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Functionalization of high density polyethylene in melt state through ultrasonic initiation and its effect on mechanical properties of glass fiber reinforced composites

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Summary

Functionalization reaction of high density polyethylene (HDPE) with γ-methacryloxy-propyltrimethoxysilane(MAS) or with MAS and MAH performed in melt state through ultrasonic initiation by a laboratory-scale ultrasonic extruding reactor was studied in this paper. The effect of ultrasonic intensity on the percentage of grafting and melt flow rate of the functionalized products was investigated. The results show that by imposing ultrasonic vibration during melt-extruding process, the scission of HDPE chain bonds can be caused to form macroradicals, the functionalization reaction of HDPE with MAS or with MAS and MAH can be realized. The percentage of grafting and the melt flow rate of the functionalized products depend upon the ultrasonic intensity and reaction temperature. The fuctionalization reaction of HDPE with MAS can be promoted by adding a second grafting monomer MAH. The ultrasonic-induced products have a higher reactivity with the coupling agents coated on the surface of glass fibers, the mechanical properties of the composite improved by the ultrasonic induced product are higher than that of by peroxide initiated product and the mechanical properties of HDPE/GF composite modified by HDPE-g-MAH-MAS are higher than that of by HDPE-g-MAH. The SEM experimental results indicate that an oriented crystal layer exists between the interface of glass fiber and the HDPE matrix, the interfacial bonding strength is the determining factor of the formation of the oriented crystal layer.

Keywords

ultrasonic vibration; functionalization reaction; HDPE, maleic anhydride

1. Introduction

In recent decades, high-intensity ultrasound has been widely applied to initiate polymerization or copolymerization to prepare the novel polymers [1, 3-11]. Cavitation in the ultrasonic field implies nucleation growth and subsequent claps of bubbles or cavities, resulting in violent shock waves with a high temperature of ~5000 K and a high pressure of ~1000 bar [2], which is highly sufficient to the scssion of chemical bonds and the formation of macro-radicals.

According to the general cavitation mechanism, when the viscosity of solution amounts to 2.0 PaS, the cavitation will disappear, which means that the scssion of chemical bonds in polymer melt will be hardly possible, the sonochemical polymerization in melt state is impossible. However, Isayev et al. [12-15] reported that the high-intensity ultrasonic wave can affect the die characteristics during polymer extrusion by reducing the pressure and die swell and postponing the melt fracture. The ultrasonic waves can also break down the molecular chains, which permanently reduce the viscosity of the original polymer melt, or rapidly break up the three-dimensional network in vulcanized rubbers through the scission of C-S, S-S, and C-C bonds. Recently works [16-20] also show that the ultrasonic oscillations can cause the degradation of polymer melt, and greatly improve the appearance and processability of polystyrene (PS), high density polyethylene and metallocene catalyzed polyethylene as well as HDPE/PS blends. Ultrasonic oscillations can also greatly enhance the compatibility and mechanical properties of HDPE/EPDM and HDPE/PS blends. It would be of very interest to apply the effect of high-intensity ultrasonic wave on polymer reactive extrusion and its mechanism.

Maleic anhydride-functionalized polyolefins may be used as a copolymer precursor in polymer blends, as an adhesion promoter with glass or carbon fiber, and as a processing aid for recycling of plastics waste etc. [21]. The methods usually adopted for functionalization consist of grafting maleic anhydride (MAH) in the presence of organic peroxide in melt state, in solid state, or in solution. For the peroxide-initiated functionalization of polyolefins in melt state, the cross-linking or chain scission may occur simultaneously with the graft reaction. For polyethylene, the dominant side reaction is cross-linking [22-26], and sometime seriously damaged the flowability and processing characteristics of the functionalized product. Therefore, besides the graft reaction itself, the suppression and avoidance of the side reactions are also of practical interest [26].

Recently our researches[27, 28] have also revealed that applying of ultrasonic vibration to the molten mixture of HDPE and MAH at the entrance of die, the MAH functionalized HDPE was prepared and the molecular structure of the functionalized products and the possible reaction mechanism were proposed. The results indicate that the functionalized product induced by ultrasonic irradiation mainly consists of the three end chain blocked products, some of which contain a double bond on the end chain. The functionalized product obtained by peroxide initiation consists of the two side chain grated products. In this article, we try to further realize the functionalization reaction of HDPE with MAS and MAH through ultrasonic vibration and illustrate the reason that the mechanical properties of HDPE/GF composites are obviously improved by the ultrasonic induced product.

2. Experimental

2.1. Materials

The high density polyethylene (HDPE 5000S, powder) with a melt flow rate of 1.1 g/10min and HDPE (2100J, granular) with a melt flow rate of 6.5 g/10 min (at 190°C and under a load of 2.16 kg) from Yang Zi Petrochemical Co. (China) were used. γ-methacryloxy- propyltrimethoxysilane (MAS) was purchased from Nanjing

Shuguang chemical factory (China). All other chemicals including maleic anhydride (MAH) are of reagent grade.

2.2. Melt extruding reaction

The ultrasonic extruding reactor consists of a 25 mm diameter plastic extruder with a length to diameter ratio L/D = 25 and an ultrasonic cross-head die attachment (Fig. 1). A 300 W ultrasonic generator, a converter, and a booster are used to provide the longitudinal vibration of the horn with a frequency of 20 kHz. The horn diameter is 15 mm. The diameter of the die opening is 3.0 mm, its length to diameter ratio (L/D) is 7. The gap between the flat face of the horn and the chamber bottom is 10 mm. The temperature of the extruder barrel and the ultrasonic intensity can be controlled; the screw rotation speed is fixed at 5 rpm.

The flow rate, the pressure at the die entry, and the temperature of grafted samples of different composition were measured, the reaction temperature is signified by the temperature of the front part of extruder barrel.

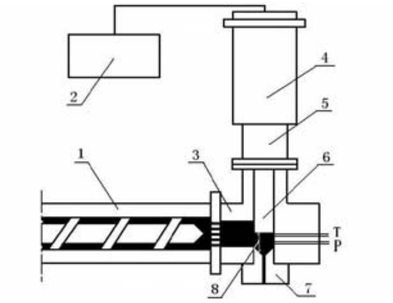


Figure 1 Schematic diagram of the ultrasonic extruding reactor. 1-extruder; 2-ultrasonic generator; 3-cross head; 4-piezoelectric transducer;5-booster; 6-cylindrical horn; 7-die; 8-gap; T-thermocouple; P-pressure transducer

2.3. Sample purification and characterization

The sample (~ 1 g) is heated in refluxing xylene for 1 h then filtered into acetone. The acetone-insoluble polymer is refluxed with acetone for 4 h, then dried under vacuum.

To determine the percentage of MAH grafting, ~ 0.2 g purified product is heated in 50 ml refluxing xylene for 30 min, followed by cooling to ~ 80°C. About 4 ml potassium hydroxide (KOH)/ethanol standard solution (~0.2N) is added, and then heated under reflux for 15 min. The surplus alkali is determined by titration with hydrochloride (HCl)/isopropanol standard solution (~0.2N). The indicator used is 0.1% phenolphthalein/ethanol solution. A blank is carried out by the same method. The percentage of MAH grafting (Pg) is expressed by:

$$Pg(\text{mass}\%)=[N(V0-V)\times 98.06] / (2\times W\times 1000)\times 100\% \tag{1}$$

where N is the concentration of HCl/isopropanol (mol/L). W is quantity of sample (g), V is the volume of HCl/isopropanol used for titration, V_0 is the volume of HCl/isopropanol used in a blank assay, 98.06 is the molecular weight of MAH. Repeated runs show that the reproducibility of the present procedure is within 5 wt %.

The purified product is pressed at ca. 180°C into thin film, infrared spectra is taken using a Nicolet 20 SXB Fourier-transform infrared spectrometer.

The percentage of MAS grafting is represented by the ratio of absorption peaks area (A_{1127}/A_{722}) of Si-O group of MAS (1127 cm^{-1}) with CH_2 group of HDPE (722 cm^{-1}) in the FTIR spectra.

The melt flow rate of the HDPE and the functionalized HDPE were measured with a CS-127 melt-flow instrument (USA) at 190°C, with a load of 2.16 kg.

The gel content of the functionalized HDPE was measured according to ASTM D2765.

The tensile (TFS, 4 mm thickness), flexural (FFS, 4 mm thickness) and impact (IFS, 10 mm thickness) fracture surfaces of HDPE/GF specimens were etched for 4h by xylene at 80°C. The samples were then dried under vacuum and coated with gold and examined by a scanning electron microscope (JSM-5900, Japan).

2.4. Sample preparation and properties measurement of HDPE/GF composite

The glass fiber reinforced HDPE composites were prepared in a diameter 25 mm co-rotating twin screw extruder. The HDPE (2100J) was mixed with the functionalized HDPE and short cut E-glass fibers, then fed to the extruder. In case the continued glass fiber was used, it was fed from the barrel side of the co-rotating twin screw extruder, the glass fiber content in the composites was controlled by adjusting the ratio of feed rotor speed and screw rotation speed. The extruder has five heating zones from hopper to die, in which the extrusion temperature was set at 190, 210, 220, 230, and 170°C in order.

The tensile strength, flexural strength and flexural modulus of the composites were measured with an Instron universal testing machine 4302 (U.K.) at room temperature. Impact strength tests were carried with an XJ-40A impact tester (China).

3. Results and discussion

3.1 Functionalization reaction of HDPE with MAS through ultrasonic initiation

Figure 2 and Figure 3 show the FTIR spectra of the functionalized product of HDPE with MAS obtained at different ultrasonic intensity and temperature. At the same reaction temperature and MAS content, the peaks at 1724 cm^{-1} and 1127 cm^{-1}, the MAS carbonyl stretching band and the absorption band of Si-O group, are

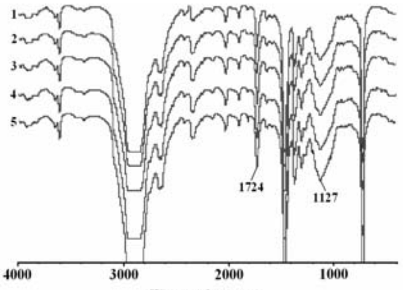


Figure 2 FT-IR spectra of HDPE-g-MAS prepared through ultrasonic initiation at 230°C. MAS content: 1.5%; ultrasonic intensity: 1-0 W; 2-100 W; 3-180 W; 4-200 W; 5-250 W

enhanced with the increase of ultrasonic intensity, and at the similar ultrasonic intensity, the peaks also are enhanced with the decrease of reaction temperature. The ratio of the absorption peaks area (A_{1127}/A_{722}) of Si-O group of MAS (1127 cm^{-1}) and -CH$_2$- group of HDPE (722 cm^{-1}) in the FTIR spectra is plotted with the ultrasonic intensity (Figure 4). It can be seen from Figure 4 that the ratio of the absorption peaks area (A_{1127}/A_{722}) obviously increases with increasing ultrasonic intensity and with decreasing reaction temperature, which indicates that the MAS content of the functionalized product increases.

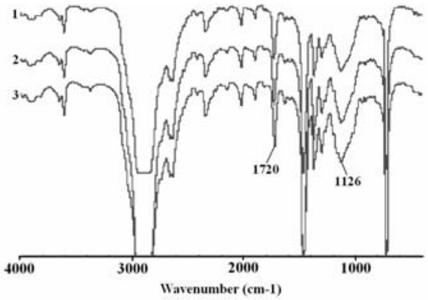


Figure 3 FT-IR spectra of HDPE-g-MAS prepared through ultrasonic initiation at different extrusion reaction temperature. MAS content: 1.5%; 1-310°C, 160 W; 2-270°C, 180 W; 3-230°C, 180 W

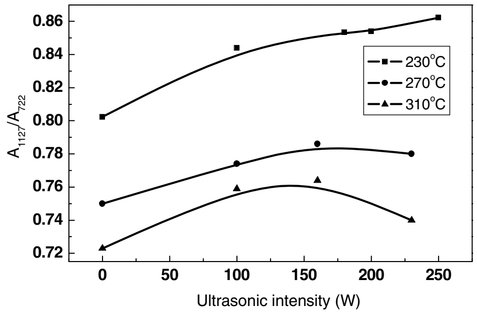


Figure 4 Influence of ultrasonic intensity on FT-IR absorbency area ratio. (A_{1127}/A_{722}) of HDPE-g-MAS (MAS content in reaction mixture: 1.5%)

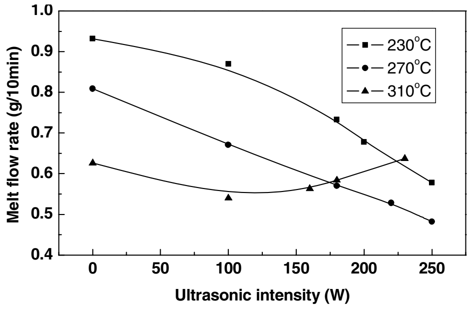


Figure 5 Influence of ultrasonic intensity on melt flow rate of HDPE-g-MAS. MAS content in reaction mixture: 1.5%

Figure 5 shows that the melt flow rate of the functionalized product of HDPE with MAS is decreased with increase of ultrasonic intensity at 230 and 270°C, but does not change obviously at 310°C, showing that the functionalization reaction of HDPE with MAS has been occurred, resulting the change of molecular weight of the product and the increase of the polarity of its chains.

3.2 Functionalization reaction of HDPE with MAH and MAS through ultrasonic initiation

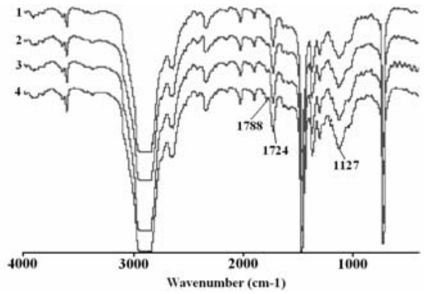


Figure 6 FT-IR spectra of HDPE-g-MAH-MAS prepared through ultrasonic initiation at 230°C. MAH content: 1.5%; MAS content: 1.5%; ultrasonic intensity: 1-0 W; 2-100 W; 3-160 W; 4-220 W

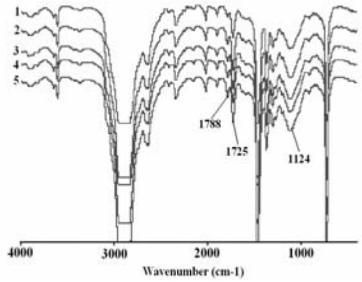


Figure 7 FT-IR spectra of HDPE-g-MAH-MAS prepared through ultrasonic initiation at 270°C. MAH content: 1.5%; MAS content: 1.5%; ultrasonic intensity: 1-0 W; 2-100 W; 3-160 W; 4-200 W; 5-240 W

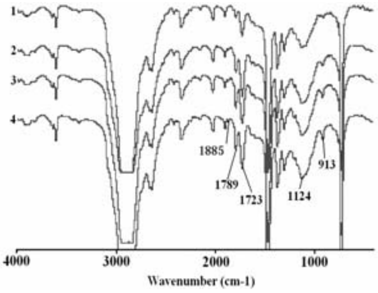


Figure 8 FT-IR spectra of HDPE-g-MAH-MAS prepared through ultrasonic initiation at 310°C. MAH content: 1.5%; MAS content: 1.5%; ultrasonic intensity: 1-0 W; 2-100 W; 3-200 W; 4-250 W

Figure 6, Figure 7 and Figure 8 show the FTIR spectra of the functionalized product of HDPE with MAH and MAS (HDPE-g-MAH-MAS) at different ultrasonic intensity. At the same of MAH and MAS content, the peak at 1788 cm^{-1}, the MAH carbonyl stretching band, is enhanced with the increase of ultrasonic intensity and with increase of reaction temperature. The peaks at 1724 cm^{-1} and 1127 cm^{-1}, the MAS carbonyl stretching band and the absorption band of Si-O group, are enhanced with the increase of ultrasonic intensity and with decrease of reaction temperature.

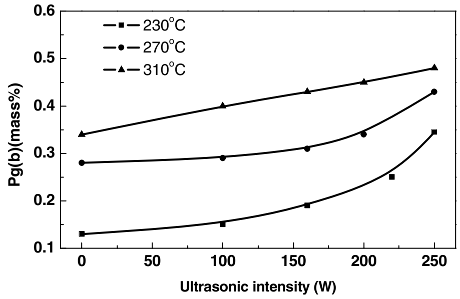


Figure 9 Influence of ultrasonic intensity on MAH% of HDPE-g-MAH-MAS. MAH content: 1.5%; MAS content: 1.5%

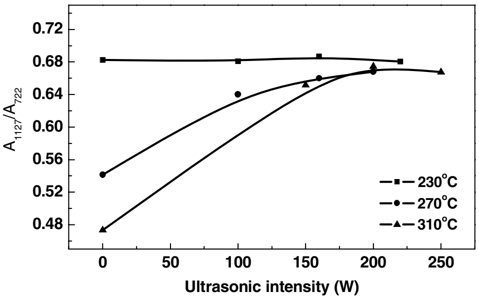


Figure 10 Influence of ultrasonic intensity on FT-IR absorbency area ratio (A_{1127}/A_{722}) of HDPE-g-MAH-MAS. MAS content in reaction mixture: 1.5%; MAH content in reaction mixture: 1.5%

The curves in the Figure 9 show that the percentage of MAH grafting of the HDPE-g-MAH-MAS product increases with increase of ultrasonic intensity and is higher than that of HDPE-MAH product [27, 28]. Meanwhile the curves in the Figure 10 show that the ratio of absorption peaks area A_{1127}/A_{722} of the product at 270°C and 310°C increase obviously with increase of ultrasonic intensity, and more obvious than that in Figure 4, showing that the fuctionalization reaction of HDPE with MAS can be promoted by adding a second grafting monomer MAH.

Figure 11 shows that with increasing ultrasonic intensity, the melt flow rate of the products do not change obviously at 230°C and 270°C, but increase obviously at 310°C and above 160W, which is also attributed to the change of molecular weight of the product and the increase of polarity of its chains.

These results show that a functionalized product (HDPE-g-MAH-MAS) with higher percentage of grafting and better melt flow property can be obtained at a lower ultrasonic intensity and a suitable reaction temperature.

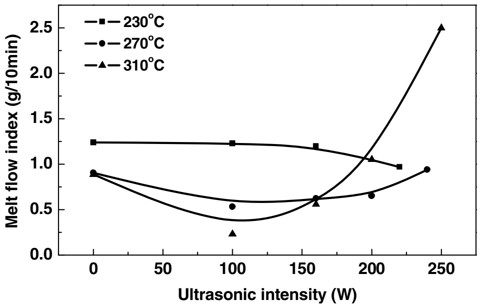


Figure 11 Influence of ultrasonic intensity on melt flow rate of HDPE-g-MAH-MAS.
MAH content: 1.5%; MAS content: 1.5%

3.3 Measurement of gel content of the functionalized product

Data listed in Table 1 show that the gel content of the functionalized products (HDPE-g-MAH-MAS) under different ultrasonic intensity and different reaction temperature is less than 1.0%, indicating that the cross-linking reaction is very small.

Table 1 Influence of ultrasonic intensity and reaction temperature on the percentage of grafting and gel content of HDPE-g-MAH-MAS*

Sample No.	Reaction temperature (°C)	Ultrasonic intensity (W)	Percentage of grafting (msaa%)	A_{1127}/A_{722}	Gel content (mass%)
1	230	0	0.13	0.643	0.46
2	230	220	0.25	0.681	0.50
3	270	0	0.28	0.542	0.23
4	270	200	0.34	0.668	0.39
5	310	0	0.34	0.473	0.59
6	310	200	0.45	0.675	0.94

* Content of MAH and MAS in reaction mixture respectively: 1.5%

3.4 Effects of functionalized products on the mechanical properties of HDPE/GF composites

Data listed in Table 2 from reference [27] are the mechanical properties of the HDPE/GF composites. The mechanical properties of the composite improved by the ultrasonic induced product are obviously higher than that of by peroxide initiated product due to the difference of their molecular structures [28], although the percentage of grafting of the peroxide initiated product is higher than that of ultrasonic induced product.

Table 3 shows that compared to the unmodified HDPE/GF composite (Sample A), the tensile strength, flexural strength and Izod impact strength of HDPE/GF composite modified by the functionalized product through ultrasonic initiation (HDPE-g-MAH, Sample B) are increased from 32.2 MPa, 46.2 MPa and 3.3 kJ/m^2 to 69.5MPa, 106.5MPa and 13.0 kJ/m^2, the tensile strength, flexural strength and Izod impact strength of the composite modified by the functionalized product through ultrasonic initiation (HDPE-g-MAH-MAS, Sample C) are increased to 73.6MPa, 114.0 MPa and 11.7 kJ/m^2 respectively.

Table 2 Mechanical properties of HDPE/GF composites improved with the HDPE-g-MAH

Sample No.	Glass fiber content (mass%)	HDPE-g -MAH content* (mass%)	Percentage of grafting (mass%)	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact strength (kJ/m^2)
1	30	12	0.54	38.7	44.1	2950	5.3
2	30	12	0.31	55.8	64.0	4320	12.7

* HDPE-g-MAH in sample 1 prepared through peroxide initiation, in sample 2 through ultrasonic initiation.

Table 3 Mechanical properties of HDPE/GF composites improved with functionalized products

Sample No.	Glass fiber content (mass%)	Functionalized Product* content (mass%)	Percentage of grafting (mass%)	Tensile strength (MPa)	Flexural strength (MPa)	Izod impact strength (kJ/m^2)
A	34.9	0		32.2	46.2	3.3
B	35.5	12.8	0.41	69.5	106.5	13.0
C	37.2	10.8	0.34	73.6	114.0	11.7

* Sample B and C modified with HDPE-g-MAH and HDPE-g-MAH-MAS respectively

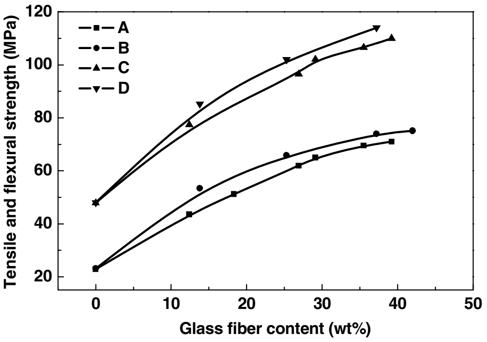


Figure 12 Tensile strength (A, B) and flexural strength (C, D) of HDPE/GF specimens versus glass fiber content. Curve A and C modified with HDPE-g-MAH, curve B and D modified with HDPE-g-MAH-MAS

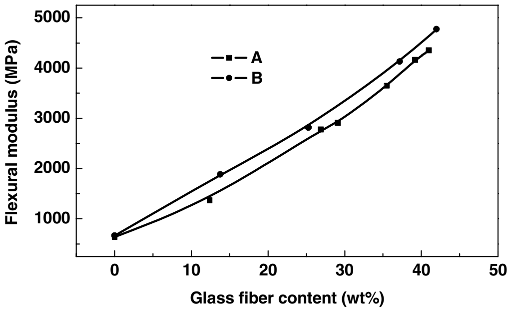


Figure 13 Flexural modulus of HDPE/GF specimens vs. glass fiber content. Curve A and B modified with HDPE-g-MAH and HDPE-g-MAH-MAS respectively

Figure 12 and Figure 13 show the mechanical properties of HDPE/GF composite modified by HDPE-g-MAH and HDPE-g-MAH-MAS. With increase of glass fiber content, the tensile strength, flexural strength and flexural modulus increases obviously, the mechanical properties of HDPE/GF composite modified by HDPE-g-MAH-MAS is obviously higher than that of by HDPE-g-MAH.

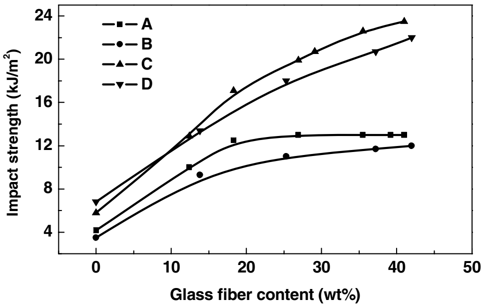
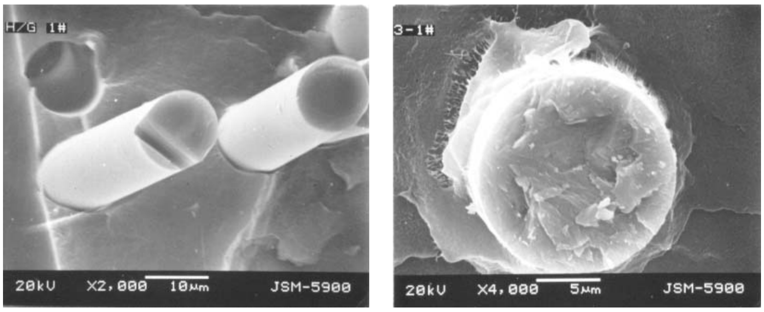
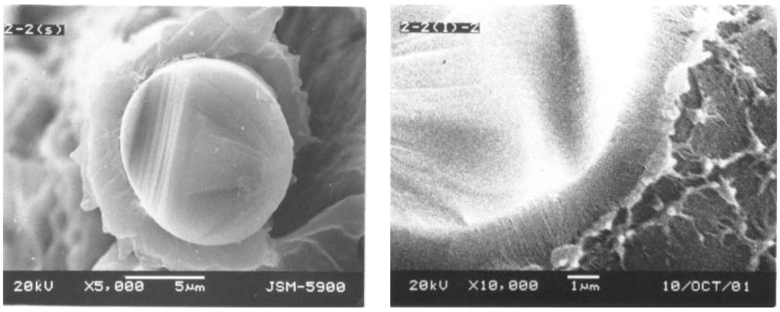


Figure 14 Izod impact strength (A, B) and Charpy notch impact strength (C, D) of HDPE/GF specimens versus glass fiber content. Curve A and C modified with HDPE-g-MAH, curve B and D modified with HDPE-g-MAH-MAS



Sample A (4 mm thickness, FFS) Sample B (4 mm thickness FFS)



Sample C (4 mm thickness, TFS) Sample C (10 mm thickness, IFS)

Figure 15 Scanning electron micrographs of the tensile (TFS), flexural (FFS) and impact(IFS) fracture surface of HDPE/GF specimens (the fracture surface was etched at 80°C by xylene) Sample A without modifying with functionalized HDPE; Sample B modified with HDPE-g-MAH; Sample C modified with HDPE-g-MAH-MAS

Figure 14 shows that the Charpy notched impact strength and Izod impact strength of HDPE/GF composite modified by HDPE-g-MAH or by HDPE-g-MAH-MAS are raised about 250%, due to the increase of glass fiber content and the effect of the functionalized product on the interface bonding strength.

Figure 15 shows scanning electron micrographs of the tensile (TFS, 4 mm thickness), flexural (FFS, 4 mm thickness) and impact (IFS, 10 mm thickness) fracture surface of HDPE/GF specimens. In the absence of the functionalized product, the surface of glass fiber of sample A is smooth, the interface adhesion is poor and there is a clear gap between the glass fiber and matrix. In the presence of the functionalized product, the connection between glass fiber and matrix in sample B and sample C becomes very strong, and a clear covered layer of glass fiber is appeared, meaning that the interfacial bonding strength is obviously enhanced.

It can be seen from SEM of the impact fracture surface of HDPE/GF specimens in Figure 15-Sample C (IFS, 10 mm thickness), there is a clear oriented crystal layer existing between the interface of glass fiber and the matrix, the interface bonding strength is obviously enhanced through the reaction of the functionalized products (HDPE-g-MAH and HDPE-g-MAH-MAS) with the coupling agents coated on the surface of glass fiber. Combining with the reference [29] results, this appearance shows that in the higher interfacial boding strength condition, the interfacial stress coming from the matrix shrinkage strain-induced the crystallization of matrix and led to the formation of the oriented crystal layer. In contrast, under the poor interfacial adhesion, the interfacial stress will be released by the formation of the interfacial cracks. The interfacial bonding strength between glass fiber and HDPE matrix is the determining factor of the formation of the oriented crystal layer.

4. Conclusions

1. The macroradicals produced due to stress-induced scission of HDPE chain caused by ultrasonic vibration during melt-extruding process will lead to the functionalization reaction of HDPE with MAS or with MAH and MAS mixture, some graft or block polymers will be formed therefrom.

2. The fuctionalization reaction of HDPE with MAS can be promoted by adding a second grafting monomer MAH. The functionalized products HDPE-g-MAH-MAS with a higher percentage of grafting, a higher melt flow rate and a lower of gel content(≤0.9%) can be prepared under a lower ultrasonic intensity and a suitable reaction temperature (200W, 270°C).

3. The ultrasonic-induced products have a higher reactivity with the coupling agents coated on the surface of glass fibers, the mechanical properties of the composite improved by the ultrasonic induced product are higher than that of by peroxide initiated product and the mechanical properties of HDPE/GF composite modified by HDPE-g-MAH-MAS are higher than that of by HDPE-g-MAH.

4. An oriented crystal layer exists between the interface of glass fiber and the matrix, the interfacial bonding strength between glass fiber and HDPE matrix is the determining factor of the formation of the oriented crystal layer.

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