

# Structure and Properties of Maleated High-Density Polyethylene

YILONG WANG,<sup>1</sup> DEQIANG JI,<sup>1</sup> CHANGLAI YANG,<sup>1</sup> HONGJIN ZHANG,<sup>1</sup> CHUAN QIN,<sup>2</sup>  
and BAOTONG HUANG<sup>2,\*</sup>

<sup>1</sup>Department of Polymer Materials, Dalian University of Technology, Dalian, 116012, People's Republic of China;

<sup>2</sup>Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,

Changchun 130022, People's Republic of China

## SYNOPSIS

Possible changes in the structure and properties of maleated polyethylene (HDPE-MA) at different degrees of grafting (D.G.) were examined. At the level of 1.6 maleic anhydride (MA)/100 ethylene units E, 70–80% of crystallinity of the parent PE was retained (DSC and WAXD). Both melting temperature and crystallization temperature decreased only slightly with increase in D.G. The lattice constants  $a$  and  $b$  of the orthorhombic PE crystallites remained constant, although  $c$  was constantly at a larger value. The presence of MA groups hampered the packing of PE chains, leading to an increase in PE crystallite sizes of  $\bar{L}_{110}$  and  $\bar{L}_{200}$  with maleation. Of the viscoelastic relaxations, dynamic mechanical analysis showed easier segmental motions and thus lowering in  $\gamma$ -,  $\alpha$ -, and  $\beta$ -relaxation temperatures with maleation. The breaking strength ( $\sigma_b$ ) increased slightly with maleation, whereas the elongation at break ( $\epsilon_b$ ) lowered due to interaction between the MA groups. In all, in HDPE-MA up to a D.G. of 1.6 MA/100 E, PE properties were maintained to be used per se or as a compatibilizer for blends involving PE or in any other usage where retention of PE properties is desired. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyolefins or their copolymers are endowed properties pertinent to polarity by, besides other avenues, functionalization with maleic anhydride (MA) or its ester moieties in the presence of a peroxide.<sup>1–4</sup> Patents related to maleation reactions and application of MA-grafted polyethylene (PE-MA) or polypropylene (PP) for a variety of purposes have been too numerous to enumerate. On the suggested chemical structure, besides that with coupled pendant polyMA on PE<sup>5</sup> or that formed through cation-radical species,<sup>6</sup> a recent investigation<sup>7</sup> indicated a monomeric substitution of the MA groups on eicosane, a model compound of PE chains, although free-radical homopolymerization of MA is also known to be possible.<sup>8,9</sup> The monomeric layout of MA groups would allow cleaner utilization of the polar functions

in further chemical modifications such as grafting through the attached MA.

It is most desirable in many cases to maintain the basic PE structure and its mechanical properties in PE-MA, when used per se or as in the case where the MA groups are brought into further reaction with a polar polymer to make a grafted copolymer to serve as a compatibilizer for a PE/polar polymer or in any other occasion where retention of the PE properties is desired. The former case includes reacting PP-MA with NH<sub>2</sub>-terminated nitrile rubber (NBR) in preparing blended thermoplastic elastomers comprising PP and NBR,<sup>10</sup> in situ coupling of ethylene-propylene rubber (EPR)-MA with nylon 6 to yield a compatibilizing agent for EPR-toughened nylon,<sup>11</sup> and similarly in alloying polyolefin/nylon blends.

Elaboration on the effect of MA substitution on the polyolefin structure and properties, however, seems lacking. Greco et al. studied the effect of the degree of grafting (D.G.) of butyl ester of maleic acid on the morphology and properties of an eth-

\* To whom all correspondence should be addressed. Also, adjunct professor, Dalian University of Technology.

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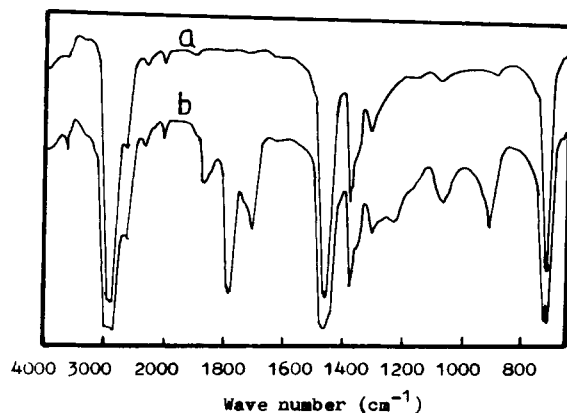
ylene-propylene copolymer.<sup>11</sup> In the present work, effort has been made to determine, by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and dynamic mechanical analysis (DMA), to what extent the D.G. of MA affects the basic structure and properties of high-density polyethylene (HDPE).

## EXPERIMENTAL

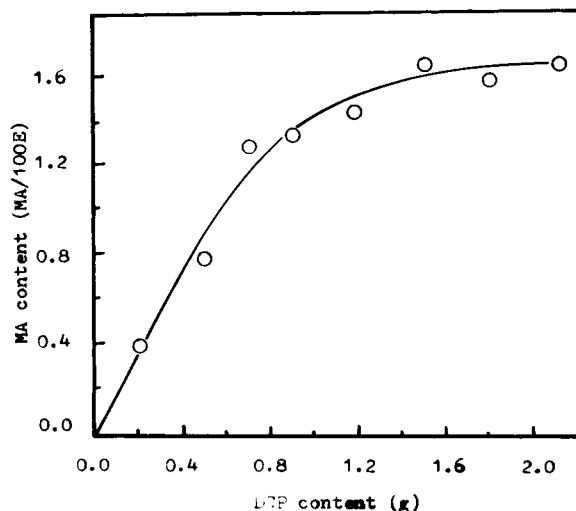
Maleic anhydride (MA) was recrystallized twice by repeatedly dissolving in chloroform under heating and stirring, and chilling the filtered solution in ice water. Dicumyl peroxide (DCP) was also recrystallized twice by dissolving in anhydrous ethanol, filtering the solution while hot, and chilling in ice water.

Maleation was carried out at 139°C for 90 min in a 600 mL xylene solution of 60 g of HDPE (GD7255, Liaoyang Chemical Fiber Co.), 30 g of MA, and varying amounts of DCP. DCP, the amount of which controls the D.G., was added to the boiling xylene solution. To get rid of the unreacted MA from HDPE-MA, the reaction product went through several cycles of being precipitated in acetone from its xylene solution, collected, and washed several times with acetone.

The content of MA in the grafted polymers (D.G.) was analyzed by adding a standard ethanolic KOH solution to a xylene solution of the samples and, after refluxing to dissolve and cooling, back-titrating the excess KOH with a standard xylene solution of acetic acid. The D.G. is calculated as the number of MA/100 ethylene units (MA/100 E).



**Figure 1** Infrared spectra of (a) HDPE and purified (b) PE-MA.



**Figure 2** Maleation of HDPE to varying degrees. Reaction conditions: HDPE 60 g; MA 30 g; xylene 600 mL, 139°C, 90 min.

## Physical Measurements

$[\eta]$  of the samples was measured in decalin at 135°C. IR measurements were made on a Shimadzu IR-408 with film samples molded at 160°C and 5 MPa in a compression molder.

WAXD samples were molded at 140°C and 9.8 MPa and slowly cooled to ambient temperature in the mold. Unit-cell parameters were found by computer modeling. The crystallite sizes  $\bar{L}_{110}$  and  $\bar{L}_{200}$  were determined from the peak width.<sup>13</sup> The crystallinity ( $X_c$ ) of the samples by WAXD was calculated according to the following equation<sup>14</sup>:

$$X_c(\%) = \frac{I_{110} + 1.46I_{200}}{0.75KI_a + I_{110} + 1.46I_{200}} \times 100$$

DSC measurements were made on a Perkin-Elmer DSC 7C with specimens as for WAXD, with a temperature increasing or decreasing rate of 10°C/min. Crystallinity of the specimens was calculated according to

$$X_c(\%) = (\Delta H_m / \Delta H_m^0) \times 100$$

taking  $\Delta H_m^0 = 7.919$  kJ/mol.<sup>15</sup>

Tensile tests were made on an Instron 1121 at 25°C with a crosshead speed of 50 mm/min. The dumbbell specimens of ca. 0.4 mm thickness with a width of 4 mm were used as for the WAXD measurements. A DDV-II-EA was used for the dynamic mechanical analysis at an amplitude of 0.200 and a programmed scanning rate of 2°C/min.

**Table I Conversion Factors for D. G. in Different Units**

From D. G. in	To D. G. in	× Factor
No. MA/100 E	g Ma/100 g PE-MA	3.5
No. MA/100 E	mmol MA/100 g PE-MA	37.5
g MA/100 g PE-MA	mmol MA/100 g, PE-MA	10.2

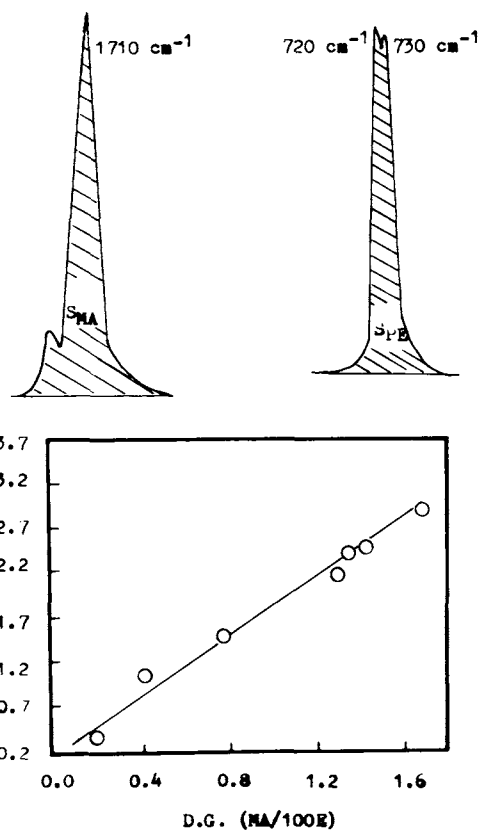
## RESULTS AND DISCUSSION

### Preparation of HDPE-MA

The reaction between MA and HDPE was carried out in the presence of DCP in xylene solution. Samples for IR measurement were purified by dissolving in xylene and precipitating in acetone for five times and then drying in vacuum at 60°C. The HDPE-MA samples exhibited a characteristic vibrational band of the carboxyl group on storage of the sample (Fig. 1).

On the basis of our previous experience in synthesizing PE-MA,<sup>1</sup> samples of HDPE-MA with various D.G. were prepared by varying the amount of DCP used in the preparation (Fig. 2). In the literature, the D.G. of PE-MA has been reported in different units. Conversion factors are thus given (Table I), which should facilitate the mutual conversion in comparing the literature values.

An empirical IR method of analyzing the MA content in HDPE-MA films was tried, using the ratio of the areas of the characteristic carbonyl absorptions at 1786 cm<sup>-1</sup> (in anhydride) and 1710 cm<sup>-1</sup> (in carboxyl) and PE absorption bands at 720 and 730 cm<sup>-1</sup>, the latter being used as the internal standard. A calibration curve of these ratios was constructed against the titration values of these samples (Fig. 3). In this manner, a sample, e.g., 0.64 MA/100 E, by titration, was found from the curve to be 0.67 MA/100 E. This preliminary result should en-



**Figure 3** Calculation of areas of characteristic absorption bands ( $S_{MA}$ ,  $S_{PE}$ ) and  $S_{MA}/S_{PE}$  vs. D.G. curve.

courage the use of this much simpler IR method for analyzing MA in PE-MA. Earlier, besides the commonly used titration (or potentiometric titration) methods, De Vito et al.<sup>4</sup> also employed an IR method for carbon tetrachloride-soluble ethylene-propylene copolymers. A calibration curve had been constructed from the ratio of absorbance of the bands at 1735 cm<sup>-1</sup> (dibutyl and diethyl succinate) and that of the solvent at 1291 cm<sup>-1</sup> at different concentrations of the ester. It is known that the grafted MA is easily hydrolyzed,<sup>16</sup> and a reversible equilibrium existed between the anhydride and the acid

**Table II Degree of Grafting (D. G.) of Samples**

	PE	Sample No.					
		1	2	3	4	5	6
D. G. (no. MA/100 E) 135°C	0	0.60	0.80	0.87	0.95	1.18	1.59
Decalin (dL/g)	12.6	12.6	11.7	11.7	9.70 <sup>a</sup>	11.2	7.30 <sup>a</sup>

<sup>a</sup> After removal of minute amount of gel.

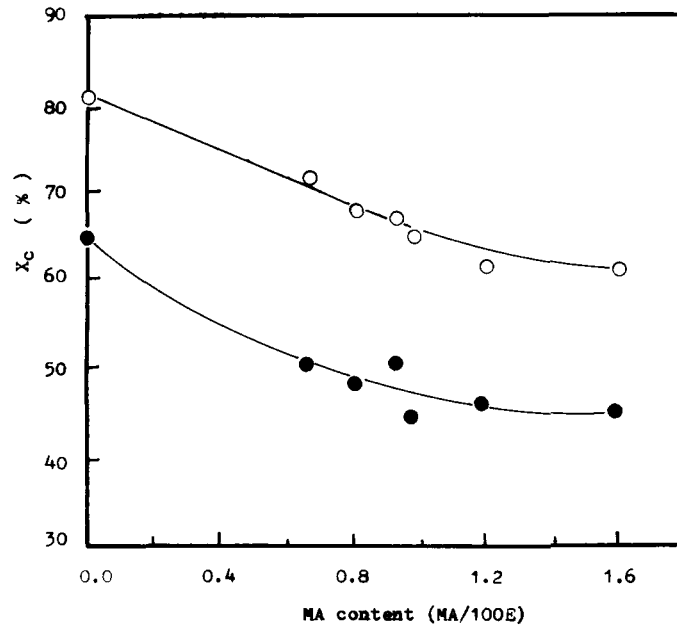


Figure 4 Crystallinity of HDPE-MA: (○) WAXD; (●) DSC.

groups.<sup>17</sup> Since the exact ratio of the anhydride/carboxyl is varying, no differentiation between them and their effect on properties is made in this work under conditions not extreme in favor of hydrolysis or vacuum drying. This distinction favors the coverage of a wider range of structures and properties.

Besides the two abnormal values where gel was noticed in the samples at a high concentration of

DCP, the  $[\eta]$  of the samples did not change to an appreciable extent with D.G. (Table II). In lieu of a knowledge of the influence of the MA groups on the chain thermodynamics, we may assume that degradation of the PE chain, if at all, had not occurred to an observable extent. This is in strong contrast to the case of maleation of polypropylene under comparable conditions.<sup>18</sup>

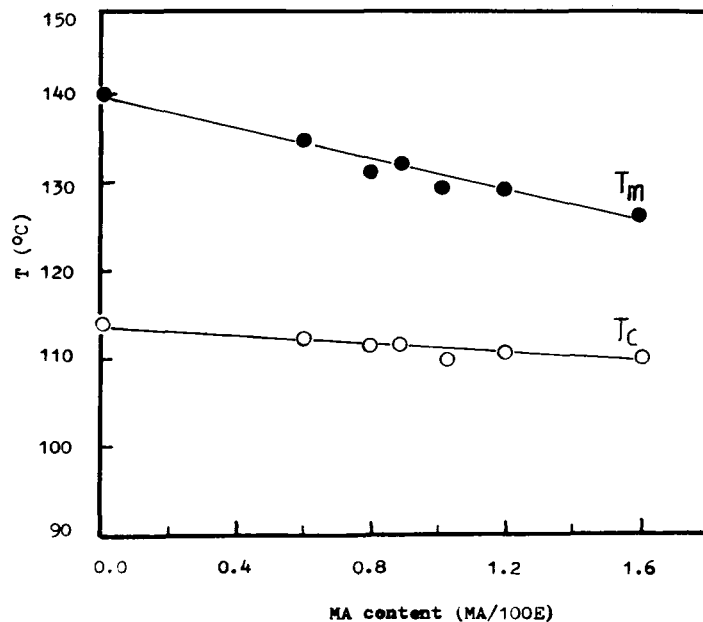


Figure 5  $T_c$  and  $T_m$  of HDPE-MA.

**Table III Lattice Constants of HDPE-MA**

	D.G. (No. MA/100 E)						
	0	0.60	0.80	0.87	0.95	1.18	1.59
$a$ (Å)	7.47	←————→		7.46 ± 0.01	————→		
$b$	4.97	←————→		4.96 ± 0.00	————→		
$c$	2.18	2.22	←————→		2.56 ± 0.00	————→	

### DSC and WAXD Characterization

The essence of the function of the PE backbone in a graft copolymer when used as a compatibilizer for blends involving PE lies in the subsistence of the inherent structure and properties of PE, so that the PE components can cocrystallize to improve the adhesion at the interface of the separated phases. Crystallinity ( $X_c$ ) of PE in the PE-MA samples (by both DSC and WAXD) showed gradual lowering with increasing amount of annexed MA moieties (Fig. 4). A retention of 70–80% of the crystallinity of the parent PE ( $X_c$  66% by DSC and 81% by WAXD) appeared with the sample of the highest degree of maleation in the present series of samples. The lowering of  $X_c$  is understandable in light of the intrusion of the bulky MA groups in the crystallite formation. An  $X_c$  of 50–60% is expected to be acceptable for PE to behave as a structural material. A residual crystallinity of  $\geq 10\%$  to  $< 2\%$  in EPR also decreased linearly with the D.G. with dibutyl maleate.<sup>19</sup>

Melting temperature ( $T_m$ ) of the PE-MA samples as measured by DSC decreased slightly with increasing amount of grafted MA (Fig. 5). This is the direct consequence of the lowering in PE crystallinity and the imperfect PE crystallites in the presence

**Table IV PE Relaxations in HDPE-MA**

	MA Content (MA/100 E)			
	0	0.60	1.18	1.59
$\gamma$ -Relaxation (°C)	-99.4	-105.4	-104.8	-110.7
$\alpha$ -Relaxation (°C)	71.4	65.8	61.9	58.3

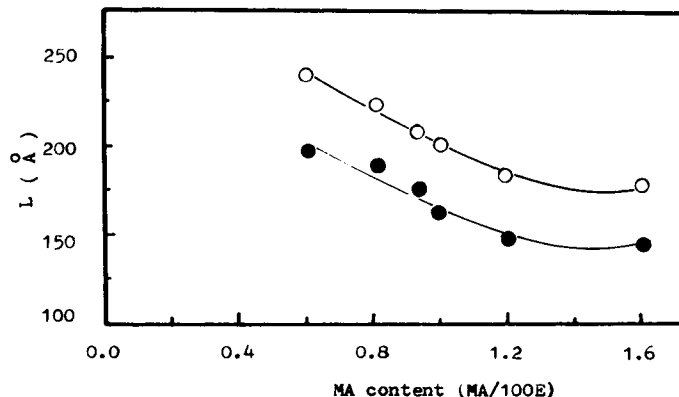
of the MA groups. The presence of MA also impeded the process of crystallization, leading to a greater extent of supercooling, and, hence, a lower crystallization temperature ( $T_c$ ) (Fig. 5).

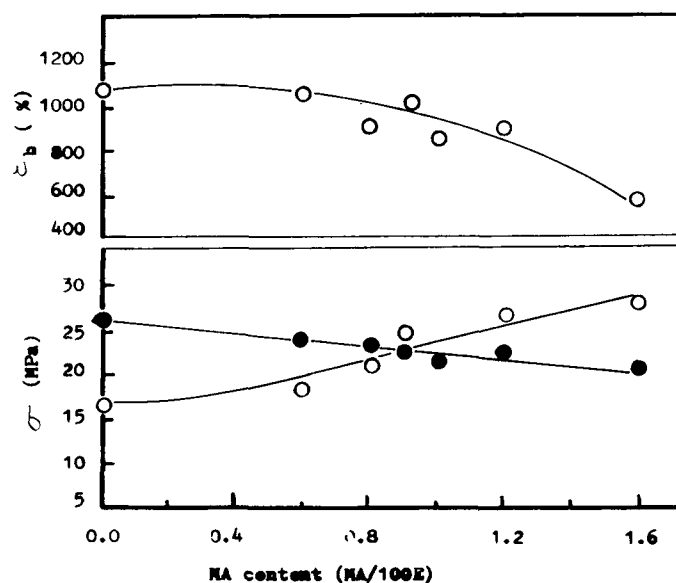
The lattice constants  $a$ ,  $b$ , and  $c$  of the grafted copolymers demonstrated the preservation of the PE orthorhombic crystalline structure, although parameter  $c$  was constantly larger than that of the parent HDPE (Table III), showing an increase in the spiral spacing along the  $c$ -axis and, in consequence, an expansion of the volume of the unit cell.

The crystallite size  $\bar{L}_{110}$  and  $\bar{L}_{200}$  of the PE in PE-MA decreased with increase in D.G. of MA (Fig. 6), showing that the presence of MA groups hampered the packing of the PE chains.

### Viscoelastic Behavior

The three relaxations in PE below their  $T_m$  have been reviewed by McCrum.<sup>20</sup> In its simplest form, the  $\alpha$ -relaxation originates from the molecular motion within the crystalline structure and the  $\gamma$ -relaxation from that of the short segments in the amorphous region, whereas the  $\beta$ -relaxation originating from the molecular motion of the side chains is proportional to the content of the side chains and thus may not appear in linear HDPE.

**Figure 6** Crystallite thickness ( $\bar{L}$ ) of HDPE-MA: (○)  $\bar{L}_{110}$ ; (●)  $\bar{L}_{200}$ .



**Figure 7** Yield strength [(●)  $\sigma_y$ ], break strength [(○)  $\sigma_b$ ], and elongation at break ( $\epsilon_b$ ) of HDPE-MA.

Examination of the damping curves of samples of varying degrees of MA grafting gives the following results (Table IV): The  $\gamma$ -relaxation, reflecting the segmental motion in the amorphous region, shifted on maleation to lower temperature with higher intensity in  $\tan \delta$ . The MA groups, owing to their plasticizing effect, increased the free volume of the system and thus facilitated the local motion of the chain segments and made the relaxation occur at lower temperatures.

The same effect applies to chain segments between lamellae and in fibrils in the crystalline region; thus, the  $\alpha$ -relaxation also occurred at lower temperature as with  $\gamma$ -relaxation. The  $\beta$ -relaxation, which was not apparent for HDPE, appeared on maleation and moved with the level of maleation to lower temperatures with increased intensity, as a result of an increase in the free volume of the system.

### Physicomechanical Properties

Our primary concern in this work centers on how the mechanical properties of PE are altered on substitution of the MA moieties. Change of yield strength ( $\sigma_y$ ), breaking strength ( $\sigma_b$ ), and elongation at break ( $\epsilon_b$ ) of PE-MA samples with varying levels of MA grafting is shown in Figure 7.

The yield strength decreased slightly with the level of MA grafting, probably due to the corresponding decrease in chain stiffness as the result of lowering in the crystallinity of the test sample. Con-

tribution to the lowering of the yield strength may also come from the expansion of the free volume in the presence of the MA groups. The increase in break strength and lowering in elongation at break may be the result of the interaction between the polar MA groups.

Anyway, grafting of MA on HDPE to the extent as in the present work (up to 1.6 MA/100 E) did not bring about deterioration of properties of PE. Thus, HDPE-MA per se as prepared in this work could be used as a structural material or should behave as a compatibilizer for blends involving PE or be good for any other usage where retention of PE properties is desired.

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