

Preparation of High-Performance Polyethylene via a Novel Processing Method of Combining Dynamic Vulcanization with a Silane-Grafted Water-Crosslinking Technique

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ABSTRACT: A novel processing method of combining dynamic vulcanization with the silane-grafted water-crosslinking technique to improve the comprehensive properties of polyethylene (PE) is reported. PE was grafted with vinyl triethoxysilane (VTEO) first, and then, *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane epoxy resin was dynamically cured in a PE-g-VTEO matrix through a twin-screw extruder to prepare PE-g-VTEO/epoxy blends. Polyethylene-graft-maleic anhydride (PE-g-MAH) was used as a compatibilizer to improve the interaction between PE-g-VTEO and the epoxy resin. The results show that the novel processing method improved the strength, stiffness, and toughness of the blends, especially

the heat resistance of the blends, by the addition of the dynamically cured epoxy resin as the reinforcement. PE-g-MAH increased the compatibility between PE-g-VTEO and the epoxy resin, which played an important role in the improvement of the comprehensive properties of the blends. In addition, after treatments in both hot air and hot water, the comprehensive properties of blends were further improved, thanks to the further curing reaction of epoxy with PE-g-VTEO. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2539–2548, 2011

Key words: crosslinking; polyethylene (PE); reactive processing; vulcanization

INTRODUCTION

Polyethylene (PE) has excellent electrical and mechanical properties, excellent resistance to cold flow, and easy processing at low cost. However, its application as a structural material still faces great challenges because of its low strength and low application temperature. To solve this issue, several methods have been applied.

The first one is the addition of inorganic fillers, such as calcium carbonate, alumina, talc, kaolin, and mica,^{1,2} to improve the stiffness of PE. However, the incorporation of inorganic fillers into PE can adversely affect its processability and ductility.³

The second is the crosslinking method. The crosslinking of PE can create a three-dimensional macromolecular structure, which leads to an improvement in its properties, including operating temperature, creep resistance, application temperature, mechanical properties, and solvent resistance.⁴ Crosslinking

methods can be further classified into radiation, peroxide, and silane grafting on the basis of various mechanisms.⁴ Each method has its own features. For example, the radiation method is expensive, and the peroxide method makes the crosslinked PE hard to reprocess. In contrast, the crosslinking of PE through silane grafting has gained much attention in recent years because of its outstanding advantages, such as good processability and low cost. Popular silanes for this purpose include vinyl trimethoxysilane and vinyl triethoxysilane (VTEO). They have conventionally been introduced into PE by melt grafting with peroxide as an initiator to form hydroxyl groups followed by silane grafting in the presence of water. The crosslinked PE has good mechanical properties and antisolvent abilities.^{5–8} However, the strict requirement remains to enhance the upper temperature limit of as-formed PE for specific applications.

The third method is the addition of a thermoset resin into the polyolefin matrix via dynamic vulcanization. Dynamic vulcanization is an effective method for preparing thermoplastic vulcanized materials through the melt-mixing process.^{9–11} This technology has led to voluminous thermoplastic and thermoset resin blends with the objective of improving the application temperature, stiffness, and impact properties.^{12–15} The improvement in the properties of PE/thermoset resin blends is restricted without any chemical bonding.

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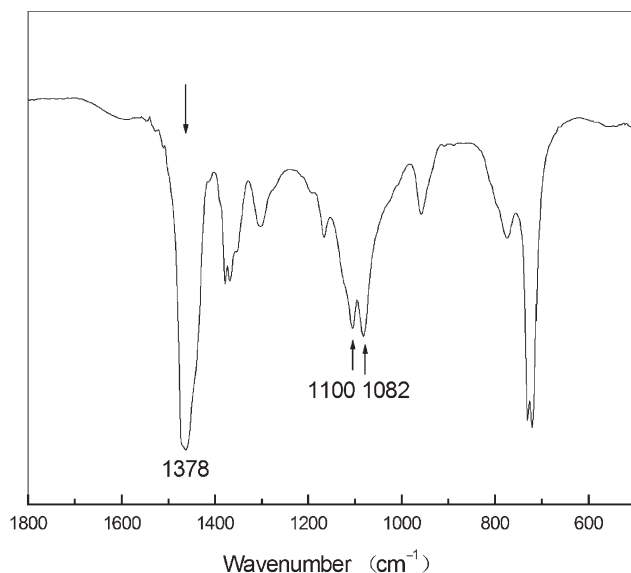


Figure 1 FTIR spectrum of a PE-g-VTEO sample.

To make full use of the advantages of these methods, a combination of dynamic vulcanization and silane grafting was designed to improve the mechanical properties, application temperature, and dimensional stability of PE. The main process steps for this PE modification were (1) PE grafting with VTEO, (2) blending with thermoset resins via twin-screw extrusion, and (3) further treatment under different conditions. In this study, *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy resin was used as the reinforcement because of its excellent heat resistance and mechanical strength. The properties of the different blends prepared with various methods were compared. The results prove that the combination of dynamic vulcanization and silane grafting was effective in improving the comprehensive performance of PE.

EXPERIMENTAL

Materials

Linear low-density PE, supplied by Sabcic Co., Ltd. (Maoming, China), had a melt flow index of 2 dg/min at 230°C under 2.16 kg of force. TGDDM was purchased from Shanghai Synthetic Resin Research Institute (Shanghai, China). Maleic anhydride

(MAH) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Dicumyl peroxide (DCP) was purchased by Shanghai Fuzhe Chemical Co., Ltd. (Shanghai, China). VTEO was supplied by Evonik Industries (Dusseldorf, Germany). Dibutyltin dilaurate (DBTDL) was supplied by Nanjing Dingchen Chemical Co. (Nanjing, China).

Sample preparation

Preparation of PE-g-VTEO

PE pellets were mixed with DCP and VTEO in a high-speed blender. The PE/VTEO/DCP weight ratio was 100/4/0.15. The as-prepared mixtures were subsequently fed into the twin-screw extruder (model ZE 25A, Berstorff GmbH, Hanover, Germany) for grafting with a temperature profile of 30/120/130/150/160/170/175/175/170°C at 120 rpm. The extrudate was then air-cooled and granulated. The extent of silane grafting was calculated according to ref. 16. It is known that PE has an absorption peak at 1378 cm⁻¹ due to -CH₃ bending vibrations (see the FTIR spectrum in Fig. 1). In silane-grafting reactions, the free radicals generated from DCP tend to attack the hydrogen at the tertiary and secondary carbons rather than the hydrogen at primary carbons. Thus, we assumed that the content of the -CH₃ group in molecules of PE should be constant throughout the grafting reaction, and so the absorption peak of the -CH₃ group at 1378 cm⁻¹ was thus used as an internal standard. The absorption peaks at 1100 and 1082 cm⁻¹ of the -Si-O-CH₂CH₃ group appearing in the curves indicated that the silane-grafting reaction occurred, and the intensities of the peaks increased with increasing amount of VTEO. Therefore, the extent of silane grafting onto PE could be determined according to eq. (1):

$$\text{Extent of silane grafting} = (I_{1100} + I_{1082})/I_{1378} \quad (1)$$

where I_{1100} , I_{1082} , and I_{1378} are absorption intensities in the FTIR spectra. The extent of silane grafting of the sample was 1.86.

Preparation of PE-g-MAH

The MAH, initiators, solvents, and PE pellets were simultaneously added to the twin-screw extruder

TABLE I
Sample Designations and Compositions

Sample code	Sample composition				
	PE-g-VTEO (phr)	DBTDL (phr)	PE-g-MAH (phr)	Epoxy (phr)	MAH (phr)
XPE	100	0.5	0	0	0
XPE/E	100	0.5	0	10	4
XPE/C	100	0.5	10	0	0
XPE/C/E	100	0.5	10	10	4

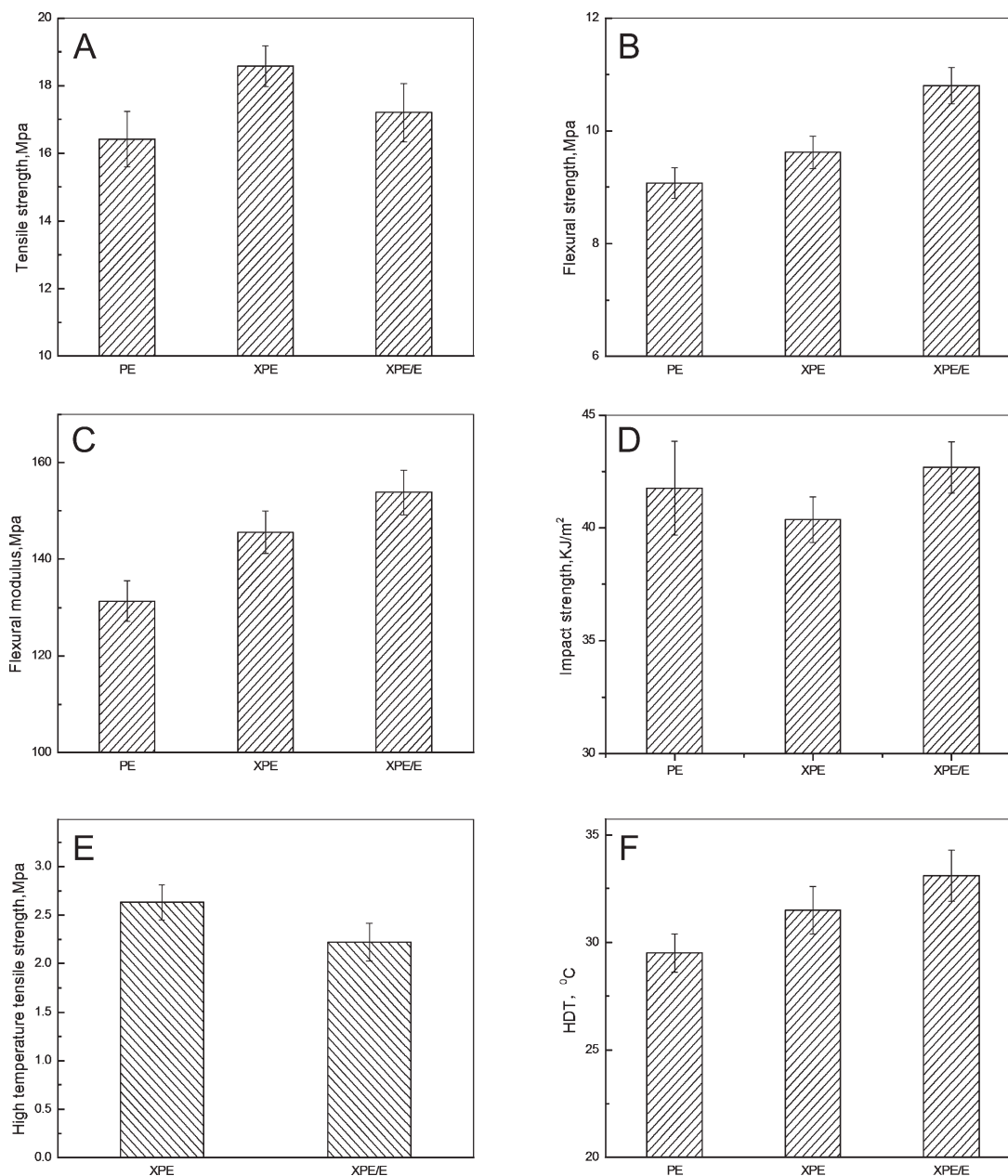


Figure 2 Mechanical properties and HDTs of pure PE, XPE, and XPE/E: (A) tensile strength, (B) flexural strength, (C) flexural modulus, (D) impact strength, (E) high-temperature tensile strength, and (F) HDT.

after dry blending, according to the preparation of ABS-g-MAH.¹⁷ The PE-g-MAH made by our group contained about 1.2 wt % MAH determined by a back-titration (the details were given in our previous article¹⁸).

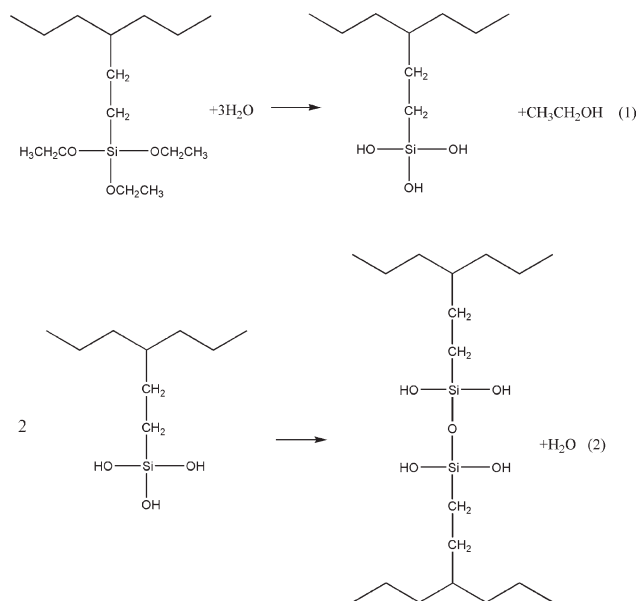
Crosslinking of PE

Table I provides sample information. In Table I, XPE stands for PE-g-VTEO, C stands for PE-g-MAH functioning as a compatibilizer in the blending systems, and E stands for the epoxy mixed with MAH. The crosslinking of PE consisted of three major steps. First, epoxy and MAH were premixed. Second,

according to the formulation in Table I, premixed epoxy, PE-g-VTEO, DBTDL, and PE-g-MAH were added to a high-speed blender; this was followed by twin-screw extrusion with a temperature profile of 30/120/130/150/160/170/175/175/170°C at 120 rpm. Third, the extrudate was air-cooled and granulated. The blend samples were obtained via injection molding for testing.

Posttreatment

To further promote the crosslinking of PE-g-VTEO with the epoxy resin, the testing samples were treated at 95°C for 10 h in an oven and hot water.



Scheme 1 Hydrolyzing crosslink mechanism of PE-g-VTEO.

Characterization

Mechanical properties

The tensile strength was measured with an Instron 4465 tester (Instron Corp., Norwood, MA) at a crosshead speed of 50 mm/min according to ASTM D 3574-86. The flexural properties were measured with the Instron 4465 tester at a speed of 2 mm/min according to ISO 178. The notched Izod impact strength was measured with a Ray-Ran Universal pendulum impact tester (Ray-Ran Polytest, Nuneaton, United Kingdom) at an impacting pendulum speed of 3.5 m/s according to ASTM D 256. The high-temperature tensile strength was determined by the Instron 4465 tester. The samples were kept in a hot chamber for 4 min at the test temperature before each run. The tests were carried out at 120°C with a crosshead speed of 50 mm/min.¹⁹

Scanning electron microscopy (SEM)

All of the samples were dipped into liquid nitrogen and forced to break up. The fractured surfaces of the samples were dried *in vacuo* and then painted with gold. A scanning electron microscope (S-2150, Hitachi, Tokyo, Japan) was used to observe the fractured surface morphological analysis.

Gel content test

The gel content test was conducted in a Soxhlet apparatus (Shanghai Bolichang, Shanghai, China) with xylene as the solvent at 160°C for more than 72 h, and the sample was dried at 60°C in a vacuum oven to a constant weight. The gel content was calculated according to eq. (2):

$$\text{Gel content} = M_c/M_0 \times 100\% \quad (2)$$

where M_0 is the initial weight of the sample and M_c is the constant weight of the sample after extraction.

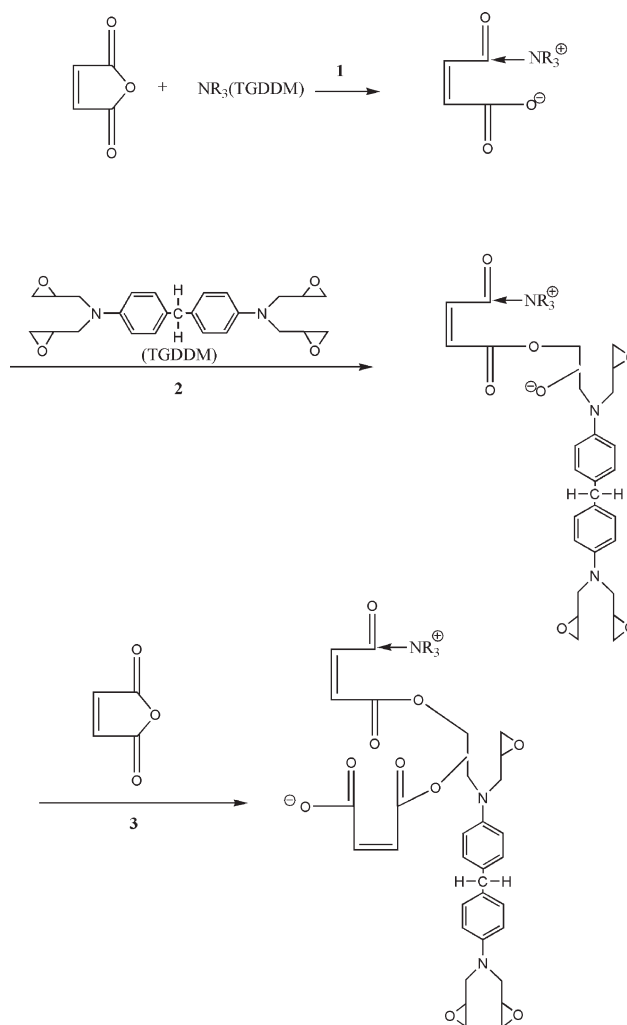
Hot deformation test (HDT)

HDT was carried out according to ISO 75-1.

RESULTS AND DISCUSSION

Influence of the crosslinking of PE and dynamically cured epoxy on the mechanical properties and HDT of the blends

To determine whether the crosslinking of PE and dynamically cured epoxy improved the strength and heat resistance of the neat PE, the mechanical properties and HDT of the blends were studied (Fig. 2). As shown in Figure 2, it was clear that the tensile strength, flexural strength, flexural modulus, and HDT of XPE improved. Meanwhile, the tensile strength at 120°C of XPE remained at 2.63 MPa, whereas the tensile strength at 120°C of neat PE was



Scheme 2 Curing mechanism of TGDDM with MAH as the curing agent ($\text{NR}_3 = \text{TGDDM}$).

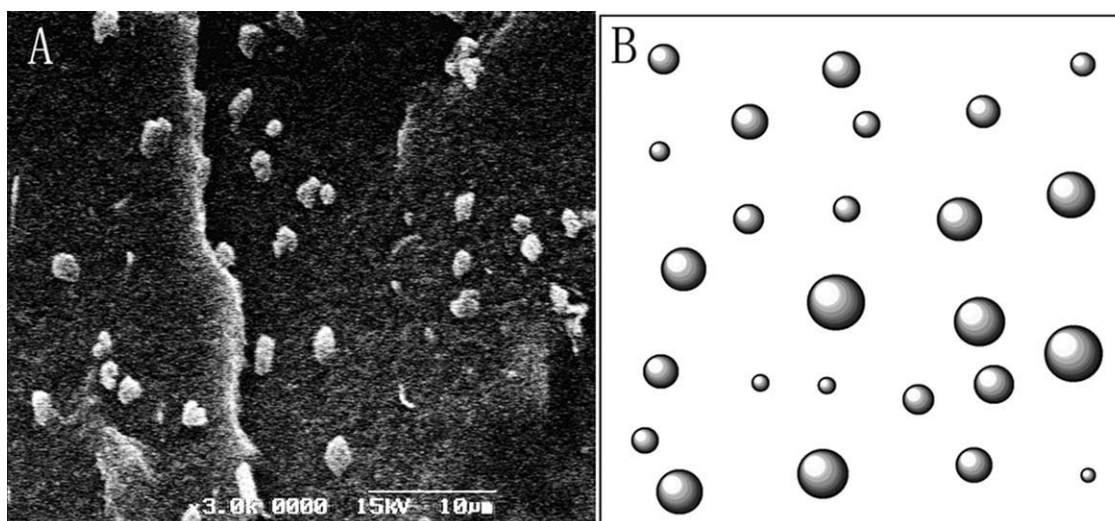


Figure 3 Morphology of XPE/E: (A) SEM photograph and (B) morphological model.

not available for its low melting temperature. The crosslinking mechanism is illustrated in Scheme 1, and PE-g-VTEO was crosslinked through the hydrolysis of the ethoxysilane group with water followed by condensation.¹⁶ However, the impact strength of XPE was slightly sacrificed because of crosslinking.

The thermoset epoxy resin had a higher heat resistance than neat PE. It made sense to add the thermoset epoxy to the PE matrix in hopes of modifying its heat resistance. In our experiment, TGDDM and MAH were chosen as *in situ* reinforcements (Scheme 2) because of their excellent heat-resistance properties and mechanical strengths.

As shown in Figure 2(B–D), the flexural strength, modulus, and impact strength of XPE/E was further improved in comparison with those of XPE, which indicated that the dynamically cured epoxy increased these properties. In other words, the cured epoxy as a hard filler resulted in the improvement of the mechanical properties of PE. However, as shown in Figure 2(A,E), although the tensile strength and high-temperature tensile strength (at 120°C) of the XPE/E were slightly higher than that of pure PE, they were lower than those of XPE.

The SEM micrograph of XPE/E, as shown in Figure 3(A), confirmed that the spherical particles 2–6 μm in diameter were well dispersed in the XPE matrix with a clear edge. Therefore, when the epoxy TGDDM was dynamically cured, it automatically became a well-dispersed reinforcing filler in the blends; this led to the enhanced properties of XPE. However, the poor compatibility between XPE and the epoxy was suspected from the sharp interface. The possible morphological model of XPE/E was conceived as shown in Figure 3(B). In Figure 3(B), the small spheres are epoxy particles, and the white background is the XPE matrix, which was cross-

linked. Because the interactive bond between the matrix and epoxy particles was very weak and the cured epoxy particles were just dispersed in the matrix of XPE as a kind of spherical filler, the cured epoxy particles could only improve the flexural strength, modulus, impact strength, and HDT of XPE/E rather than the tensile strength (at 25 and 120°C).

In general, the crosslinking of XPE increases the tensile strength, flexural strength, modulus, high-temperature tensile strength (at 120°C), and HDT, but not the impact strength, of PE. The addition of dynamically cured epoxy further enhanced the flexural strength, modulus, impact strength, and HDT of the XPE/E blends because of its reinforced filler function, whereas the poor compatibility between XPE and the epoxy decreased the tensile strength, especially at a high temperature (at 120°C).

Compatibilizing effect of PE-g-MAH on the improvement of the properties of the blends

As previously mentioned, the poor compatibility between the XPE and epoxy decreased the tensile strength at a high temperature (at 120°C). Therefore, PE-g-MAH was used as a compatibilizer to modify their compatibility to improve the mechanical properties of the blends. Because MAH was used as a curing agent of the epoxy, we expected that the MAH group of PE-g-MAH would have a good compatible effect on the cured epoxy and PE chain segments of PE-g-MAH and XPE. The effects of PE-g-MAH on the mechanical properties and HDT of XPE/C/E were evaluated, as shown in Figure 4. As shown in Figure 4, when the PE-g-MAH was added to the XPE matrix, all of the mechanical properties of XPE/C almost remained the same as those of

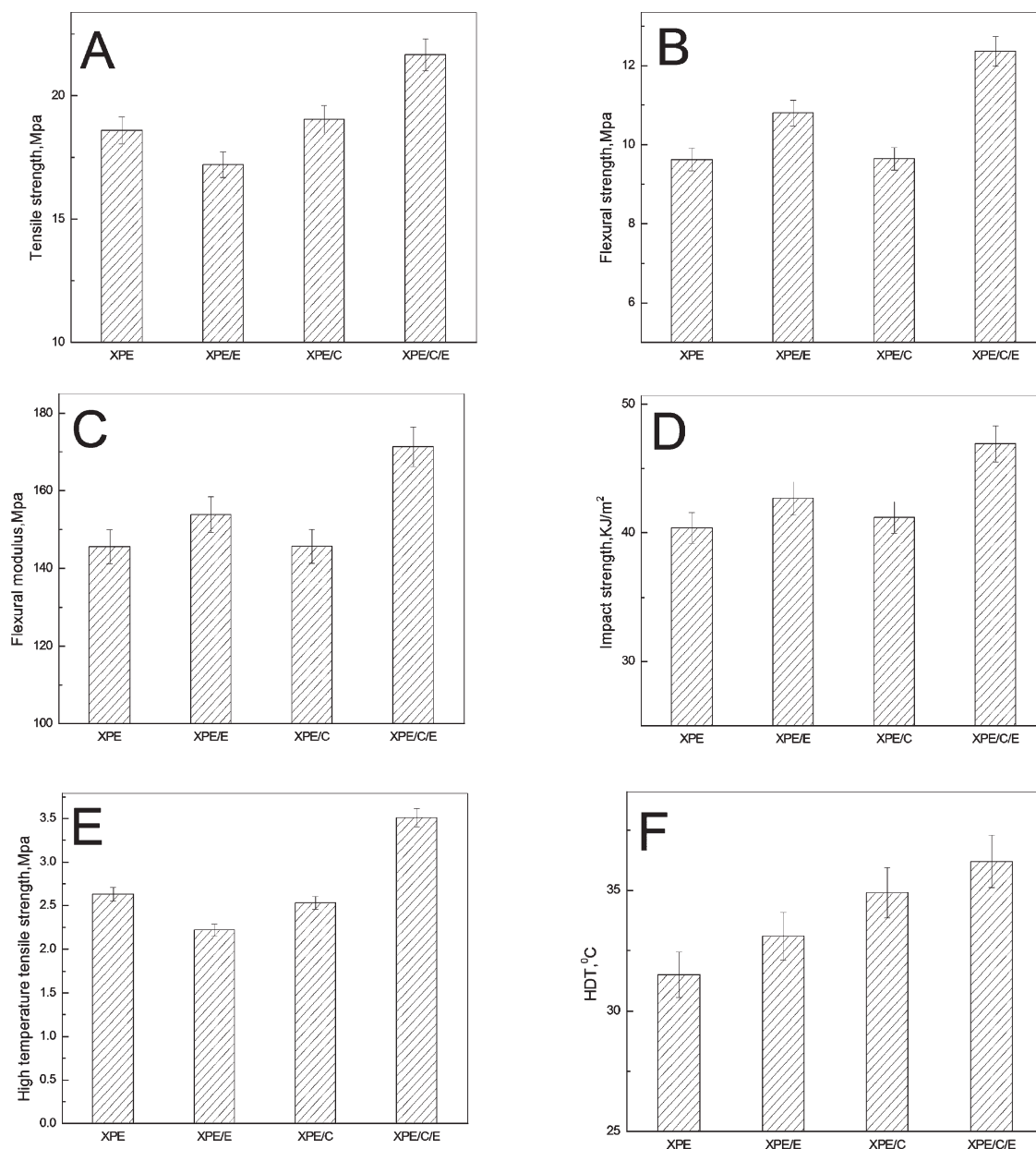


Figure 4 Mechanical properties and HDTs of XPE, XPE/E, XPE/C, and XPE/E: (A) tensile strength, (B) flexural strength, (C) flexural modulus, (D) impact strength, (E) high-temperature tensile strength, and (F) HDT.

XPE, which indicated that the mechanical properties of PE-g-MAH were close to those of XPE. Thus, the addition of PE-g-MAH did not affect the contribution of PE-g-MAH to the compatibility of the blends and the improvement of the mechanical properties.

The tensile strength and the high-temperature tensile strength (at 120°C) of XPE/E were initially lower than those of pure XPE because of the poor compatibility. Although PE-g-MAH was added to the XPE/E blends as the compatibilizer, the tensile strength (21.65 MPa) and the high-temperature tensile strength (at 120°C; 3.51 MPa) of the XPE/C/E blends were remarkably improved. The good compatibility enhanced the molecular interaction

between XPE and the epoxy and resulted in the improvement of the tensile strength (at 25 and 120°C) of the XPE/C/E blends.

Figure 5(A) shows the SEM micrographs of the XPE/C/E blends, in which fine epoxy particles about 100–500 nm in size were well distributed in the XPE matrix (much smaller than that of XPE/E) and their edge was vague. This indicated that the epoxy particles could have been well embedded in the dynamically cured XPE/C/E blends with the help of PE-g-MAH. A similar structure of three-component polymer/compatibilizer/filler systems was reported by other authors.²⁰ We concluded that PE-g-MAH improved the compatibility between XPE

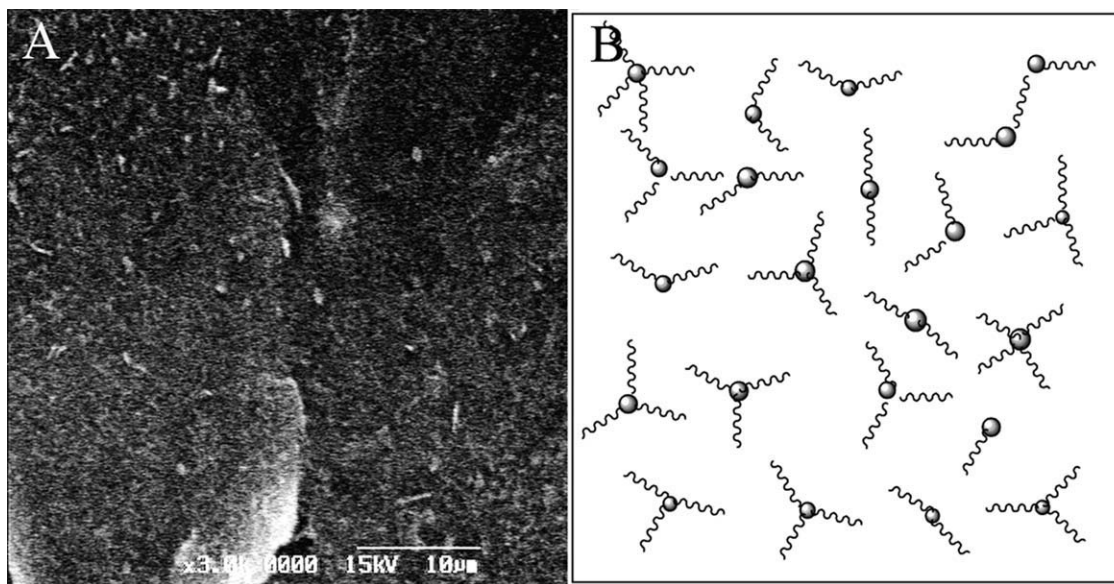
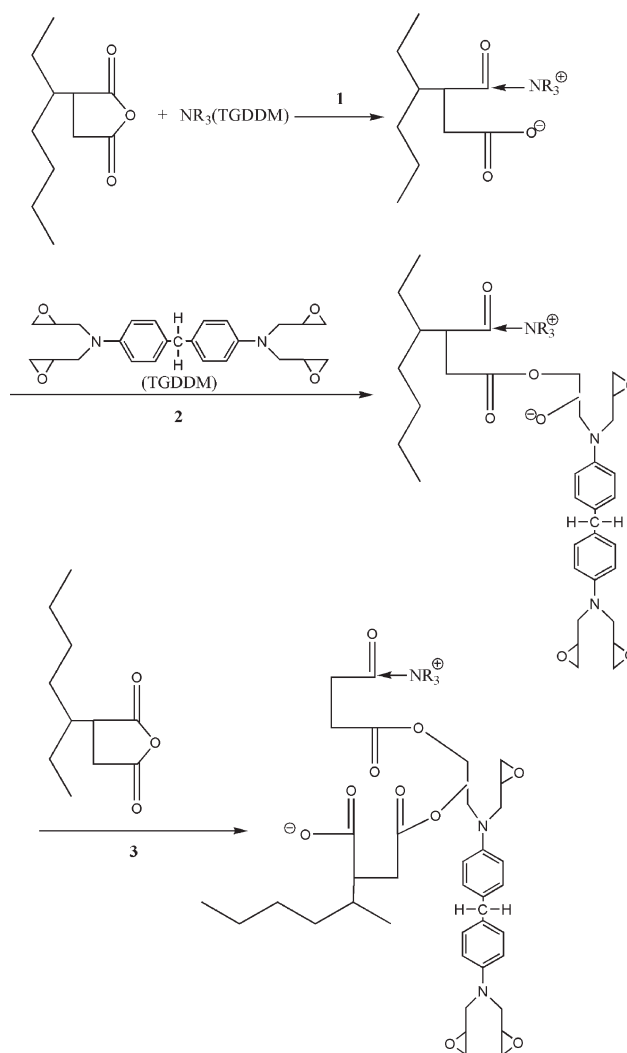


Figure 5 Morphology of XPE/C/E: (A) SEM photograph and (B) morphological model.

and the epoxy resin. The main reaction mechanism is shown in Scheme 3.²¹

In the first step of the reaction, the tertiary amino group of TGDDM induced the MAH group of PE-g-MAH to generate oxygen anion, and then, the oxygen anion of PE-g-MAH reacted with the epoxy group in TGDDM to form a chemical bond between PE and TGDDM. Thus, TGDDM was not only the reagent but also the catalyst for the curing reaction. The reaction took place in the XPE/C/E blends to form a graft copolymer, which acted as a compatibilizer to promote a fine dispersion of the epoxy resin phase. However, the MAH content in PE-g-MAH was too low to characterize the reaction between PE-g-MAH and the epoxy. The reaction between PE-g-MAH and the epoxy increased the interaction between the two immiscible phases to promote the compatibility between XPE and the epoxy and led to improved properties. On the basis of the previous analysis, the possible reinforcing mechanism model was established and is shown in Figure 5(B). In Figure 5(B), the small spheres are epoxy particles, the white background is the XPE matrix, which had already been crosslinked, and the short chains on the epoxy spheres are the PE-g-MAH. One side of the PE-g-MAH chain connected with the epoxy and residual chain of PE-g-MAH tangled with the crosslinking chain of XPE. In this way, the small epoxy particles dispersed randomly as the reinforcement in the matrix to improve the overall properties of the XPE/C/E blends. Likewise, the flexural strength, modulus, impact strength, and HDT were improved, thanks to the compatibilizing effect of PE-g-MAH. As shown in Figure 4(B–D,F), the flexural strength, modulus, impact strength, and HDT of XPE/C/E were much higher than those of XPE and XPE/E.



Scheme 3 Reaction mechanism of TGDDM with the MAH-g-PE curing system ($\text{NR}_3 = \text{TGDDM}$).

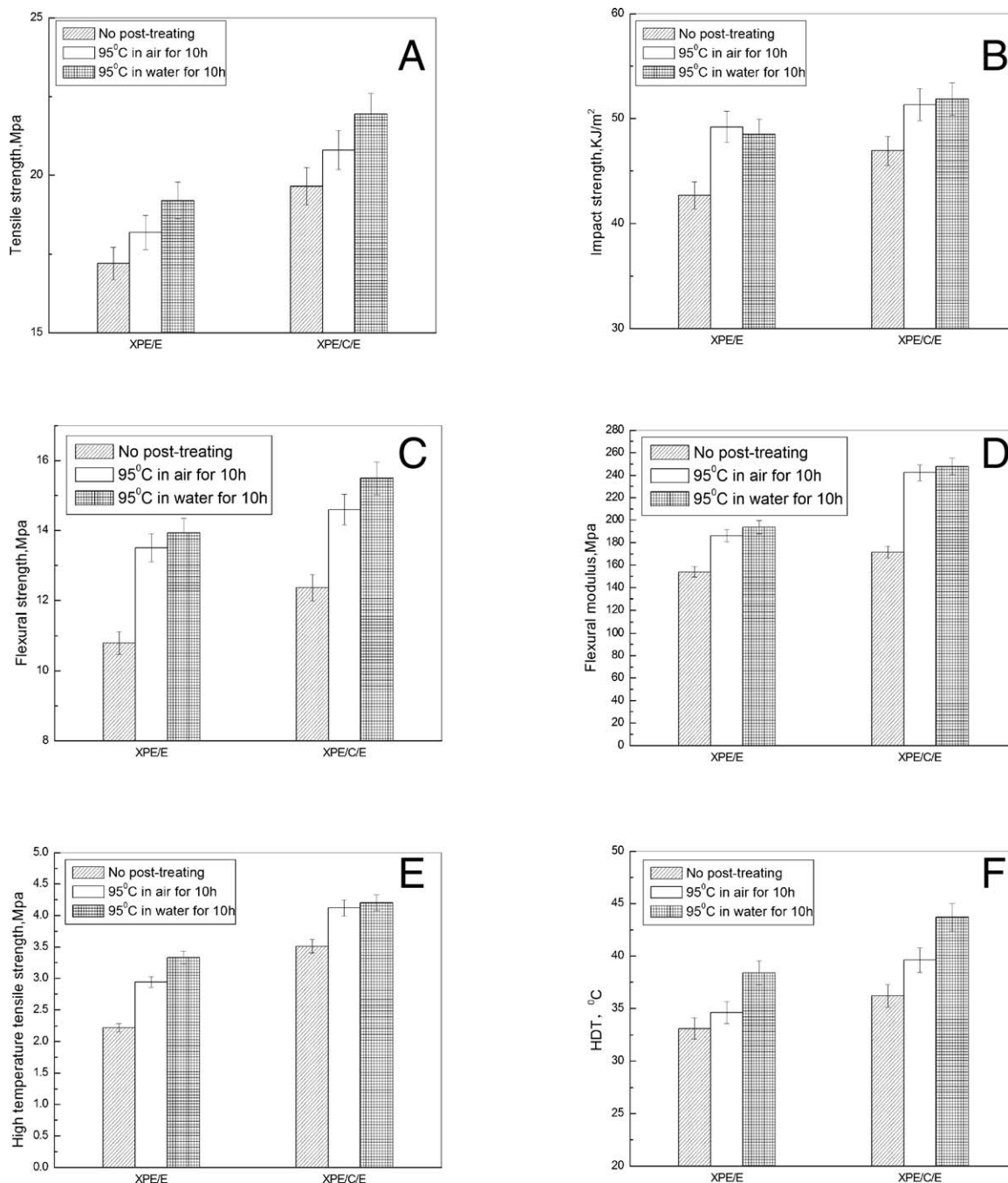


Figure 6 Effects of the posttreatment conditions on the properties of the XPE/E and XPE/C/E blends treated under different conditions: (A) tensile strength, (B) flexural strength, (C) flexural modulus, (D) impact strength, (E) high-temperature tensile strength, and (F) HDT.

In summary, PE-g-MAH was an effective compatibilizer that helped the dynamically cured epoxy to improve both the mechanical properties and HDT of the XPE/C/E blends.

Effects of the different postprocessing conditions

Mechanical properties and HDT

It is well known that the crosslinking of silane requires water for a period of time, and the curing

of epoxy also requires a certain time to complete its reaction with a curing agent, even at high temperatures. Thus, we estimated that neither the silane water crosslinking nor the epoxy resin curing reaction could be completed after the extruding process. Taking those factors into account, we found it necessary to study the effect of different postprocessing conditions to further improve the properties.

Figure 6 shows the mechanical properties of XPE, XPE/E, XPE/C, and XPE/C/E treated under

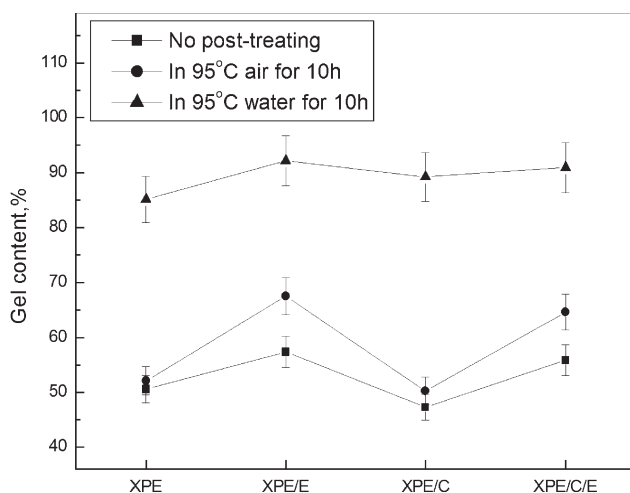


Figure 7 Gel contents of the XPE, XPE/E, XPE/C, and XPE/C/E blends treated under three disposal conditions.

different conditions at 95°C for 10 h. As shown in Figure 6, the tensile strength, flexural strength, modulus, and impact strength of the blends were improved compared to those of the samples with no postprocessing. This was attributed to the epoxy particles dispersed in blends cured entirely in the 95°C air for 10 h.

After treatment at 95°C in water for 10 h, the tensile strength, flexural strength, and modulus of the blends were further increased compared to those of the blends treated at 95°C in air for 10 h. The reason for this phenomenon was that the treatment in hot water for 10 h not only made the XPE matrix crosslinked completely but also enabled epoxy particles as reinforcements to further cure. However, the impact strength of the blends treated at 95°C in water for 10 h slightly decreased because of the incremental crosslinking of XPE.

The high-temperature tensile strength (at 120°C) and HDT of XPE/E and XPE/C/E, shown in Figure 6(e,f), also changed accordingly. The treatment in air at 95°C for 10 h improved the high-temperature tensile strength (at 120°C) and HDT of the blends, and the treatment at 95°C in water for 10 h promoted the heat-resistance properties even further. Particularly, the high-temperature tensile strength (at 120°C) and HDT of the XPE/E blends treated at 95°C in water for 10 h reached 4.2 MPa and 43.7°C, respectively; these values were much higher than those of pure PE.

Gel content

To study the dimensional stability of the blends, the gel content of the samples treated under different conditions, which were categorized into no-disposal, 95°C air for 10 h, and 95°C water for 10 h, was measured. The results are listed in Figure 7.

Before posttreatment, the gel content of the samples had a relatively low value, in the vicinity of 50%, which indicated that the XPE might not crosslink completely. When the samples were treated in 95°C air for 10 h, their gel content increased because of the further curing of the epoxy. However, the content of epoxy in the blends was 10 wt %; thus, the improvement of the gel content was not significant.

The gel contents of XPE and XPE/C after treatment in water at 95°C for 10 h reached 85.10 and 89.20%, respectively. The addition of PE-g-MAH decreased the gel contents of the blends, most likely because of the good compatibility between PE and PE-g-MAH. When the dynamically cured epoxy was added to the XPE matrix, the gel contents of the XPE/E and XPE/C/E blends increased to 92.17 and 90.90%, respectively. This was because the cured epoxy was a kind of thermoset resin that did not dissolve in hot xylene in the extracting process.

On the basis of the previous analysis, the treatment at 95°C in water for 10 h further promoted the crosslinking of XPE and the curing of the epoxy, so the XPE/C/E blends had excellent dimensional stability.

CONCLUSIONS

A novel processing method that combined dynamic vulcanization with the silane-grafted water-crosslinking technique was used to improve the comprehensive properties of PE. The important results are as follows:

1. The novel processing method enhanced the flexural strength, modulus, impact strength, and HDT of the XPE/E blends by the crosslinking of XPE and the contribution of reinforced epoxy fillers. However, the poor compatibility between the XPE and epoxy slightly lowered the tensile strength (at 25 and 120°C).
2. PE-g-MAH was an effective compatibilizer, which improved the compatibility between the XPE and epoxy particles and resulted in the improvement of the interaction and the properties.
3. Postprocessing further improved the mechanical properties and gel content of the blends, especially for the posttreatment in hot water for 10 h.
4. A high-performance crosslinkable PE-graft-silane composite was successfully prepared via this novel processing method.

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