for EPDM/PP blends.⁴³ EPDM can act as a nucleating agent for PP. However, X_c decreases in the presence of EPDM, and this indicates that this nucleating effect of EPDM does not necessarily imply an increase in the crystallinity.⁴⁴ An increase in the melting temperature of PP in the blends is directly related to the size of the PP crystals.⁴³

Figure 7 shows the polarized optical micrographs of PP, PP/epoxy (70/30), PP/MAH-g-PP/epoxy (60/10/30), and dynamically cured PP/epoxy (60/10/30/1.2) blends. The spherulites of PP are about 80 μm in diameter and obviously larger than those of PP in all the PP/epoxy blends. The spherulites of PP in the PP/epoxy (70/30) blend are larger than those of PP in the PP/MAH-g-PP/epoxy (60/10/30) and dynamically cured PP/epoxy (60/10/30/1.2) blends. This shows that the addition of the epoxy resin results in a decrease in the size of the spherulites of PP in all the

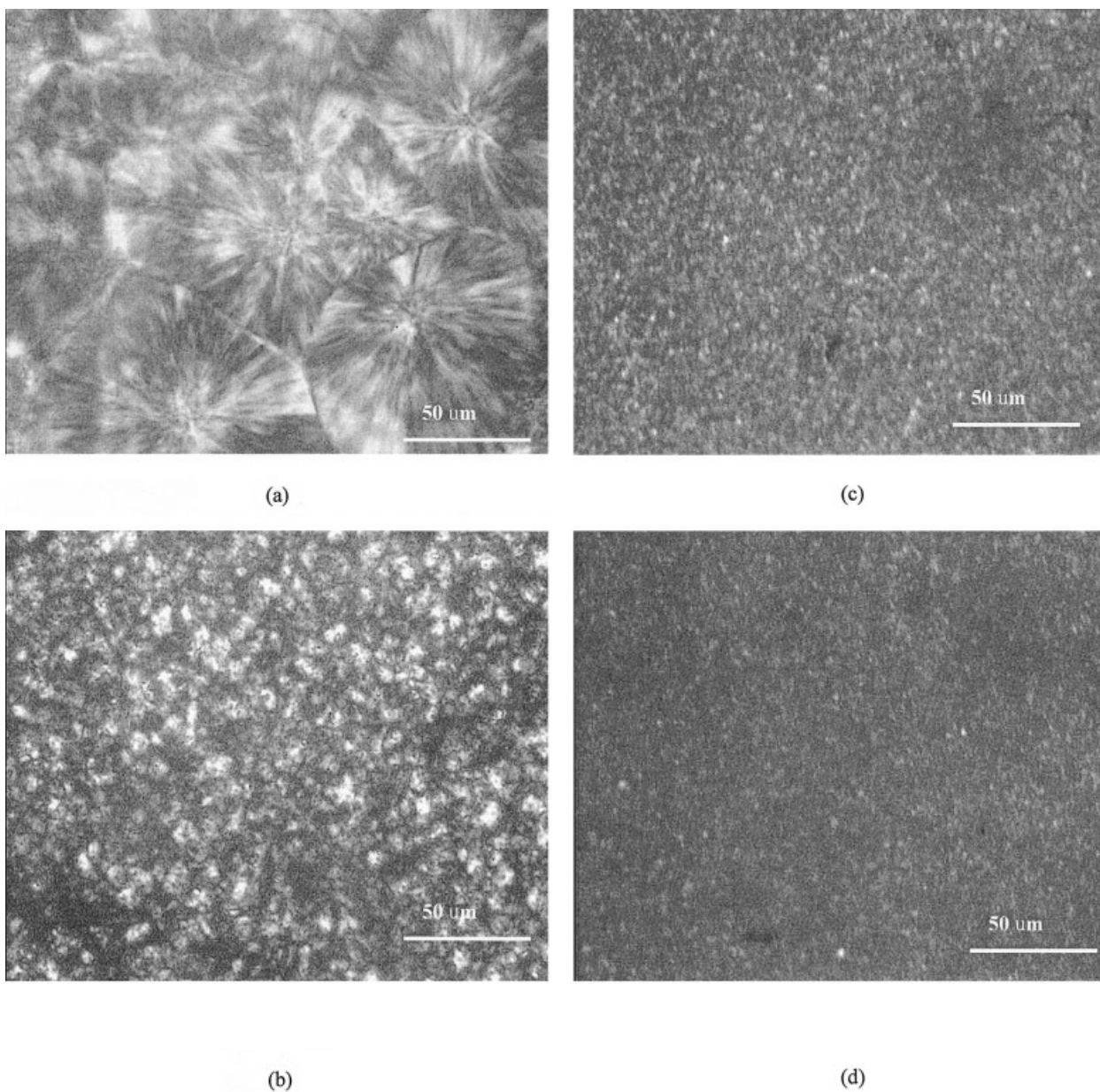


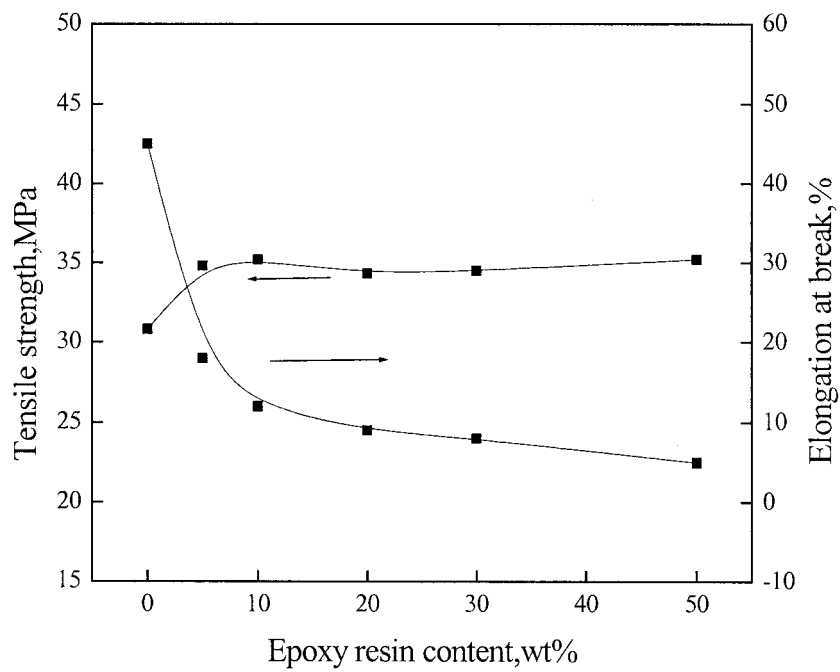
Figure 7 Polarized optical micrographs of PP, PP/epoxy, PP/MAH-g-PP/epoxy and dynamically cured PP/epoxy blends at 136°C for 30 min: (a) PP, (b) 70/30 PP/epoxy, (c) 60/10/30 PP/MAH-g-PP/epoxy, and (d) 60/10/30/1.2 PP/MAH-g-PP/epoxy/EMI-2,4.

PP/epoxy blends, and some spherulites are too small to be seen in the polarized optical micrographs. We believe that the epoxy resin particles become the nucle-

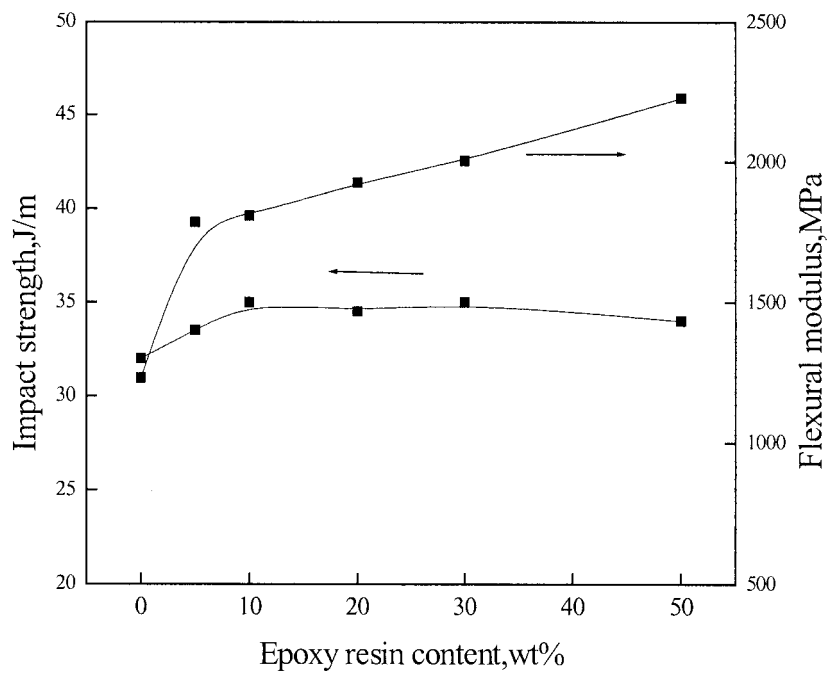
ating sites, the number of spherulites increases dramatically, and the size of the spherulites decreases significantly. Zhang et al.⁴⁵ reported that the addition of an

TABLE II
Mechanical Properties of PP and Different Systems of PP/Epoxy Blends

Composition	Impact strength (J/m)	Tensile strength (MPa)	Elongation at break (%)	Flexural modulus (MPa)
PP	30	30.8	300	1250
PP/epoxy (70/30)	18	25.6	12	1577
PP/MAH-g-PP/epoxy (60/10/30)	25	35.2	21	1659
PP/MAH-g-PP/epoxy/EMI-2,4 (60/10/30/1.2)	35	35.0	24	2003



(a)



(b)

Figure 8 Effect of the epoxy resin content on the mechanical properties of dynamically cured PP/epoxy blends.

ethylene–octene copolymer to the PP matrix could also considerably reduce the spherulite size of PP.

Mechanical properties

Table II shows the mechanical properties of the PP and PP/epoxy blends. The addition of 30 wt % epoxy resin to the PP matrix improves the flexural modulus but reduces the impact strength, tensile strength, and elongation at break because of the poor compatibility between PP and the epoxy resin. Through the addition of 10 wt % MAH-g-PP (used as a compatibilizer), the PP/MAH-g-PP/epoxy (60/10/30) blend has a higher flexural modulus and tensile strength but a lower elongation at break than pure PP. The dynamically cured PP/epoxy (60/10/30/1.2) blend has the highest flexural modulus (2003 MPa) and impact strength (35 J/m), which increase by 60 and 20%, respectively, in comparison with those of pure PP. The tensile strength of the dynamically cured PP/epoxy (60/10/30/1.2) blend is almost the same as that of the PP/MAH-g-PP/epoxy (60/10/30) blend, but it is higher than that of pure PP. The elongation at break of the dynamically cured PP/epoxy (60/10/30/1.2) blend is much lower than that of pure PP. As shown in Table II, the dynamically cured PP/epoxy blends have better mechanical properties than the PP/epoxy and PP/MAH-g-PP/epoxy blends.

The effect of the epoxy resin content on the mechanical properties of the dynamically cured PP/epoxy blends is shown in Figure 8. With increasing epoxy resin content, the flexural modulus of the blends increases gradually. The flexural modulus of the dynamically cured PP/epoxy blends at an epoxy resin content of 5 wt % increases by 50% in comparison with that of PP/MAH-g-PP blend. The impact strength and tensile strength of the dynamically cured PP/epoxy blends slightly increase with an increasing epoxy resin content, whereas the elongation at break decreases rapidly. When the epoxy resin content is greater than 10 wt %, the impact strength and tensile strength of the blends slightly vary. These results show that the modulus and stiffness of the dynamically cured PP/epoxy blends obviously increase with the addition of the epoxy resin.

CONCLUSIONS

The dynamic vulcanization process has been successfully applied to PP/epoxy blends. The blends have been prepared in the mixing chamber of a Haake rheometer through the dynamic curing of an epoxy resin in molten PP, and they have been called dynamically cured PP/epoxy blends. Because the epoxy resin and PP are immiscible, MAH-g-PP has been used as a compatibilizer. The dynamically cured PP/epoxy

blends have the structure of the epoxy resin particles finely dispersed in the PP matrix. The PP/epoxy blends compatibilized with MAH-g-PP have finer domains than the PP/epoxy blends. The crystallization peaks move to a higher temperature for all the PP/epoxy blends, and this indicates that the epoxy resin particles can act as effective nucleating agents. The spherulites of pure PP are larger than those of PP in the PP/epoxy, PP/MAH-g-PP/epoxy, and dynamically cured PP/epoxy blends. The dynamically cured PP/epoxy blends have better mechanical properties than the PP/epoxy and PP/MAH-g-PP/epoxy blends. With increasing epoxy resin content, the flexural modulus of the dynamically cured PP/epoxy blends increases gradually, and the impact strength and tensile strength increase slightly, whereas the elongation at break decreases rapidly.

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