

The Influence of Acrylic Acid Groups on the Microstructure of HDPE/BT System Studied by Positron Annihilation

Hongmei Wang,^{1,2} Zhe Chen,^{1,2} Pengfei Fang,^{1,2} Shaojie Wang,^{1,2} Yuzhen Xu,³ Zhengping Fang³

¹Physics Department, Wuhan University, Wuhan 430072, China

²Hubei Key Laboratory of Nuclear Solid State Physics, Wuhan University, Wuhan 430072, China

³Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, China

Received 1 February 2007; accepted 23 October 2007

DOI 10.1002/app.27682

Published online 28 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two types of composites, high-density polyethylene (HDPE)/Bentonite (BT) and high-density polyethylene grafted with acrylic acid (HDPE-g-AA)/(BT), are prepared by melt compounding. The microstructure of the composite has been studied by the means of positron annihilation lifetime spectroscopy (PALS). It has been found that the mean free volume size is nearly the same in composites and HDPE matrices with different BT concentration. While the *ortho*-positronium (*o*-Ps) intensity decreased for HDPE-g-AA and its lifetime distribution is narrower

than that for pure HDPE. With the increasing of BT content, the *o*-Ps intensity increases for HDPE-g-AA/BT composites and the *o*-Ps intensity decreases for HDPE/BT composites. It is found that the carboxyl group of Acrylic acid plays a significant chemical inhibition on positronium formation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1557–1561, 2008

Key words: grafting; HDPE; microstructure; positron annihilation

INTRODUCTION

In the past decades, polymer/clay nanocomposites have motivated vigorous research in the polymer industries due to the concurrent dramatic enhancements of material properties that have been achieved by the nanodispersion of clay layers. Compared to pure polymers, these nanocomposites demonstrate excellent properties such as improved storage modulus,¹ decreased thermal expansion coefficients,² and reduced gas permeability,³ and enhanced ionic conductivity.⁴ It is a challenge to fabricate polyolefins-based nanocomposites due to their nonpolar backbone which can be overcome by introducing polar group functionalized polyolefins, such as maleic anhydride-grafted polyethylene (MAPE).^{5,6} It is known that beside maleic anhydride, acrylic acid (AA) is commonly used as compatibilizer for polyolefins and particulate fillers. Moreover, HDPE-g-AA/BT nanocomposites have been successfully prepared in the literature.⁷ Although the method to prepare the HDPE-g-AA/BT nanocomposites has been elucidated to some extent, the microstructure of these

materials has not yet been clearly clarified, which must be understood concerning their modifications and applications. Therefore, comparative study of microstructure of HDPE/BT and HDPE-g-AA/BT composites not only can lead to the modification of HDPE, but also has significant theoretical meaning.

Positron annihilation lifetime spectroscopy (PALS) has been used as a unique technology to probe the free volume properties of polymers and polymer-based nanocomposites.^{8,9} PALS is able to give direct information about the free volume at atomic scale in polymers and polymer-based nanocomposites. The positron (e^+) is an antiparticle to electron, and has properties identical to those of electron except for the charge being positive. The positron preferentially localizes in the sample region of minimal positive charge density because of the repulsive interaction between positron and the positive nucleus. By introducing positrons from a radioactive source into a polymer sample, they diffuse at the free state or may form a bound-state positronium (Ps)⁸ after the positrons are thermalized. The typical lifetime of the free positron is in the range of 0.3–0.5 ns, whereas the lifetime of Ps atom depends on the spin state. The *para*-positronium (*p*-Ps) with the singlet state annihilation is in about 0.1 ns. The *ortho*-positronium (*o*-Ps) with the triplet state has an intrinsic lifetime of 140 ns in vacuum. However, in polymers the *o*-Ps atoms are preferentially localized in the atomic-scale holes and their lifetime is shortened to about 1–5 ns by the

Correspondence to: S. J. Wang (sjwangh@yahoo.com.cn).

Contract grant sponsor: Chinese National Foundation of Natural Science Research; contract grant numbers: 10475062, 20304009.

pick-off annihilation with an electron from the surrounding molecules. The *o*-Ps lifetime directly correlates to the free volume hole size and its intensity contains information about the free volume concentration.⁸ The relationship between the *o*-Ps lifetime τ_3 and the radius R has been established by an empirical equation.¹⁰

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \frac{2\pi R}{R_0} \right]^{-1} \quad (1)$$

where $R_0 = R + \Delta R$ and ΔR ($=1.656\text{\AA}$) is the fitted empirical electron layer thickness. Equation 1 is obtained under the assumption that the hole has a spherical geometry and has an infinite potential for the Ps localizing.

In this work, HDPE/BT and HDPE-*g*-AA/BT composites were prepared by melt compounding. The PALS is used to investigate the changes of the ortho-positronium (*o*-Ps) lifetime and its intensity in two types of composites with different content of BT. The aim is to study the influence of AA grafting modification on the microstructure of the HDPE-based composites.

EXPERIMENTAL

Materials

The organically modified bentonite was supplied by Zhejiang Huate Group, Hangzhou, China, which was ion-exchanged with octadyl trimethyl ammonium. High-density polyethylene (5502#, MFR = 0.35 g/10 min) was from Daelim Corp., Korea. Acrylic acid and dicumyl peroxide (DCP) were bought from Shanghai Chemical Group. All chemicals were used without further purification.

Sample preparation

HDPE and organic bentonite were melted compound in a Thermo Haake Rheomix with a screw speed of 60 rpm for 20 min at a temperature of 160°C. The mixture was press molded to get a plate of about 1.5-mm thick. The content of bentonite was set as 0, 2, 3, 4, wt% and the acquired materials were defined as HDPE, HDPE2, HDPE3, and HDPE4, respectively. The high-density polyethylene-grafted acrylic acid (HDPE-*g*-AA) and organic bentonite were mixed in the same procedure as above and the materials were named as HDPEA, HDPEA2, HDPEA3, and HDPEA4 correspondingly.

Sample characterization

A $10^6\text{Bq } ^{22}\text{Na}$ positron source sealed in two sheets of Ni foils (1 g/cm^2) was sandwiched between two

identical samples. A conventional ORTEC-583 fast-fast coincident lifetime spectrometer is used for PALS measurement at room temperature. To minimize the artifact, charging of each sample is performed in the same position as marked. Each spectrum contained ~ 1 million and 4 million counts for PATFIT and MELT, respectively.^{11–14} The time resolution is found to be a sum of two Gaussians with $\text{FWHM}_1 = 280\text{ ps}$ (90%) and $\text{FWHM}_2 = 320\text{ ps}$ (10%). Analysis of positron lifetime spectra were performed using finite-term lifetime analysis PATFIT program and the continuous analysis technique (maximum entropy lifetime method) MELT program. Moreover, to reduce artificial effects, spectra were resolved using the same parameters.

RESULTS AND DISCUSSION

PATFIT analysis

The measured positron lifetime spectra have been well resolved into three components using PATFIT after the background and positron source correction were subtracted. All the variations of the fit (χ^2) were smaller than 1.2. The shortest-lived component τ_1 (~ 0.12 – 0.15 ns) is attributed to the self-annihilations of *para*-positronium (*p*-Ps) and “free” positron annihilation. The intermediate-lived component, $\tau_2 \approx 0.30$ – 0.40 ns , is assigned to annihilation of positron trapped in various vacancies. The two short components τ_1 and τ_2 are found to exhibit no correlation with the free volume properties,¹⁵ but the second component (τ_2 and its intensity I_2) contains the structure formation of interfacial layers.¹⁶ Since the third component (the longest-lived *o*-Ps lifetimes) can be related to the properties of the pores in the samples, the following discussions are mainly based on the annihilation characteristics of the third component.

The variation *o*-Ps lifetime τ_3 with the filler content in HDPE/BT and HDPE-*g*-AA/BT composites are shown in Figure 1. From Figure 1, the *o*-Ps lifetime τ_3 in composites is not different from that in HDPE matrices. So the free volume size in composites is nearly as same as that in HDPE matrices. The results imply that the silicate platelet did not enter into the free volume hole and Ps is only formed and annihilated in HDPE matrices for both pure HDPE and the composites. Furthermore, the variation of *o*-Ps lifetime nearly unchanged with increasing BT concentration, which indicates the BT concentration does not influence the free volume hole size of HDPE matrices.

As shown in Figure 2, with the increasing of BT content, the *o*-Ps intensity increases obviously for HDPE-*g*-AA/BT composites and decreases for HDPE/BT composites. For HDPE/BT composites, the changes of *o*-Ps intensity have been found in sev-

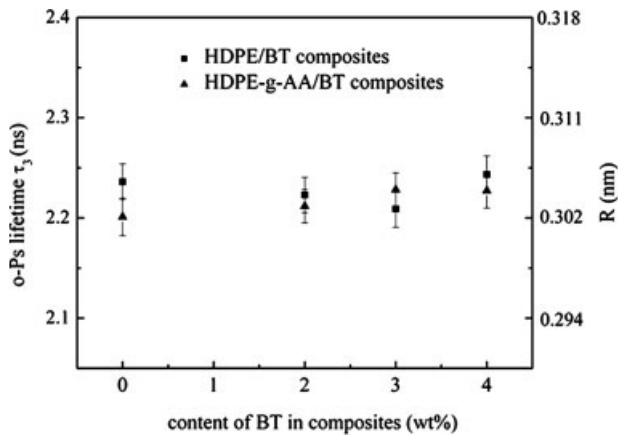


Figure 1 Content dependence of the *o*-Ps lifetime τ_3 .

eral polymers.^{9,17,18} In this article, the *o*-Ps intensity is mainly influenced by the free volume concentration and the chemical inhibition.

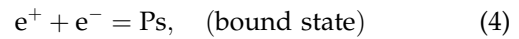
For the pure HDPE-based composites, HDPE chains are confined by the interfacial layer, the layers can be therefore regarded as impermeable walls to restrict HDPE chain conformations, and the HDPE chains interfacial region may be treated as adsorbed chains with one end attached to a plane, which is named tail chains.^{19,20} The conformational number of confined chains is smaller than that in the free chains. Wu calculated the conformational number of tail chains using the model of NRW (normal random walk) and deduced the ratio (α) of conformational number of the model tail chains to that of the free chains for linear polymer structure,²¹ as the segmental length $N \rightarrow \infty$, the ratio is

$$\alpha^{(d)}(N) \approx \frac{1}{\sqrt{2d\pi}} N^{-1/2} \quad (2)$$

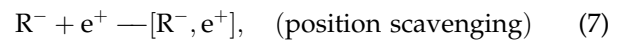
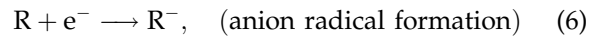
where d is the dimension of the lattice. From this equation, the conformations reduced when the HDPE chains were confined by fillers, i.e., there is less room for the confined chain motion, thus the mobility of the confined HDPE chains in the interfacial region was reduced by the filler. From the free volume theory, the free volume is related to the chain segment mobility. As aforementioned, the size of free volume is nearly unchanged, so the free volume concentration might decrease. Therefore, in the HDPE/BT composites, the *o*-Ps intensity I_3 decreased.

But for HDPE-*g*-AA/BT composites, the *o*-Ps intensity is remarkably different from that observed in HDPE/BT composites. From Figure 2, the *o*-Ps intensity I_3 in HDPE-*g*-AA is less than that in pure HDPE and I_3 increases with the increasing of BT content. So there should be positronium inhibition in this system. The results can be explained in the following.

In terms of the spur reaction model,²² the Ps formation process in polymer is taken as a reaction of thermalized positron and one of the excess electrons generated in the terminal positron spur when the positron loses the last part of its energy during the slowing down process:²³



The Ps formation probability I_3 will be influenced by the positronium formation process which must be competed with other process, such as electron-cation recombination, the diffusion of positrons and electrons out of the spur, and electron or positron scavenging:



HDPE-*g*-AA has carboxyl groups and carboxyl groups behave like electronegative molecules. The *o*-Ps formation probability I_3 of HDPE-*g*-AA is 15% lower than that of pure HDPE. The large effect on I_3 could be explained by considering that the strongly bound electron belonging to the carboxyl groups can not be ionized, or, even the surrounding free electrons are available, the recombination process would happen immediately, leading to the positron having less chance to form Ps atom in the local environment. This mechanism which can significantly reduce I_3 can be described as the following equation:

$$I_3 = \frac{I_3^0}{1 + \sigma C}, \quad (8)$$

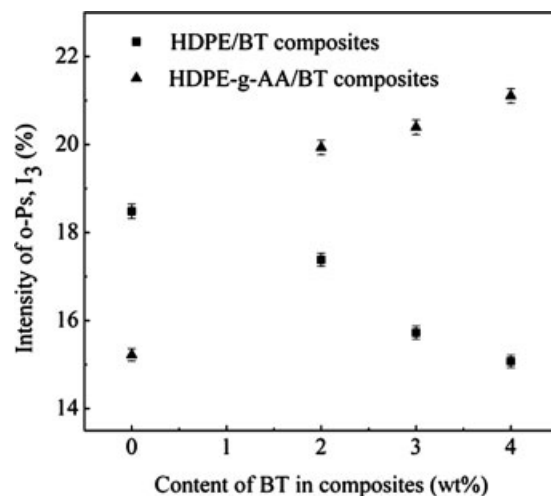


Figure 2 Content dependence of the *o*-Ps intensities I_3 .

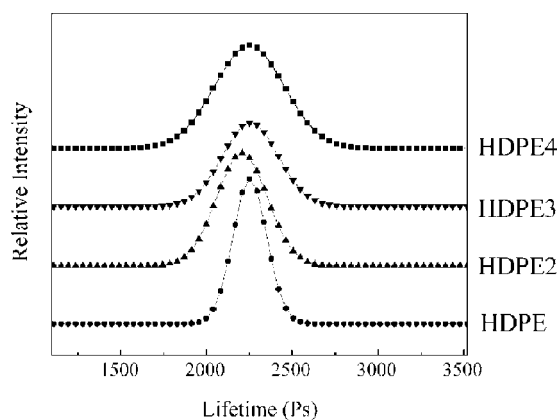


Figure 3 Dependence of *o*-Ps lifetime distribution on the BT content of HDPE/BT composites.

where C is the concentration of scavenger in units of mol/L, s the fitting parameter called inhibition constant, and I_3^0 the ideal *o*-Ps yield assuming $C = 0$, that is to say, only considering the free volume effect on *o*-Ps yield. The inhibition constant characterizes the efficiency of scavenger relative to Ps formation probability. As shown in Figure 2, the I_3 increases with the increasing of BT content for HDPE-*g*-AA/BT composites. We can infer that C decreases with the increasing of BT content. It is probably because that when the organically modified BT is added into the HDPE-*g*-AA system, the carboxyl groups of HDPE-*g*-AA chains can react with BT layers and easily enter into the BT layers. Yu et al. indicates that the *o*-Ps is harder to access and annihilation in interspacing of BT layer.²⁴ Thus with the increase of BT content, more carboxyl groups of HDPE-*g*-AA chains can enter into BT layers and the inhibition of Ps formation decreases. As a result, the *o*-Ps intensity of HDPE-*g*-AA/BT composites increases with increasing the BT content.

From Figure 2, the *o*-Ps intensity of HDPE-*g*-AA/BT composites with different BT content is larger than the HDPE/BT composites. It can be explained in the following. In melt compound process, the degradation such as chain scission would happen, especially in the grafting reaction,²⁵ which may lead to the increase of free volume concentration. Consequently, the I_3^0 of HDPE-*g*-AA is larger than HDPE. While adding enough BT content, most of the carboxyl groups enter into the BT gallery, which means there is less Ps inhibition. As a result, *o*-Ps intensity is mainly related to the intrinsic free volume concentration of the matrices.

Melt analysis

Shukla et al. has developed a program named the maximum entropy method (MELT) and MELT is a promising method for finding a reliable *o*-Ps distri-

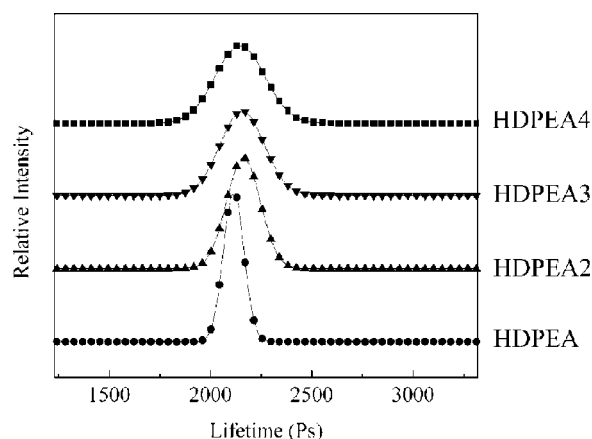


Figure 4 Dependence of *o*-Ps lifetime distribution on the BT content of HDPE-*g*-AA/BT composites.

bution of a positron lifetime spectrum in polymers.^{26,27}

In this article, the MELT program was used to obtain the free volume distribution in order to discuss the effect of AA grafting modification on the miscibility of HDPE-based composites. Figures 3 and 4 show the free volume distributions for HDPE/BT and HDPE-*g*-AA/BT composites, respectively. Parameters of the *o*-Ps lifetime τ_3 for different samples are given in Table I. It is observed that the maximum of the distribution has little shift with increasing BT content, which is in good agreement with the discrete analysis as shown in Figure 1. On the other hand, it is very interesting to find the difference in the free volume distribution between HDPE/BT composites and HDPE-*g*-AA/BT composites. The distribution of HDPE-*g*-AA/BT composites is quite narrow, but extremely broad for HDPE/BT composites. It is well known that the free volume distribution should have very similar Gaussian-like distributions in the miscible system, while the distribution is broader in the immiscible system.^{28–31} So the miscibility of HDPE-*g*-AA/BT composites is better than that of HDPE/BT composites, which indicates that the miscibility is greatly affected by AA grafting. The AA grafting modification could enhance the dispersion of BT in HDPE matrix, and strength interaction between the HDPE matrix and BT layers.

TABLE I
Parameters of the *o*-Ps Lifetime τ_3

Sample name	Center positron (ps)	FWHM (ps)
HDPE	2249	276
HDPE2	2204	296
HDPE3	2258	327
HDPE4	2250	398
HDPEA	2212	100
HDPEA2	2252	166
HDPEA3	2241	219
HDPEA4	2236	244

CONCLUSIONS

The unique information on the microstructure in HDPE/BT and HDPE-*g*-AA/BT systems is provided by PALS. In this article, it is found that the *ortho*-positronium (*o*-Ps) intensity decreases $\sim 15\%$ for HDPE-*g*-AA and its lifetime distribution is narrower than that for pure HDPE. Carboxyl groups have an inhibition effect on Ps formation. With the increase of BT content, the *o*-Ps intensity increases for HDPE-*g*-AA/BT composites and the *o*-Ps intensity decreases for HDPE/BT composites. It is probably an evidence for the carboxyl groups entering into the BT galleries. And the distribution of HDPE-*g*-AA/BT composites is quite narrow, but the extremely broad for HDPE/BT composites. It indicates that the miscibility of HDPE-*g*-AA/BT composites is better than that of HDPE/BT composites. The results also show that high-intensity polyethylene composites with good dispersion can be obtained by proper modification of HDPE.

References

1. Yao, K. J.; Song, M.; Hourston, D. J.; Luo, D. Z. *Polymer* 2002, 43, 1017.
2. Sun, T.; Garces, J. M. *Adv Mater* 2002, 14, 128.
3. Usuki, A.; Tugigase, A.; Kato, M. *Polymer* 2002, 43, 2185.
4. Wu, J. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J. *Chem Mater* 1993, 5, 835.
5. Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J. *Macromolecules* 2002, 35, 5529.
6. Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y.S.; Chung I. J. *Polymer* 2001, 42, 9819.
7. Xu, Y. Z.; Fang, Z. P.; Tong, L. F. *J Appl Polym Sci* 2005, 96, 2429.
8. Jean, Y. C. *Microchem J* 1990, 42, 72.
9. Beckker, O.; Cheng, Y. B.; Varley, R. J.; Simon, G. P. *Macromolecules* 2003, 36, 1616.
10. Nakanishi, H.; Wang, S. J.; Jean, Y. C.; Positron Annihilation Studies of Fluids; Sharma, S. C., Eds. World Science: Singapore, 1988; p 292.
11. Kikegaard, P.; Eldrup, M.; Mogensen, O.; Pertersen, N. J. *Comput Phys Commun* 1981, 23, 307.
12. Wästland, C.; Maurer, F. H. *Macromolecules* 1997, 30, 5870.
13. Dammert, R. M.; Maunu, S. L.; Maurer, F. H. J. *Macromolecules* 1999, 32, 1930.
14. Süvegh, K.; Klapper, M.; Domján, A.; Mullins, S. *Macromolecules* 1999, 32, 1147.
15. Wang, C. L.; Wang, S. J. *J Phys Rev B* 1995, 51, 8810.
16. Wang, S. J.; Wang, C. L.; Zhu, X. G.; Qi, Z. N. *Phys Status Solidi A* 1994, 142, 275.
17. Wang, Y. Q.; Wu, Y. P.; Zhang, H. F.; Zhang, L. Q.; Wang, B.; Wang, Z. F. *Macromol Rapid Commun* 2004, 25, 1973–1978.
18. Olson, B. G.; Peng, Z. L.; Srithwatpong, R.; McGervy, J. D.; Shida, H.; Jamieson, A. M.; Manias, E.; Giannelis, E. P. *Mater Sci Forum* 1997, 255–257, 336.
19. Takahashi, A.; Kawagushi, M. *Adv Polym Sci* 1992, 48, 1.
20. Whittington, S. G. *Adv Chem Phys* 1982, 51, 1.
21. Wu, D. C. K. *J Sci China Ser B* 1996, 39, 608.
22. Mongesen, O. E. *Positron Annihilation in Chemistry*; Springer-Verlag: Berlin, 1995.
23. Dai, Y. Q.; He, C. Q.; Li, S. Q.; Fang P. F.; Chen Y. Y.; Wang S. J.; *Chin Phys Lett* 2000, 17, 457.
24. Yu, D. H.; Wang, B.; Feng, Y.; Fang, Z. P. *J Appl Polym Sci* 2006, 102, 1509.
25. Chen, Z.; Fang, P. F.; Wang, H. M.; Zhang, S. P.; Wang, S. J. *J Appl Polym Sci* 2006, 101, 2022.
26. Hoffmann, L.; Shukla, A.; Peter, M.; Barbiellini, B.; Manuel, A. A. *Nucl Instrum Methods A* 1993, 355, 276.
27. Shukla, A.; Peter, M.; Hoffmann, L. *Nucl Instrum Methods A* 1993, 335, 310.
28. Stlund, C. W.; Berndtsson, H.; Maurer, F. H. J. *Macromolecules* 1998, 31, 3322.
29. Chen, Z. Q.; Uedono, A.; Li, Y. Y.; He, J. S. *Jpn J Appl Phys* 2002, 41, 2146.
30. Liu, J.; Jean, Y. C.; Yang, H. *Macromolecules* 1995, 28, 5774.
31. Zhu, Y. C.; Wang, B.; Gong, W.; Kong, L. M.; Jia, Q. M. *Macromolecules* 2006, 39, 9441.