In-situ reactive compatibilization of HDPE/GTR blends by dicumyl peroxide and phenolic resin without catalyst

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Abstract: In-situ reactive compatibilization of high-density polyethylene (HDPE)/ground tire rubber (GTR) blends by dicumyl peroxide (DCP) and HY-2045—a kind of thermoplastic phenolic resin without catalyst was investigated by studying the morphology, stress and strain behavior, dynamic mechanical properties and crystallization performance of the blends. Scanning electron microscopy (SEM) results show that there are a lot of fibrous materials distributing in the interface, which connects the dispersed phase with the matrix and obtains better interfacial strength for prominent mechanical properties. The addition of compatibilizers results in the decrease of crystallinity of the blends and the disappearance of an obvious yield phenomenon, which was proved by the differential scanning calorimeter (DSC) test and X-ray diffraction (XRD) characterization. Although the crystallinity of the blends decreases, the tensile strength and tensile strain of the blends significantly increases, especially for the HDPE/GTR/DCP/HY-2045 blends, which is possibly attributed to the good compatibility of the blends owing to the in-situ interface crosslinking. In addition, it is found that the compatibilizing HDPE/GTR blends shows a higher tanδ peak temperature and a broaden transition peak for GTR phase.

Key words: in-situ reactive compatibilization; high-density polyethylene (HDPE); ground tire rubber (GTR); thermoplastic phenolic resin; dicumyl peroxide (DCP)

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0 Introduction

A kind of thermoplastic elastomer could be prepared by the combination of thermoplastics such as high-density polyethylene (HDPE), polypropylene (PP), etc. and ground tire rubber (GTR) by using the melt blending method[1-4]. The approach above to the management of GTR not only accomplishes the recycling of rubber resources, but also brings benefits to environmental protection.

However, the blends based on thermoplastics (i.e. HDPE, PP) and GTR are thermodynamic incompatible, which leads to weak interfacial strength and unstable morphology. Therefore, the synthetic mechanical properties are poorer compared to their components. Some methods are used to improve the compatibility and interfacial adhesion of the system to obtain excellent properties, for example, the addition of block copolymer or graft copolymers[5], i.e. non reactive compatibilizers, acting as emulsifying agents localized at the interface among plastic and rubber phases. Also, reactive compatibilizers, such as peroxide[6], novolacs[7,8] as well as functionalized polymers[9], have been used to improve the compatibility of the GTR and the thermoplastic. Among those, the crosslinking agents (peroxide or novolacs) used as compatibilizers will efficiently promote the interfacial reaction between plastic and rubber phases, which leads to higher interface adhesion and stabler morphology. Moreover, this subject has been studied by various researchers due to the advantages of low cost and prominent thermal stability of the polymer with reactive compatibilizers.

Magioli et al. reported a significant compatibiliza-

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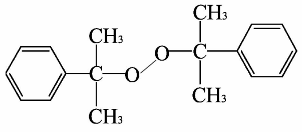
Corresponding author: LI Ying-chun (liyingchun@nuc.edu.cn) tion of the bismaleimides/dicumyl peroxide (BMI/DCP) as crosslinking agents system on the thermoplastic vulcanizates (TPVs) based on PP and GTR[4]. Generally, adding DCP into the blends with PP matrix always results in beta scission of PP molecular chains[10], as a result, the mechanical properties of polymer will deteriorate. Thus the authors used BMI as co-crosslinking agent in preparation of the composite to both reduce the degradation of PP and promote the compatibility of PP and GTR. Finally, we found that the compound had the highest interface adhesion and prominent properties with the BMI/DCP ration of 6 : 1. Whereas the HDPE/GTR powder blends were prepared based on a free radical mechanism, taking the DCP as reactive compatibilizers[6]. On the contrary, DCP can cause the HDPE matrix to crosslink unlike the fact described above. It was found that both the self-crosslink in HDPE matrix and the interfacial co-crosslink occur in HDPE/GTR (50/50) blends, especially, the latter plays an important role in improving the compatibility of the composites. However, the crystallinity content of the matrix decreases, which leads to the deterioration of the mechanical properties of the blends, with an excessive amount of DCP content (a DCP/HDPE ration is more than 0.01). Also, the literature has provided examples on the role of the phenolic resin in achieving sufficient interfacial adhesion between GTR and thermoplastic matrix. Soni et al.[8] successfully prepared the isotactic polypropylene (iPP)/ethylene-propylene diene rubber (EPDM)/nitrile rubber (NBR) elastomeric blends with or without phenolic resin as a cross linking agent and studied the compatibilization effect of the phenolic resin on the mechanical properties and morphology of the blends. And the co-crosslink reaction among the interface, promoting the generation of the graft copolymer as compatibilizer and reducing the interfacial tension thereby imposing the interfacial adhesion, occurred in the dynamic vulcanization process, which was indirectly illustrated by brittle-ductile transition in stress-strain behaviors at low elastomer content and the markedly plastic deformation in micrograph. The similar results were obtained in the literature[7, 11], where the linkage between nature rubber (NR) and HDPE molecules was generated by reactions taking place through methylol groups in the phenolic molecules and un-saturation in the HDPE molecules and NR molecules, respectively, which improved the interface adhesion among the plastic and rubber phases.

Whereas the stannous chloride, used as catalyst to accelerate the rate of co-crosslink reaction, easily corroded the experimental equipment and was harmful to laboratory technicians because of its toxicity. Moreover, the phenolic resin was able to crosslink NR without catalyst and also compatibilize the PP and NR, which was indirectly illustrated by micrograph of the blends at high temperature[12]. However, it is known that the degree of un-saturation in HDPE is small[13], which limits the quantity of phenolic resin modified HDPE (PhSP-PE) playing an important role in compatibilizing HDPE and GTR[7]. Accordingly, considering the fact that DCP would initiate co-crosslink among plastic and rubber phases above, the HDPE/GTR compounds were prepared with the addition of DCP and HY-2045 (one kind of phenolic resin), which would well compatibilize the HDPE and GTR. The performances of in-situ compatibilization were evaluated by studying the morphology, the stress-strain behavior and dynamic mechanical properties of the blends. The crystallization behaviour was also determined by means of DSC and X-ray diffraction (XRD) measurements.

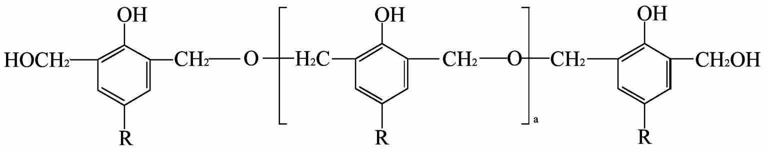
1 Experement

1.1 Materials

The GTR, with the mean particle size of 250 μm, was supplied by Hongrui rubber Co. Ltd. (Jiaozuo, China). The HDPE was an extrusion grade (5 000 S, a melt flow index at 190 ℃, under 2.16 kg load at 0.8—1.2 g/10 min and a density of 0.949—0.953 g /cm^3) and was manufactured by Lanzhou Chemical Co. Ltd. (Lanzhou, China). The DCP with purity of 98% supplied by Baoman Biological Technology Co. Ltd. (Shanghai, China) axis used as a crosslink agent. HY-2045, a kind of phenolic resin, was also used as a crosslink agent and purchased from Shanxi Provincial Institute of Chemical Industry (Taiyuan, China). The chemical structural formula of crosslink agents above was shown as follows:



DCP with purity of 98%



R=-C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$

HY-2045 with methylol content of 10%-14%

1.2 Preparation of HDPE/GTR blends

HDPE/GTR blends were prepared at a fixed ratio of HDPE/GTR = 40/60, whose accurate formulations are shown in Table 1. The polymer blending was carried out in an internal mixer, KCCK, model XSM-1/70 (Shanghai KCCK Co. Ltd., China), at a rotor speed of 60 r/min, at 180 ℃. HDPE and GTR compounds were mixed for 6 min in the mixer before adding crosslink reagents. Then DCP was added into the mixing chamber for 2 min. The HY-2045 was loaded in the last step and mixed until the constant torque was obtained. Subsquently, the blends were removed immediately and then compressed into a 2 mm thick sample at 180 ℃ under a pressure of 10 MPa for 7 min by using a SLB-15 compression molding machine (Changzhou SUYAN Co. LTD, China). Finally, the sheets obtained above were mechanically shaped into specimens used for mechanical testing.

Table 1 Compounding formulations used to prepare HDPE/GTR blends

Ingredients	Quantity (phr)		
HDPE	40	40	40
GTR	60	60	60
DCP	—	0.3	0.3
HY-2045	—	—	4.0

Note: phr means parts per hundred of the blends.

1.3 Morphology characterization

The morphology of the HDPE/GTR blends was investigated by a JEOL scanning electron microscope model JSM-7001F (JEOL Ltd., Japan). Before morphological observation, the cryogenically fractured faces of the samples and the tensile fracture surface of the dumbbell shaped specimens were coated with a thin layer of gold to prevent electrostatic charging buildup during observation.

1.4 Mechanical testing

Tensile testing was performed at room temperature according to ISO 37:2005 using an SANS CMT6104 universal testing machine (SANS group, China) at a crosshead speed of 500 mm/min and the testing sample was Dumbbell shaped specimens (type Ⅰ).

1.5 Dynamic mechanical properties analysis

The dynamic mechanical properties of HDPE/GTR blends were measured using DMA/SDA861e DMTA (METTLER, Switzerland) at a strain of 0.01% and a frequency of 1 Hz. The small tension-molded samples with dimensions of 20 mm×4 mm×2 mm were used for testing. The samples were tested in a temperature range from −80 to 150 ℃ at a heating rate of 3 ℃/min.

1.6 Thermal analysis

The DSC (METTLER TOLEDO DSC 1, Switzerland) test was performed by using approximately 5 mg samples, dried completely in vacuum oven before being used for the measurement, to investigate the crystallinity and crystallization behavirs of the HDPE and HDPE/GTR blends. The samples were heated from 25 to 210 ℃ at a rate of 10 ℃/min under a nitrogen atmosphere and was maintained at 210 ℃ for 10 min to eliminate thermal history completely. Then the samples were cooled to 25 ℃ at a rate of 5 ℃/min to observe the nonisothermal crystallization behavior. The degree of crystallinity was calculated via the total enthalpy method as

$$X_c = \frac{\Delta H_m}{W_t \times \Delta H_m^0} \times 100\%, \qquad (1)$$

where X_c is the degree of crystallinity, W_t is the content of HDPE component in the blends, ΔH_m is the specific enthalpy of melting, and ΔH_m^0 is the specific melting enthalpy for 100% crystalline polyethelene (PE). The heat of fusion (ΔH_m^0) of HDPE used is 289 J/g[14].

1.7 Wide angle XRD measureme-nts

Wide angle X-ray diffraction (WAXD) was performed by a TD3500 X-ray diffractometer (Dandong Tongda science and technology Co., Ltd., China) with a copper target (CuKα). The samples were scanned from 5 to 50° (2θ) at a scanning speed of 0.08° 2θ/s with an operating voltage of 35 kV and current of 25 mA.

2 Results and discussion

2.1 Morphology analysis

The effect of the compatibilizers such as DCP and HY-2045 on the morphology of the HDPE/GTR TPV was studied by analyzing the cryogenically fractured surface and interfacial adhesion information obtained from SEM micrographs. As shown in Fig. 1(a′), there is a mass of random fringes formed during the cryogenic fracture process, and an irregular surface which exhibits the HDPE/GTR blend is an incompatible system.

Comparatively, the fracture surfaces of the HDPE/GTR blends become relatively flat when the crosslink agents, especially for HY-2045, were incorporated into the system, as shown in Figs. 1(b′) and (c′). Furthermore, the oriented fringes with ridge-shaped erections occur on the surface of composites (Fig. 1(c′)), meaning that the material undergoes a light brittle failure process[15]. The possible reason that strong interface adhesion by chemical crosslink bonding contributes to the transition of stress through phases interface and avoids the crack propagation along the interfacial boundry, ultimately promoting the generation of flat surface (Fig. 2(c′)).

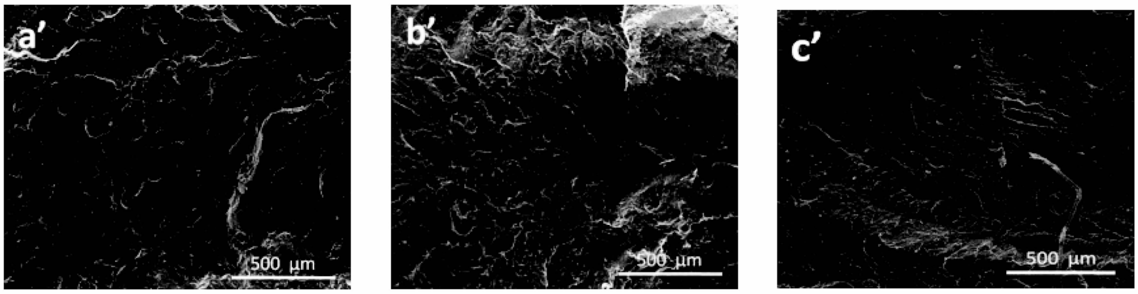


Fig. 1 SEM micrographs: cryogenically fractured surface of (a′) HDPE/GTR blends, (b′) HDPE/GTR/DCP TPV and (c′) HDPE/GTR/DCP/HY-2045 blends

In order to further demonstrate the existence of the interfacial interaction, that is to say, the prominent in-situ reactive compatibilization of HY-2045, the tensile fracture surface (perpendicular to the tensile direction) of dumbbell specimen was investigated by SEM method. Since the conclusion that the relative smooth part in the tensile fracture surface of thermoplastic elastomer (TPE) is considered to be crosslinked rubber according to the literature[16], the flat dispersed phases in fracture surface of HDPE/GTR blends should be GTR particles, as shown in Figs. 2(a)—(c). There are obvious phase interface existing in either plastic-rubber phases or rubber phases and slight plastic deformation in HDPE matrix, as shown in Figs. 2 (a)—(a2). In other words, the system of HDPE/GTR blends is incompatible, creating poor mechanical property, which will be discussed in the following paragraphs. Some fibrous materials exist in the phase interface and connect the rubber phase with HDPE matrix (Figs. 2(b1)—(b2)), which are generated from the interface co-crosslink reaction via the free radical mechanism[6] and promote the compatibility of HDPE and GTR when the crosslink agent (DCP) is incorporated into the system. Consequently, the strong interfacial strength due to the in-situ reactive compatibilizion of DCP causes the larger plastic deformation, (Fig. 2(b)) of HDPE matrix in the tensile test compared with that of the HDPE/GTR system without crosslink agent. Figs. 2(c)—(c2) show the influence of compatibilizers (DCP and HY-2045) on interfacial morphology between HDPE matrix and GTR. It can be seen that the content of fibrous materials is more than that of HDPE/GTR/DCP blends due to the prominent reactive compatibilization of DCP and HY-2045.

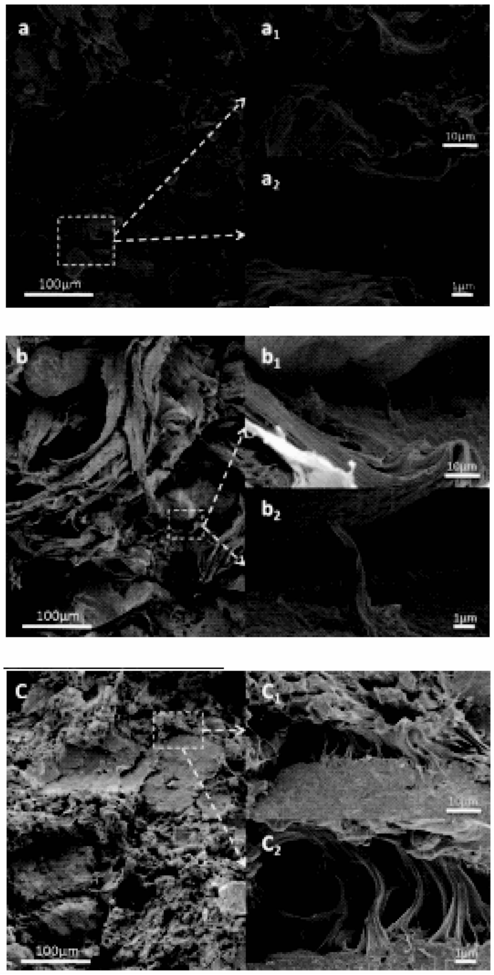


Fig. 2 SEM micrographs: tensile fracture surface of (a) HDPE/GTR blends, (b) HDPE/GTR/DCP TPV and (c) HDPE/GTR/DCP/HY-2045 blends

2.2 Mechanical properties analysis

Fig. 3 shows nominal stress-strain curves of HDPE and HDPE/GTR blends under uniaxial tension at room temperature. Obviously, it exhibits yield phenomenon and incomplete necking process followed by a rather brittle fracture[17] in the tensile test of neat HDPE. This is possibly attributed to the cavitation in plastic deformation process which easily causes the fracture of HDPE sample[18,19]. And the slope of the curves, the characterization of Young's modulus, presents a decreasing trend from curve 2 to curve 4 (Fig. 3), which is possibly due to the lower crystallinity obtained from DSC and XRD measurements, as listed in Table 2. Similarly, no unobvious yield phenomenon appears in the stress-strain curves of HDPE/GTR blends with or without the compatibilizers.

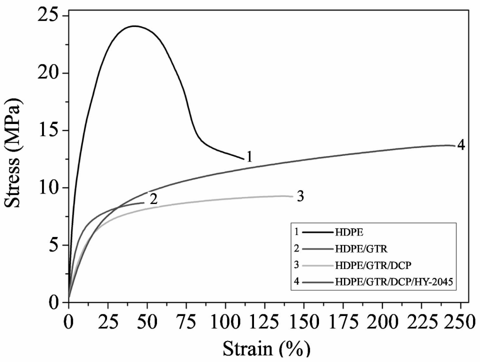


Fig. 3 Tensile stress-strain curves of HDPE and HDPE/GTR blends

Table 2 Melting temperature (T_m), heat of fusion (ΔH_m), degree of crystallinity (X_c) and crystallization temperature (T_c) of HDPE and HDPE/GTR blends

Samples	ΔH_m(J/g)	T_m(℃)	X_c(%)	T_c(℃)
HDPE	129.72	131.38	44.89	119.49
HDPE/GTR	92.07	130.81	31.86	119.86
HDPE/GTR/DCP	61.18	131.16	21.17	119.67
HDPE/GTR/DCP/HY-2045	45.83	131.22	15.86	119.86

Additionally, the HDPE/GTR blends, with DCP and HY-2045, show the highest tensile strain; without crosslink agent, the lowest tensile strain; with the DCP alone, intermediate tensile strain. These results can be explained by a hypothetical deformation model illustrated in Fig. 4, inspired by the previous literatures[20,21], which closely depends on an unsimultaneously deformation of the HDPE matrix and the strong interface adhesion between the plastic and rubber phases. When the strain of HDPE/GTR blends increases gradually from curve 2 to curve 4 (Fig. 3), generally, the GTR phase easily causes stress concentration of the blends when the HDPE/GTR tensile samples without any compatibilizers are subjected to tensile force. Thus the debonding between the GTR particles and the HDPE matrix happens instantaneously, leading to the minimum tensile strain.

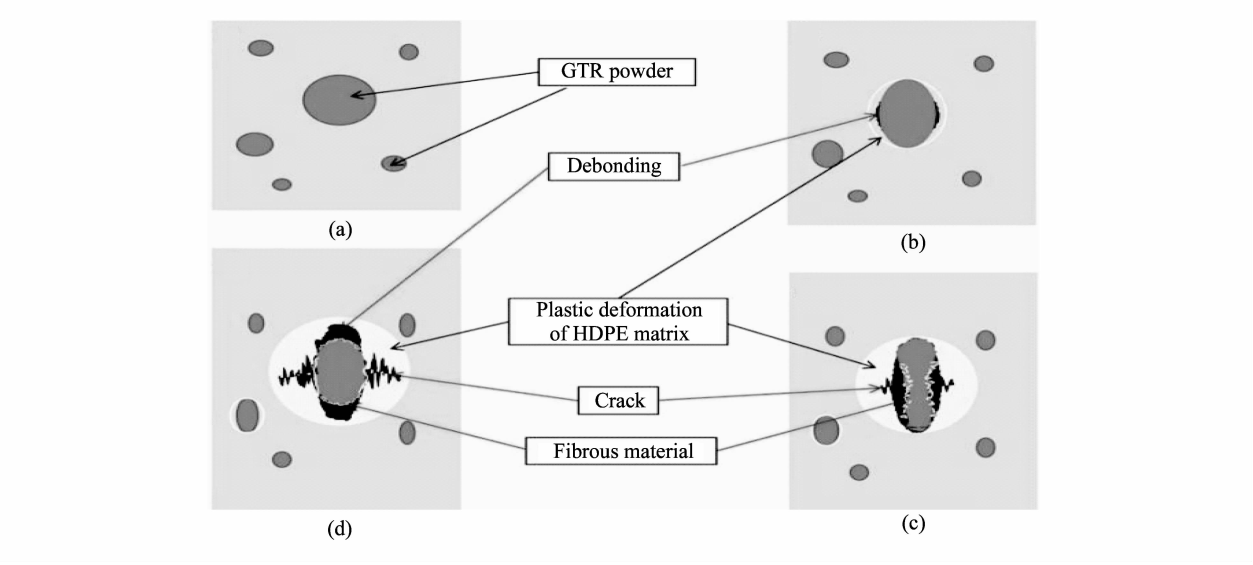


Fig. 4 Sketch illustrating the deformation and fracture behavior (parallel to the tensile direction) of the HDPE/GTR blends

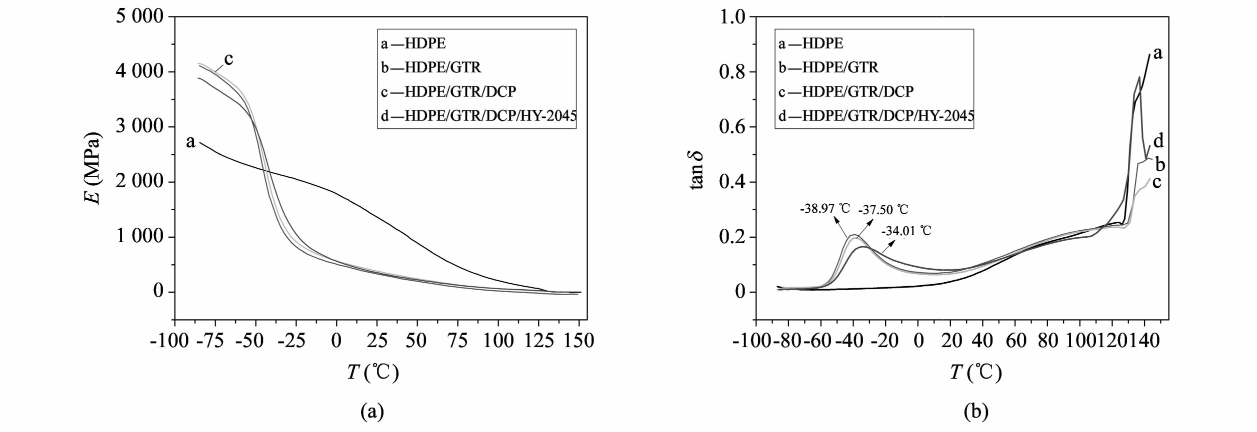
Considering that the unsimultaneous deformation of the HDPE matrix, the strain of HDPE/GTR blends with DCP and HY-2045 as compatibilizers is the maximum compared with those of the others. Usually, elastic modulus of rubber is inferior to plastic one, which means that rubber is prone to deformation under the external force. Consequently, the equatorial region of the dispersed GTR particles will form a stress concentration zone under tensile force. For compatibilizing HDPE/GTR blends, the GTR particles are elongated due to the strong interface adhesion, especially for the blends with HY-2045 and DCP. Therefore, the stress generated in the equatorial region of the dispersed rubber can transfer from GTR powder to the plastic phase through the interface layer, causing the surrounding matrix deformation. The increasing stress can induce yield, and plastic deformation as well, with strain harden of HDPE matrix surrounding the GTR powder, when the tensile force increases in the stretching process. Similarly, the deformation above will progressively expand in the HDPE matrix at the region that is far away from GTR powder until the debonding between GTR phase and HDPE matrix occurs in the phase interface nearby the equatorial region of the dispersed rubber (Fig. 4(b)), i. e. the occurrence of local fracture. Then the equatorial region of the dispersed rubber will resile and elongate in the polarization direction under the tensile force. Meanwhile, the cracks generated from the local fracture above expand in the HDPE matrix (Fig. 4(c)). Finally, the debonding between HDPE matrix and GTR will occur in the polar part of GTR particles when the tensile force increases continually and then the deformed GTR recovers to their original shape (Fig. 4(d)). However, the size of the dispersed GTR is not uniform, thus the force described above is not of equal size due to the inhomogenous deformation of GTR phase, which leads to unsimultaneously deformation of the HDPE matrix. The debonding between GTR and HDPE and the voids in the matrix will appear when the tensile strain continuely increase, however, those deficiencies are not enough to cause material fracture. The larger tensile force and the strong interface adhesion will produce plastic deformation to the most matrix and more voids in HDPE phase which can cause the ultimate fracture of the blends sample.

2.3 Dynamic mechanical analysis

To study the in-situ reactive compatibilization of HY-2045 and DCP on the HDPE/GTR blends, the thermal transitions of the composites—the dynamic response was evaluated from −100 to 150 ℃ by dynamic mechamical analysis (DMA) measurement. The dependence of storage modulus (E') and tanδ with temperature for the HDPE/GTR blends with different compatibilizers is shown in Figs. 5(a) and (b), respectively.

All samples show a steep decrease in storage modulus (E') value in the temperature range from -100 to 0 ℃ except for neat HDPE, followed by a rubbery plateau. It also can be seen that the E' of all HDPE/GTR blends is higher than that of HDPE, of which the modulus of HDPE/GTR/DCP blends is the highest; followed by the HDPE/GTR blends, HDPE/GTR/DCP/HY-2045 blends is the lowest prior to its glass transition, as shown in Fig. 5(a).

In fact, the E' of the blends just increases slightly by the addition of DCP. This is possibly due to the poor interface strength, which can be proved indirectly that there are few fibrous materials existing at interfacial boundry of the fracture surface in tensile specimen, as shown in Fig. 2(b). Theoretically, the storage modulus is positively correlated to the crosslinking density according to the literature[22,23]. However, the HY-2045 promotes the interfacial reactive compatibilization and forms the stable interfacial layer, which is proved by the broadening tanδ transition peak and the higher tanδ temperature (T_g), as shown in Fig. 5(b).



(a) (b)

Fig. 5 Storage modulus and loss tangent versus temperature for the HDPE/GTR blends

The similar conclusions were obtained in the research[24,25]. Although the strong interfacial adhesion is beneficial to the increase of E' of the HDPE/GTR blends with DCP and HY-2045, a small amount of DCP and HY-2045 can cause the crosslinking of the matrix phase which leads to a considerable reduce in crystallinity, as listed in Table 2. Therefore, the E' of blends decreases by the reduction of crystallinity. The α-relaxation transition from 30 and 100 ℃ of HDPE and HDPE/GTR blends refers to the some types of chain segments relaxation transition in the crystalline phase[26] of HDPE matrix. It is found that the marked α-relaxation transition appears in the E' versus temperature curve of neat HDPE. However, there is no obvious change in similar curves of other HDPE/GTR blends, which is possibly due to the huge decrease in crystallinity (Table 2) of the blends compared with the neat HDPE and the prominent reactive compatibilization of DCP and HY-2045 on the blends. The alpha star transition (T_α^*) in high temperature region (Fig. 6(b)) is associated with the slippage between the crystallites. This transition is very susceptible to processing induced changes and can be enlarged or decreased by the applied heat history, processing conditions, etc. [27]

2.4 Crystallization performance analysis

The crystallization performance of HDPE and HDPE/GTR blends was investigated by means of DSC and WAXD diffraction measurements. The melting and crystallization curves of HDPE and HDPE/GTR blends without or with compatibilizers are shown in Fig. 6. Table 2 shows the melting and crystallization temperatures, heat of fusion ΔH_m(the first melting process) and degree of crystallinity determined by DSC measurements, for HDPE and HDPE/GTR blends with compatibilizers. It can be seen that the melting temperature and crystalline temperature remain essentially unchanged at about 131 and 119.5 ℃, respectively.

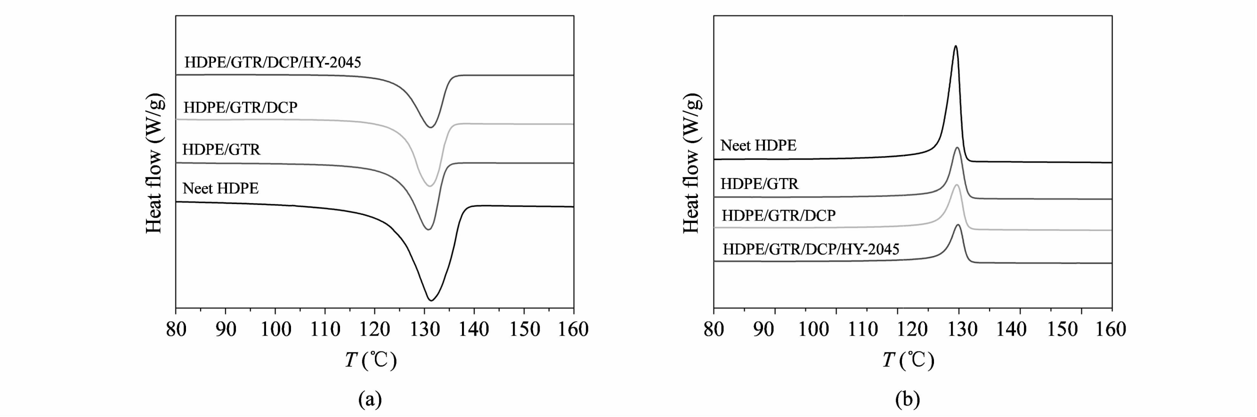


Fig. 6 Melting and crystallization curves of HDPE and the HDPE/GTR blends

Additionally, two visible crystal diffraction peaks can be seen at around $2\theta=21.5°$ and $23.8°$ (Fig. 7), which represent (110) and (200) crystallographic planes of HDPE matrix[18].

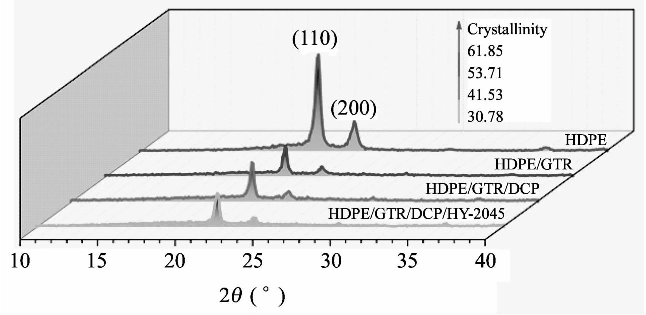


Fig. 7 XRD patterns for HDPE and HDPE/GTR blends

Accordingly, the addition of GTR and compatibilizers such as DCP and HY-2045 hardly affect the crystalline structure of HDPE during blending. Generally, the crystallinity estimated by WAXD method is higher than that by DSC measurements, which is consistent with the results in literature[28,29].

Nevertheless, it is also found that the crystallinity calculated by the measurements above both decreases by the addition of GTR with compatibilizers, which demonstrates the similar decreasing tendency in Young's modulus, i. e. changing tendency in the slope of the stress-strain curves (Fig. 3).

On the one hand, the GTR components hinder molecular chain segments from arranging into the crystalline region, leading to the reduction in crystallinity of the HDPE/GTR blends, especially for the incorporation of DCP and HY-2045 because of its reactive compatibilization. On the other hand, DCP or HY-2045 also causes the HDPE matrix self-crosslinking, which will results in the decrease in crystallinity. Note that the crystallization temperature, obtained from the cooling process in DSC measurements, slightly increases when the compatibilizers are added into the system. This is possibly attributed to that the distributed crosslinking junctions may act as nucleating agent whereby the crystallization starts at higher temperature[30].

3 Conclusion

The role of DCP and HY-2045 in in-situ compatibilizing HDPE/GTR blends has been investigated by several methods. It is found that the stable interfacial layer exists in the interface between HDPE and GTR phases of the HDPE/GTR blends, which has been directly illustrated in DMA and SEM study results. The stable layer above makes the strong interface adhesion and promotes the transition of stress in GTR phase generated from tensile process through the interface, which results in significant improvements in the mechanical properties, especially in strain of the HDPE/GTR/DCP/HY-2045 blends. Meanwhile, the incorporation of DCP and HY-2045 leads to the decrease in crystallinity and Young's modulus of blends, to some extent, which has a negative impact on its practical application.

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过氧化二异丙苯和酚醛树脂对 HDPE/GTR 共混物的原位反应性增容

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摘　要： 采用过氧化二异丙苯(DCP)和热塑性酚醛树脂(HY-2045)在未添加催化剂时实现了对高密度聚乙烯(HDPE)/废旧轮胎胶粉(GTR)共混物的原位反应性增容，并研究了其对共混物的微观形貌、应力-应变曲线、动态力学性能和结晶性能的影响。扫描电镜结果显示，共混物橡塑界面处有大量的纤维状物质同时嵌入到基体相和分散相中，使得共混物的界面强度得到显著增加，从而获得较好的综合力学性能。差式扫描热量(DSC)和 X 射线衍射(XRD)测试结果表明，原位增容后的共混物的结晶度显著降低，致使其明显的拉伸屈服现象消失。由于反应型增容剂 DCP 和 HY-2045 使得共混物在界面处形成化学交联，尽管其结晶度有所降低，但是其拉伸强度和断裂伸长率还是得到了显著的增加。另外，动态力学性能测试表明，增容后的 HDPE/GTR 共混物中 GTR 相的玻璃化转变峰变宽，玻璃化转变温度升高。

关键词： 原位反应性增容；高密度聚乙烯；废旧轮胎胶粉；热塑性酚醛树脂；过氧化二异丙苯

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