Effect of the Graft Yield of Maleic Anhydride on the Rheological Behaviors, Mechanical Properties, Thermal Properties, and Free Volumes of Maleic Anhydride Grafted High-Density Polyethylene

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ABSTRACT: The rheological behavior, thermal properties, and molecular mobility of a series of maleic anhydride (MA) grafted high-density polyethylenes were characterized and evaluated. The rheological behavior was studied with a Haake minilaboratory. The viscosity of the samples in their melt state decreased with an increase in the graft yield, and this could be attributed to the higher molecular mobility for samples with a higher degree of grafting. The thermal properties were investigated with dynamic mechanical analysis and differential scanning calorimetry. Positron annihilation lifetime measurements were used to study the effect of the degree of grafting on the chemical environment and the atomic-scale free-volume properties. It was found that the grafted MA group played a significant chemical inhibition role in positronium formation when the graft yield was low. The results also indicated that the higher the degree of grafting was, the broader the free-volume distribution was. The relationship between the microstructure and rheological behavior is discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 985–992, 2008

Key words: melt; microstructure; polyethylene (PE); viscosity

INTRODUCTION

The modification of polymers has become a major route for obtaining structural and functional polymers with desired physical and chemical properties at lower cost than the development of completely new polymers. Several methods, such as solution processing,[1] UV processing,[2] and reactive extrusion processing,[3] have been investigated for carrying out graft copolymerization for reactive compatibilizers and interfacial active agents. The reactive extrusion process has been used to produce a wide variety of polymer products because of its low cost and widespread applications in engineering. Polyolefins are the most preferred polymers for this process.

Polyethylene (PE) exhibits excellent toughness, chemical stability, biocompatibility, and good process rheological properties, but it is a hydrophobic polymer. For PE to be used effectively in applications requiring adhesion to polar fillers (i.e., clay, glass fiber, and metallic microparticles or nanoparticles) or polymers (i.e., nylon), it must be modified to incorporate polar functionality onto the PE backbone to avoid a coarse and unstable phase morphology and poor interfacial adhesion along the interphases or interfaces. The functionalization of PE with polar monomers, particularly maleic anhydride (MA), is one of the most common examples of PE modification. Many attempts have been made to study the parameters affecting the MA grafting reaction. Razavi Aghjeh et al.[4] showed that the reactant concentration (MA and reaction initiator) plays a major role in the determination of the graft yield and the extent of chain branching/crosslinking as competitive side reactions. Gaylord et al.[5] demonstrated that electron donor materials, which inhibit the formation of MA excimers, can reduce the extent of chain branching/crosslinking. This process may occur at the expense of the graft yield. Chandranupap and Bhattacharya[6] examined the effect of the presence of comonomers on the grafting reaction of MA onto PE and showed that the use of vinyl monomers could lead to a higher degree of grafting and less crosslinking. Covas et al.[7] studied the free-radical melt grafting of MA onto PE with an emphasis on the physicochemical phenomena developing along the screw axis of a twin-screw extruder for different PEs.

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In this study, maleic anhydride grafted high-density polyethylenes (MA-g-HDPEs) with different contents of MA were prepared and characterized by different means. The effect of the MA graft content on the microstructure and local chemical properties was studied.

EXPERIMENTAL

Materials and preparation

High-density polyethylene (HDPE; PE-LA-500012) was purchased from Daqing Petroleum Chemical Plant (Daqing, China). MA and dicumyl peroxide (DCP) were supplied by Shanghai Chemical Group (Shanghai, China).

A corotating twin-screw extruder (SHJ-20, Nanjing Giant Machinery Co., Ltd.) with three separate temperature-controlled barrel zones was used for the free-radical melt-grafting processes. The diameter of the screw was 21 mm, and the total barrel length was 672 mm. All experiments were conducted at a screw speed of 300 rpm and a feed rate of 6.5 kg/h. Before the processing, desired amounts of HDPE and MA were mixed for 5 min in a mixer. The barrel temperature was maintained at 160°C in the feed section and at 190°C in the next two zones and the die holder. The extrudate was then continuously cooled in a water bath and then pelletized.

All the blends were dried at 80°C for 4 h before injection molding. Some specimens for tests were prepared on a microinjection molding machine (Thermo Electron Corp.). The injection time was 30 s, the injection pressure was 0.55 MPa, the injection temperature was 190°C, and the mold temperature was 40°C.

Characterization

Fourier transform infrared (FTIR) analysis

Each sample (2 g) was weighed and put in a flask with 100 mL of xylene; the flask was then heated. After the grafter was completely dissolved in xylene, the solution was poured into 250 mL of acetone. The precipitate was filtered and dried at 60°C for 24 h. The dried precipitate was pressed into a film 0.1 mm thick and characterized with a Nicolet 5700 FTIR apparatus (Thermo Electron).

Degree of Grafting of MA-g-HDPE

The filtered and dried precipitate (0.2–0.4 g) was put in a flask with 50 mL of xylene and completely dissolved. Then, the cooling solution was poured into 20 mL of ethanol/potassium hydroxide, and the solution was heated and refluxed. After 4 h, the chemical titration of this solution was carried out with a hydrochloric acid/ethanol solution. Therefore, the

graft yield of MA could be calculated according to the following formula:

Degree of grafting (%)
$$= [(V_1 - V_2)NM/1000W] \times 100\% \quad (1)$$

where V_1 is the volume of hydrochloric acid in the base experiment, V_2 is the volume of hydrochloric acid of the grafter MA-g-HDPE, N is the concentration of hydrochloric acid, M is the molecular weight of MA, and W is the weight of the precipitate.

Rheology

Rheological measurements were performed with a Haake Mini-Lab twin-screw extruder (Thermo Electron) with a recycle circuit, which allowed viscosity–time curves to be recorded. The samples were processed at 50 rpm and 190°C with a counterrotating screw configuration.

Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were conducted on a DMA 242C instrument from Netzsch Instruments Co., Ltd. The three-point bending mode was selected. Tests were performed at 1 Hz, and the temperature programs were run from −50 to 130°C under a controlled sinusoidal strain at a heating rate of 2°C/min.

Differential scanning calorimetry (DSC)

A PerkinElmer DSC7 differential scanning calorimeter with nitrogen as the purge gas was used. Samples of 4–4.5 mg were analyzed via heating from 30 to 200°C at a rate of 10°C/min. The degree of crystallinity (χ) was then calculated as $\chi = \Delta H_f / \Delta H_{f0}$, where ΔH_f is the heat of fusion and ΔH_{f0} is the heat of fusion of fully crystalline PE ($\Delta H_{f0} = 293$ J/g).

Positron annihilation lifetime spectroscopy (PALS)

PALS was performed with a conventional Ortec 583 fast–fast coincident system at room temperature. The time resolution of the system was 290 ps. A [22]Na positron source with 1.0×10^6 Bq was sandwiched between two sample disks. The positron lifetime spectrum contained 10^6 counts, which were analyzed with the PATFIT[8] program to be decomposed into several lifetime components, and there were 4×10^6 counts for the MELT[9] analysis, which resolved the continuous distribution of the $ortho$-positronium (o-Ps) lifetime in the polymer.

RESULTS AND DISCUSSION

The intensity of the absorption peak at 1790 cm^{-1} corresponding to the anhydride-type carbonyls and at 1710 cm^{-1} for the acid-type carbonyl, divided by that of the CH$_2$ absorption peak at 720 cm^{-1}, was used as a measure of the degree of grafted MA.[4,10] The degree of grafting for each sample was determined with a calibration curve obtained on the basis of titration and FTIR spectroscopy results, as shown in Figure 1.

Effect of the graft yield on the rheological behavior

The curve of the viscosity versus the processing time for each sample is shown in Figure 2. The variation of the viscosity can be divided into two stages. In the first stage, the viscosity sharply increases, and this can be ascribed to feeding the material into the Haake. In the second stage, the viscosity value decreases with increasing handling time for each sample. As the viscosity is directly related to the molecular weight, main-chain scission should be observable if the viscosity decreases. The shear and heat to which the polymer is exposed during extrusion cause thermomechanical degradation, such as chain scission.[11] Therefore, the viscosity of each sample becomes lower with an increase in the processing time. Similar results have also been found in ethylene vinylacetate copolymer (EVA) material.[12] For the samples with higher graft yields, the viscosity curve has a sharper decrease. It implies that a higher degree of grafting of MA on PE would more easily cause degradation in melt extrusion. In fact, melt-phase processing of a polyolefin is often accompanied by side reactions. These include (1) radical-induced crosslinking of the polyolefin substrate, (2)
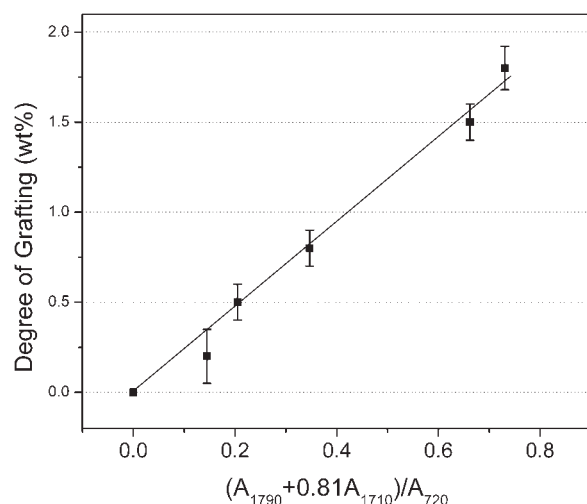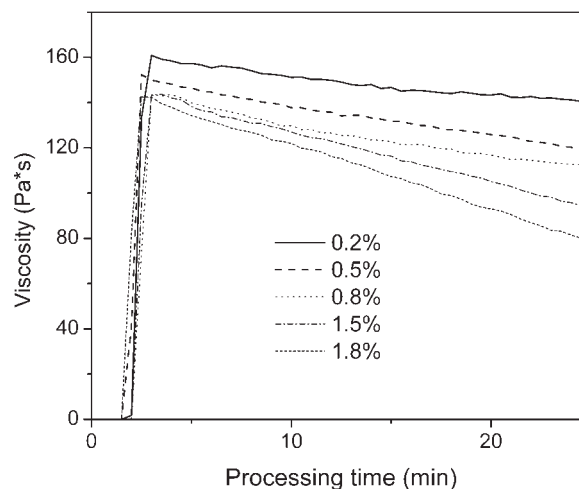

Figure 2 Viscosity of samples with different graft yields versus the processing time.

radical-induced chain scission of the polyolefin substrate, and (3) shear-induced degradation of the polyolefin substrate.[3] An increase in the MA content increased the MA excimer formation,[5] which intensified the hydrogen abstraction from the PE backbone. As a result, a sample with a higher degree of grafting should be easier to degrade in shear processing than one with a lower degree of grafting.

The initial period relates to the feeding period, and a longer processing time will lead to degradation of the material. Therefore, the viscosity value can be used to characterize the rheological property of a sample when the processing time is about 5 min. The viscosity becomes lower with an increase in the graft yield, and this should be ascribed to MA and DCP leading to degradation of the HDPE matrix in reactive extrusion.

Effect of the graft yield on the dynamic mechanical properties

DMA was performed over a temperature range of −50 to 130°C. The storage modulus characterizes the stiffness of the investigated material and its ability to store the energy. The loss modulus (E'') characterizes the material's capacity for energy dispersion, that is, the viscous properties of the material. The damping factor (tan δ) reflects the internal and external friction and expresses the ratio of dispersed energy in one deformation cycle to energy accumulated during the deformation process.

The variations of E'' with an increase in temperature are shown in Figure 3. The peak of E'' shows a higher intensity and a shift to a lower temperature when the graft yield increases from 0.2 to 0.8%. Then, with the graft yield increasing from 0.8 to 1.8%, the intensity of the peak becomes lower, and the position of the peak shifts to a higher temperature. The higher values of E'' suggest greater mobility of the polymer
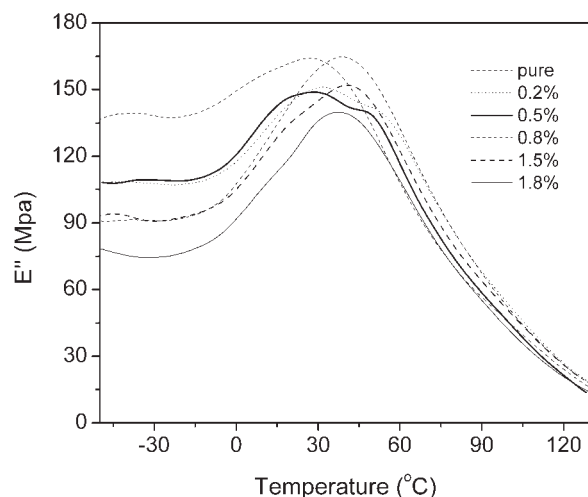

Figure 1 Calibration curve for the quantitative measurement of the degree of MA grafting on PE obtained with titration and FTIR results.

Figure 3 E'' of samples as a function of temperature at 1 Hz.

Figure 4 Tan δ of samples as a function of temperature at 1 Hz.

chains associated with the dissipation of energy when the polymer is subjected to deformation.[13] Adding grafted groups to the polymer chain implies a mixed morphology, and this would increase the heterogeneity of the microstructure. When the graft yield is low, increasing the number of grafted groups merely destroys the homogeneity of the microstructure around MA groups, and this induces easier backbone mobility. Therefore, the E'' values increase with the graft yield increasing from 0.2 to 0.8%. However, when the MA group concentration becomes higher, an increasing number of MA groups implies a greater possibility of molecular interactions between the grafted chains, so some local ordering structure may be formed. As a result, E'' decreases with increasing graft yield (from 0.8 to 1.8%).

The curves plotted from the values of tan δ versus temperature for different samples are shown in Figure 4. The samples with a low graft yield (0.2 or 0.5%) show a broader distribution in tan δ. As interpreted previously, the MA groups can influence only the microstructure in the local area around them. In this case, there is heterogeneity in MA-g-HDPE when the graft yield is low. When more MA groups are grafted in the polymer chains, the relaxation seems to split into two peaks. This could be ascribed to the interaction between the MA groups, which may lead to some local ordering structure.

Effect of the graft yield on the thermal properties

The results of the DSC measurements are shown in Figure 5. The neat HDPE has a melting transition in a narrow temperature range, reflecting its original crystalline structure. Table I compiles thermal parameters such as the transition temperatures, fusion enthalpy, and crystallinity for each of the samples.
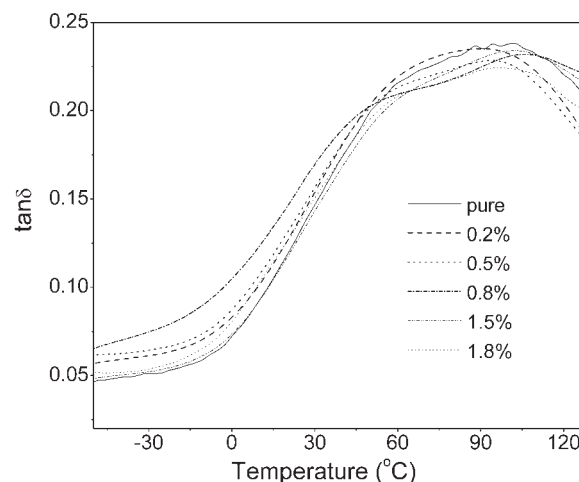
With the grafting rate increasing, the melting temperature shifts to a lower temperature slightly and then increases a little. The variation of the melting temperature measured by DSC agrees with the DMA results. Furthermore, the transition point of the melting temperature appears in the sample with the graft yield of 0.8%. A transition is also obtained by DMA when the degree of grafting is 0.8%. This suggests that a higher graft yield may induce a different microstructure than that of a sample with a degree of grafting lower than 0.8%. As shown in Table I, the introduction of the MA group leads to an evident decrease in the crystallinity. In Collar et al.'s opinion,[14] HDPE is a kind of fully regular polymer that has very few tertiary atoms. If polar groups were introduced to the repetitive unit on the crystalline phase, the system response would be sharply affected by a need to accommodate a much more
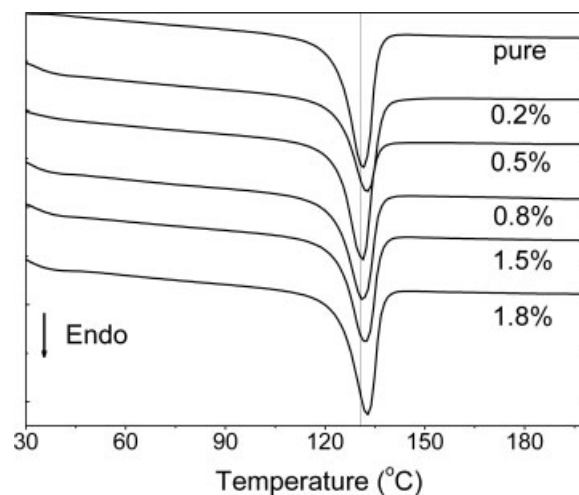

Figure 5 DSC thermograms showing the fusion peaks of samples. The lines are guides for the eyes.

Thermal Parameters of the Samples

Degree of grafting (wt %)	Melting temperature (°C)	Melting enthalpy (J/g)	Crystallinity (%)
0	131.7	149.2	50.9
0.2	132.9	112.8	38.5
0.5	131.4	124.1	42.4
0.8	130.9	123.0	42.0
1.5	131.6	123.6	42.2
1.8	132.8	139.7	47.7

voluminous amorphous phase. Therefore, the crystallinity of each grafted sample is lower than that of pure HDPE. With an increase in the graft yield, the crystallinity increases slightly. This suggests the formation of another local ordering structure related to the graft yield.

Effect of the graft yield on the microstructure of MA-*g*-HDPE

The free-volume concept is central in the interpretation of many properties of polymeric materials. It was introduced to explain the molecular motion and physical behavior of glassy and liquid states. However, its implementation as a quantitative measure of the structural disorder in a polymer is a challenging problem. Several investigations have explored the possibility of employing spectroscopic techniques to directly probe the free volume in polymeric materials.[15] PALS has been developed as probably the most successful technique for studying local free volumes.[16] The technique involves using a positron source (e.g., ^{22}Na) to emit positrons into a sample. After the positrons thermalize, they diffuse at the free state or form a bound state of the positron electron, which is known as positronium (Ps). o-Ps has an intrinsic lifetime of 140 ns *in vacuo*; however, in polymers, the o-Ps atom is preferentially localized in the free-volume holes, and its lifetime is reduced to 1–5 ns by the pick-off annihilation with an electron from the surrounding molecules. If a spherical shape of the free-volume hole can be supposed, the relationship between τ (ns), which is the average lifetime of o-Ps, and R (Å), which is the radius of the free-volume hole, is

$$\tau = 1/\lambda = 0.5[1 - R/(R + R_0)$$
$$+ (1/2\pi)\sin(2\pi R/(R + R_0))]^{-1} \quad (2)$$

where λ is the annihilation rate and $R_0 = 1.656$ Å is an empirical parameter.[17]

Dlubek[18] reported a critical analysis of the physical meaning of the lifetime components obtained by a three- and four-term decomposition of lifetime spectra in PE. The conclusion is that the constrained four-component fit gives a consistent physical picture of positron annihilation in semicrystalline PE. The shortest lifetime (τ_1) is ascribed to self-annihilation of the *para*-positronium, the bound singlet state of a positron and an electron. The second lifetime component (τ_2) is supposed to be due to free (not bound) positron annihilation, and the two longest lived components (τ_3 and τ_4) are considered to originate from o-Ps annihilation in crystalline and amorphous regions of the polymer, respectively. Of course, other views about lifetimes have also been published.[19]

In this study, the positron lifetime spectra were measured as a function of the degree of grafting and resolved into three components with the program PATFIT. After the background and source component were subtracted, the variance of fit was less than 1.2. The longest lived component was assigned to the o-Ps annihilation in the free volume.

The variations of o-Ps lifetime τ_3 and its intensity I_3 with the degree of grafting are shown in Figures 6 and 7. With an increase in the graft yield, τ_3, the longest lifetime of the grafted samples, becomes a little larger, and I_3 decreases first and then increases.

Qi and Zhang[20] found o-Ps lifetime τ_3 and its corresponding intensity I_3 to be related to the properties of side groups in the macromolecular chains. In this study, the mean free-volume size changed slightly with the graft yield.

The positron free-volume model, in which the o-Ps intensity is assumed to be simply proportional to the free-volume concentration, cannot convincingly explain why the addition of MA strongly influences the hole concentration (characterized by I_3). The spur reaction model,[21] which allows us to relate the Ps formation process to chemical effects, can explain these results, as described later. In this system, Ps formation is partially inhibited by positron trapping and annihilation with polar groups, such as the MA
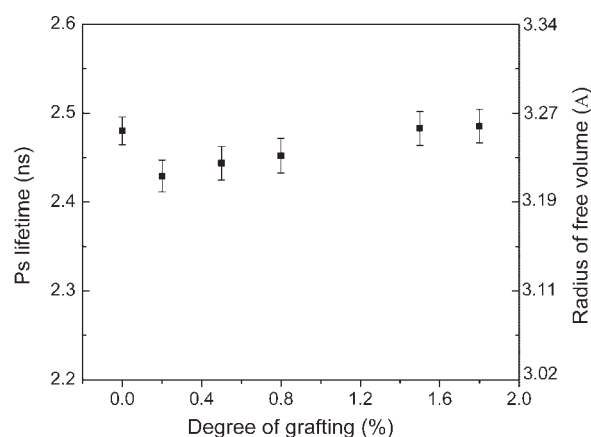

Figure 6 o-Ps lifetime for MA-*g*-HDPE as a function of the degree of grafting.
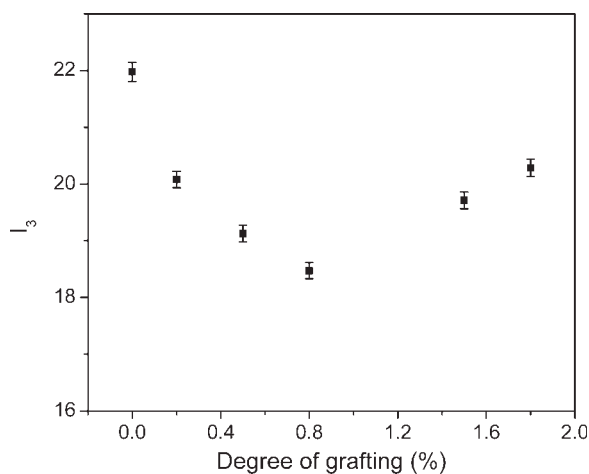
Figure 7 *o*-Ps intensity for MA-*g*-HDPE as a function of the degree of grafting.

Figure 8 *o*-Ps distribution of MA-*g*-HDPE with different degrees of grafting.

group. When inhibition of Ps formation occurs, it is seen as a decrease in the *o*-Ps intensity.[22] In He et al.'s study,[23] for a very low concentration of the inhibitors, the inhibition effect influenced the Ps formation distinctly; however, for a higher concentration of the polar groups, the inhibition effect was similar. It also has been suggested that the total fraction of *o*-Ps formed (I_3) in the polymer is related to the number of free-volume holes in the matrix. The probability of *o*-Ps formation is assumed to be proportional to the number of regions of low electron density in which *o*-Ps can locate. When the microstructure of MA-*g*-HDPE differs in reactive extrusion, the free-volume hole will be influenced by the degree of grafting.

Therefore, in MA-*g*-HDPE materials, the *o*-Ps intensity is influenced by two factors: the concentration of the free volume and the Ps inhibition effect. Increasing the free-volume concentration will lead to more *o*-Ps being formed, and increasing the MA group in samples will result in a decrease in the *o*-Ps intensity. With a low graft yield (0.2–0.8%), the MA group leading to the inhibition of *o*-Ps is the predominant factor influencing the *o*-Ps intensity; with a high graft yield (0.8–1.8%), the variety of microstructures of the polyolefin substrate in reaction extrusion results in the increase in the *o*-Ps intensity.

To carefully investigate the effect of the graft yield on the free-volume property, positron annihilation lifetime spectra with 4 million counts were measured at room temperature. As determined with eq. (2), the *o*-Ps lifetime distributions obtained by MELT that relate to the free-volume size distributions are shown in Figure 8. With the Gaussian fitting, the full width at half-maximum (FWHM) of the *o*-Ps lifetime for different samples is shown in Table II.

FWHM of the *o*-Ps distribution increases gradually with increasing graft yield, and this means that the
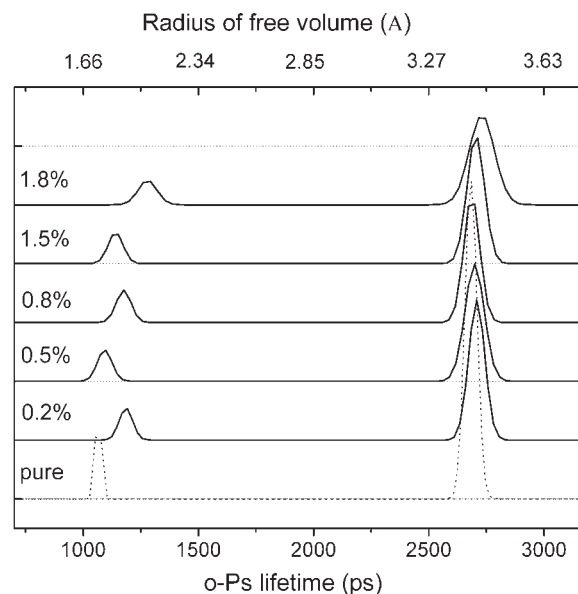
free-volume radius distribution becomes broader. When the MA group is functionalized to the backbone of HDPE, the appearance of heterogeneity will influence the microstructure. In addition, there will be more polymer chains cut off in the grafting process, and this may lead a broader free-volume distribution. Therefore, with an increasing degree of grafting, the microstructure should be more and more inhomogeneous. As a result, the free-volume distribution will be broader as the MA concentration increases.

Correlation between the rheological behavior and positron annihilation parameters

Doolittle[24] disclosed that the relation between the viscosity (η) and fractional free volume (f) is logarithmic:

$$\eta = A \exp(B/f) \tag{3}$$

where A and B are constants. Cohen and Turnbull[25] placed this expression on a solid theoretical basis by showing that eq. (3) can be derived under the

TABLE II
FWHM Values of the *o*-Ps Lifetime Distribution of Different Samples

Degree of grafting (wt %)	FWHM for τ_3 (ps)	FWHM for τ_4 (ps)
0	21	53
0.2	73	81
0.5	83	92
0.8	82	93
1.5	83	103
1.8	106	129

assumption that a distribution of hole sizes exists, and the jump probability is determined only by the chance of finding an adjacent local free volume of sufficient size into which to jump. For diffusive motion to occur, there must appear a hole large enough to permit a significant displacement of molecules.

Generally, the effective free-volume hole fraction (f), from the application of semiempirical quantum mechanical and volumetric and free-volume hole models,[17] can be thought of as the product of the average hole size and the hole concentration:

$$f = CvI \tag{4}$$

where C is the constant coefficient, v is the mean free volume, and I is the ideal o-Ps yield under the assumption of no polar group and under the consideration that the variance of I is related only to the free-volume concentration.

From the analysis in the former sections, it is found that some new local ordering structure may be formed when the graft yield is higher than 0.8%. In this case, the positron annihilation parameters may be influenced by other effects. Therefore, we just consider the samples with a low graft yield (0–0.8%). Because the MA group will lead to the inhibition of o-Ps, we assume that inhibited o-Ps is proportional to the degree of grafting when the graft yield is low (<0.8 wt %) according to a Stern–Volmer-type equation:

$$I = I_3(1 + \gamma X) \tag{5}$$

where I is the ideal o-Ps yield if we consider only the free-volume effect on the o-Ps yield, I_3 is the o-Ps intensity measured from PALS, X is the degree of grafting, and γ is the proportional factor.

On the basis of the concept mentioned previously, we obtain the following relationship:

$$\frac{1}{vI_3(\ln \eta - \ln A)} = \frac{C}{B}(1 + \gamma X) \tag{6}$$

Utracki and Sedlacek[26] reported the free-volume dependence of the polymer viscosity, and the parameters have been carefully calculated. For HDPE, $\ln A \ll \ln \eta$. For the sake of simplicity, the equation can be interpreted as follows:

$$\frac{1}{vI_3 \ln \eta} = \frac{C}{B}(1 + \gamma X) \tag{7}$$

To justify eq. (7), the experimental data have been calculated and are presented in Figure 9. The results suggest that the correlation between the viscosity and positron annihilation parameters can be approached by eq. (7). The empirical relation from the experimental data can be linearly fitted as follows:
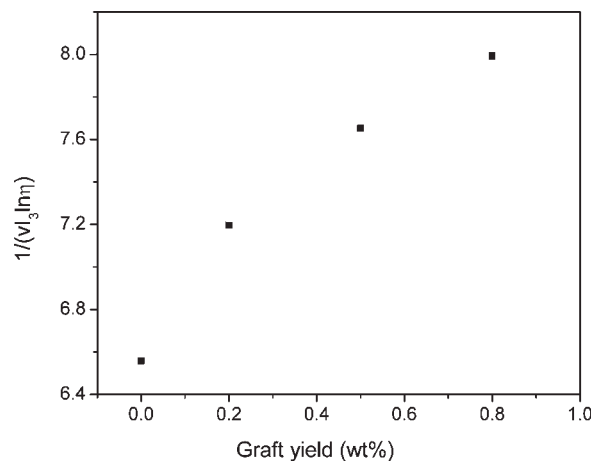

Figure 9 Plot of $1/(vI3 \ln \eta)$ versus the graft yield for samples.

$$\frac{1}{vI_3 \ln \eta} = 6.70 + 173X = 6.70 \times (1 + 25X) \tag{8}$$

Therefore, proportional factor γ is about 25 and can characterize the inhibiting effect of the MA group.

CONCLUSIONS

In this study, we investigated the properties of MA-g-HDPE with different graft yields with a HAAKE Mini-Lab, DMA, and PALS. All the results are in good agreement. The following conclusions can be drawn. The viscosity of MA-g-HDPE decreases with the processing time, and this shows that the degradation of MA-g-HDPE is mainly due to thermomechanical scission of the polymer chain. A higher degree of grafting leads to faster degradation. The viscosity of a sample with a lower graft yield was larger than the viscosity of a sample with a higher graft yield. This could be attributed to the chain scission in reactive extrusion. The melting temperature of the grafted samples decreases when the graft yield increases from 0.2 to 0.8% and then shifts to a higher temperature with the degree of grafting increasing. The o-Ps intensity variation can be interpreted in terms of free-volume properties and an inhibiting effect. The local physicochemical environment of HDPE is changed significantly after MA is grafted onto the backbone. With a lower graft yield, the MA group in the polymer matrix plays an important role of inhibition of Ps. The relation between the rheological results and positron annihilation parameters can be interpreted well by free-volume theory.

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