

SEM Study of the Morphologic Change of High-Density Polyethylene Surface Grafted with Glycidyl Methacrylate

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ABSTRACT: Scanning electron microscopy (SEM) study of the morphologic change of high-density polyethylene (HDPE) surface grafted with glycidyl methacrylate (GMA) was reported. Radiation-induced grafting of GMA onto HDPE was carried out in acetone and dichloromethane solution, respectively. The effects of irradiation dose, atmosphere, and swelling time on grafting were investigated. Generally, the extent of grafting increased with irradiation dose, but for the grafting carried out in acetone solution, the extent of grafting initially increased with irradiation dose and then remained almost constant. The extent of grafting was higher in acetone solution than in dichloromethane solution at the same irradiation dose. The extent

of grafting in nitrogen was higher than that in air. The successful grafting of GMA onto HDPE was confirmed by weighing and FTIR analysis. SEM investigations showed that the morphologies of the PE samples grafted in acetone solution were quite different to those grafted in dichloromethane. The grafting of GMA carried out in acetone was mainly on HDPE surface and that carried out in dichloromethane was mainly in the bulk of HDPE. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 185–191, 2007

Key words: graft copolymers; high-density polyethylene; morphology; scanning electron microscopy; radiation; glycidyl methacrylate

INTRODUCTION

Polyethylene (PE) has been widely used in many industrial and civil fields. However, PE films, sheets, or injection molded items are difficult to be bonded, electroplated, coated, printed, etc., because their surfaces are chemically inert and have a very low surface energy. PE should have much more applications if its surface can be modified or functionalized. Radiation-induced grafting has become a very common and a powerful technique to modify the physical-chemical properties of PE (e.g., wettability, adhesion, adsorption, and surface reaction), because of its significant advantages over other methods.¹

Glycidyl methacrylate (GMA) is a multifunctional reactive monomer. Several kinds of grafting methods, such as photografting,^{2,3} melt grafting, or the reactive extrusion grafting,^{4–11} were used to graft GMA onto polymeric materials; however, work done on the radiation-induced grafting of GMA is quite rare.^{12,13} Once GMA is grafted onto the surface of polymeric material, the surface property of the polymeric material has been changed. Moreover, the epoxy group on GMA molecule can further react with other chemicals to endow the surface with properties as required. For example, GMA was grafted onto PE

to improve the compatibility of polyamide-6/PE,^{14,15} polyester/PE⁹; GMA was grafted onto low-density polyethylene (LDPE) and then aminated with ethylenediamine; the aminated GMA-grafted sample had the ability to adsorb cupric ions;¹⁶ GMA was grafted onto plasma-pretreated PE by UV-induced graft polymerization for improvement of antithrombogenicity.¹⁷ GMA was also grafted onto PE to improve its adhesion property.^{18,19}

Recently, we reported the radiation-induced grafting of GMA onto high-density polyethylene (HDPE) and the radiation lamination of HDPE by mutual bulk grafting of GMA.²⁰ Very strong adhesion could be obtained when using GMA as the monomer to laminate HDPE by γ -irradiation-induced bulk grafting. But when the grafting of GMA was carried out in different solvents, the grafted HDPE samples had significantly different adhesion properties. Some had good adhesion, but some had no adhesion at all. The adhesion property of the grafted samples is strongly affected by two main factors:²¹ (1) where the grafts are, i.e., on the surface or in the bulk of polymer substrate, and (2) the microstructure of the grafted chains. No strong adhesion can be obtained if the grafted GMA is grafted mainly in the bulk or highly branched. There is still not a direct method to measure the microstructure of the grafted chains. But some methods have been developed to determine the location of the grafts. Hill et al.²¹ developed a spectroscopic method to know the penetration depth

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of grafted material in polymer substrate. Transmission optical microscopy and scanning electron microscopy (SEM) are the convenient methods.^{22,23}

We found that adhesion property of the HDPE surface grafted with GMA when the grafting was carried out in acetone solution was better than that carried out in dichloromethane solution; the latter had nearly no improvement when compared with that of pristine HDPE surface. When examined with SEM, it was found that the morphologies of the grafted surfaces were quite different. Very possibly, the difference in the morphologies of the grafted surface is the reason for their different final adhesion properties. In this article, we report the radiation-induced grafting of GMA onto HDPE carried out in acetone and dichloromethane and the significant differences in the morphologies of the grafted samples studied by SEM.

EXPERIMENTAL

Materials

HDPE (melt flow index: 0.39 g/10 min; density: 0.949 g/cm³) was supplied by Nova Chemicals (Sania, Ontario, Canada). HDPE films were prepared by heating at 160°C for 7 min and molded under a pressure of 20 MPa for 3 min and quenched immediately in tap water. The HDPE film was cut into 10 mm × 20 mm (≈ 0.3 mm in thickness) rectangle samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Monomer glycidyl methacrylate (GMA, 97%) was from Mitsubishi Gas (Tokyo, Japan). The solvent acetone and dichloromethane (AR grade) were from Beijing Beihua Fine Chemicals (Beijing, China). All the chemicals were used without further purification.

Grafting

The grafting procedure was the same as reported previously.²⁰ All the samples were irradiated with different doses at a dose rate of 213 Gy/min. The reaction temperature was not strictly controlled. Room temperature 10–15°C was taken as the reaction temperature.

The extent of grafting was expressed as the weight increase per surface area of the sample, and was calculated from the following equation:

$$G = \frac{W_g - W_0}{S} (\mu\text{g}/\text{cm}^2)$$

where W_g and W_0 are the weights of PE sample after and before grafting, and S is the surface area of PE sample.

The average value of five samples is taken as the final extent of grafting. Typically, the five samples gave values within 10%.

FTIR characterization

FTIR spectra were obtained from pristine HDPE film and HDPE films grafted with GMA on an Avatar-360 spectrometer (Nicolet Analytical Instruments, Madison, WI). The number of scans was 32 at a resolution of 4 cm⁻¹.

SEM investigations

The morphologies of the pristine and grafted PE samples were examined with a Hitachi X-650 scanning electron microscope (Tokyo, Japan). The scanning electron micrographs of the cross section of the grafted HDPE films were obtained with a Hitachi S-4800 SEM. The samples were coated with gold.

RESULTS AND DISCUSSION

Grafting

The grafting of GMA onto HDPE was carried out in acetone and dichloromethane solution in air or N₂, respectively. The monomer concentration was 1 mol/L; the reaction temperature was 10–15°C.

Similar to our previous results,²⁰ the γ -irradiation-induced grafting of GMA onto HDPE occurred very easily both in acetone and in dichloromethane solution.

Generally, the extent of grafting increased with irradiation dose, but for the grafting carried out in acetone solution, the extent of grafting initially increased with irradiation dose and then remained almost constant. As shown in Figure 1(a), for the grafting carried out in acetone solution in air, there was no grafting after 5 kGy irradiation, and after that, the extent of grafting increased with irradiation dose till 25 kGy, where the extent of grafting was about 4000 $\mu\text{g}/\text{cm}^2$, and after that, the extent of grafting remained almost constant; for the grafting carried out in N₂, the extent of grafting increased quickly with irradiation dose from 5 kGy, where the extent of grafting was about 1500 $\mu\text{g}/\text{cm}^2$, to 10 kGy, where the extent of grafting was more than 4000 $\mu\text{g}/\text{cm}^2$, and after that, the extent of grafting increased slowly till 20 kGy, and then remained constant at about 6000 $\mu\text{g}/\text{cm}^2$. The extent of grafting in nitrogen was much higher than that in air at the same irradiation dose, especially when the irradiation dose was less than 20 kGy.

As shown in Figure 1(b), for the graftings carried out in dichloromethane solution in air or N₂, the extent of grafting increased almost linearly with irra-

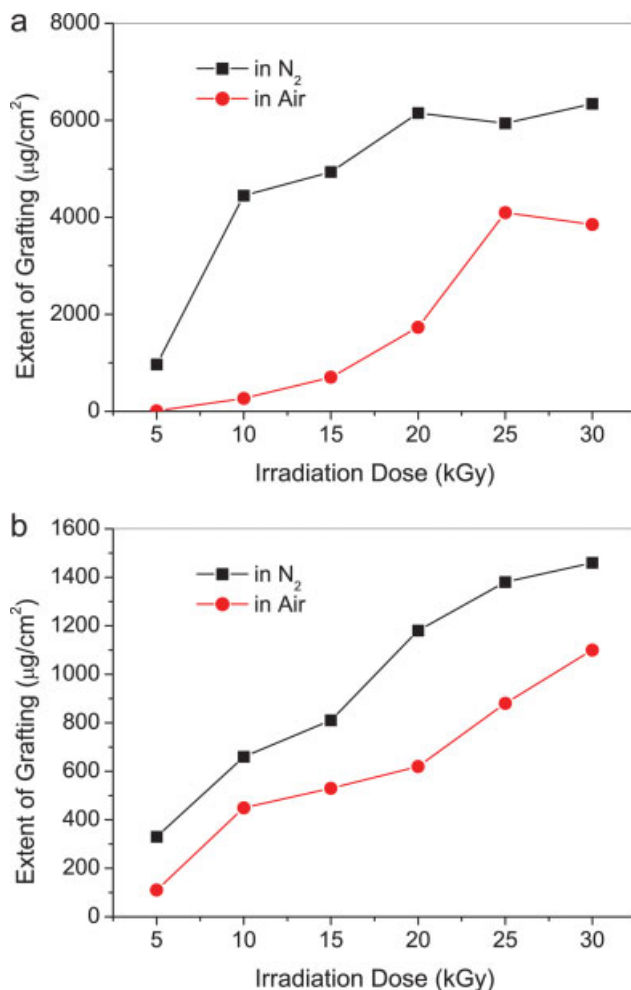


Figure 1 Extent of grafting as a function of irradiation dose. Grafting carried out in 1M GMA solution: (a) in acetone and (b) in dichloromethane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

diation dose. Similar to that in acetone solution, although the difference was not so significant, the extent of grafting in nitrogen was also higher than that in air at the same irradiation dose.

The extent of grafting was much higher in acetone solution than that in dichloromethane solution at the same irradiation dose, no matter in air or in N₂.

Swelling time on grafting

Swelling time significantly affected the grafting of GMA onto HDPE when dichloromethane was used as the solvent. On the contrary, the grafting carried out in acetone was only very slightly affected by swelling time. Figure 2 shows the effect of swelling time on the grafting carried out in dichloromethane in air. When the irradiation dose was less than 15 kGy, the extent of grafting of the HDPE samples swollen for different time was very similar and was

only about 500 µg/cm² after 15 kGy irradiation. However, when the irradiation dose was 20 or 30 kGy, the extent of grafting of the HDPE samples swollen for different time was different. At the same irradiation dose, the extent of grafting of the sample swollen for longer time was higher than that of the sample swollen for shorter time. The extent of grafting of the sample swollen 7 days was about 4000 µg/cm² after 30 kGy irradiation, whereas that of the sample swollen for 1 day was only about 1000 µg/cm².

FTIR characterization

The grafting of GMA onto HDPE was confirmed by FTIR spectroscopy, as illustrated in Figure 3(a) for pristine HDPE film and in (b,c) for the grafted HDPE films. Figure 3(a) shows that the pristine HDPE spectrum has no absorption band near 1731 cm⁻¹, which is the characteristic absorption band of the carbonyl group (C=O). In the FTIR spectra of the grafted samples [Figs. 3(b,c)], stronger absorption bands occurring at about 1731 cm⁻¹ appear, and the absorbance increases with the increase of the extent of grafting. The FTIR spectra demonstrate that radiation-induced grafting of GMA on HDPE films has taken place.

SEM analyses

Banded spherulites are the common morphologic features for crystalline polymers. HDPE is a semi-crystalline polymer, and it also has banded spherulites. The spherulites are made of lamellas. Figure 4(a) shows the scanning electron micrograph of pristine HDPE surface; it clearly shows the lamellar structure of HDPE.

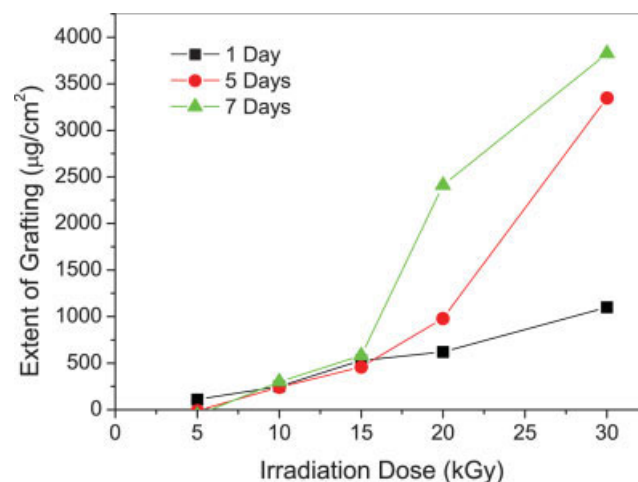


Figure 2 The effect of swelling time on grafting carried out in dichloromethane in air. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

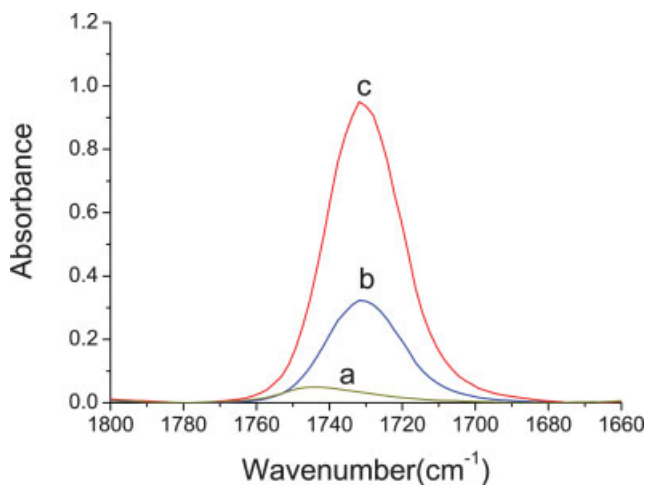


Figure 3 FTIR spectra of pristine HDPE film (a), HDPE film grafted with $750 \mu\text{g}/\text{cm}^2$ (b), and $1100 \mu\text{g}/\text{cm}^2$ (c) GMA. Grafting carried out in dichloromethane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figures 4(b–d) show the micrographs of the HDPE samples grafted in 1M GMA acetone solution in air after 1.07, 2.13, and 5.12 kGy irradiation, respectively. Compared with pristine HDPE surface [Fig. 4(a)], no obvious change can be found in the morphology of HDPE after 1.07 kGy irradiation; the lamellar structure of HDPE is clearly shown in the micrograph [Fig. 4(b)]. Figure 4(c) shows the micrograph of HDPE surface after 2.13 kGy irradiation; the lamellar structure of HDPE can also be found, but it is not so clear as that in Figures 4(a,b). Significant change could be found in the morphology of HDPE after 5.12 kGy irradiation [Fig. 4(d)]; it is obviously different to those in Figures 4(a–c). The surface became much smoother, and it is difficult to find clear lamellar structures of HDPE. It may be suggested that the HDPE surface has been fully covered with grafted materials. The extent of grafting was very low after 5 kGy irradiation in air [Fig. 1(a)], and so the thickness of grafted layer was very small, possibly in nanometers. This assumption can easily explain the protuberances with the shape of lamellar structure on HDPE surface [Fig. 4(d)]. Because the thickness of the lamellar structure of HDPE is 2–6 nm,^{24,25} when the grafted layer is in nanometers, the shape of some lamellas can still be found. Just like when a hand is fully covered with a thin layer of salad dressing, you cannot see the hand, but you can see its shape. When the irradiation dose was less than 5 kGy, no grafting could be found by weighing the sample since the grafted amount was too less.

Figures 5(a–c) shows the micrographs of the HDPE samples grafted with 450, 1900, and $3450 \mu\text{g}/\text{cm}^2$ GMA, respectively. These samples were grafted in 1 mol/L GMA acetone solution in air.

When the extent of grafting was $450 \mu\text{g}/\text{cm}^2$ [Fig. 5(a)], the HDPE surface became quite smooth and totally different from the pristine HDPE surface. It suggests that the HDPE surface has been fully covered with grafted GMA. With the increase of the extent of grafting, as shown in Figures 5(b,c), the morphologies of HDPE grafted with more GMA change dramatically; they are quite different from those of pristine HDPE and HDPE grafted with less amount of GMA (Fig. 4). Rough surface with orderly structures is the feature of the morphologies of HDPE grafted with 1900 and $3450 \mu\text{g}/\text{cm}^2$ GMA. For the HDPE sample grafted with $1900 \mu\text{g}/\text{cm}^2$ GMA, as shown in Figure 5(b), some square or rectangular structures with side length in the range of 5–15 μm , as well as some grains or strips and irregular structures could be found on the surface. These regular or irregular structures are arrayed in straight lines. For the HDPE sample grafted with $3450 \mu\text{g}/\text{cm}^2$ GMA, its surface morphology is a little different from that of the sample grafted with $1900 \mu\text{g}/\text{cm}^2$ GMA; grains are the main structure of the grafted material and they become bigger. The grains are also arrayed in straight lines. The reason for the orderly arrangement of grafted GMA on HDPE surface is still unknown and needs further study.

The SEM analyses results confirm that the grafting of GMA onto HDPE carried out in acetone mainly

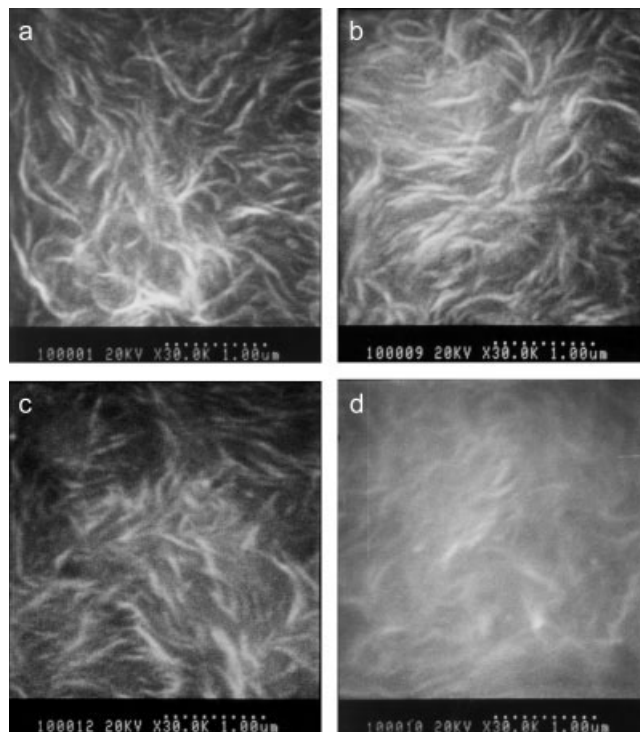


Figure 4 Scanning electron micrographs of pristine HDPE and HDPE grafted in acetone solution in air for different time. (a) Pristine HDPE; (b) 5 min, 1.07 kGy; (c) 10 min, 2.13 kGy; (d) 24 min, 5.12 kGy.

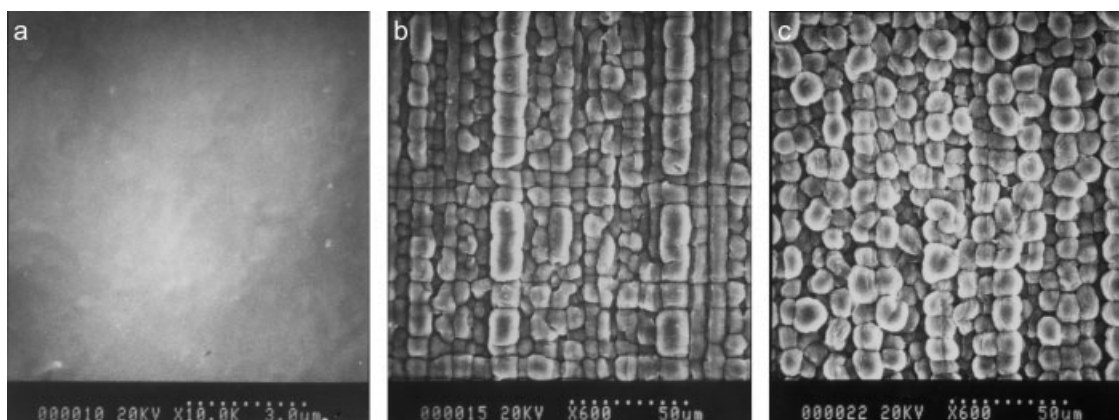


Figure 5 Scanning electron micrographs of HDPE grafted with different amount of GMA. Grafting carried out in 1 mol/L GMA acetone solution in air. (a) 450 $\mu\text{g}/\text{cm}^2$; (b) 1900 $\mu\text{g}/\text{cm}^2$; (c) 3450 $\mu\text{g}/\text{cm}^2$.

occurs on HDPE surface. Once the surface is fully covered with grafted GMA, the grafting occurs on the grafted layer; therefore, very thick (in μm) grafted layer can be obtained.

When the grafting was carried out in dichloromethane and the grafting time was short, the micrographs of the samples were almost the same as those grafted in acetone solution for a short time. The lamellar structure of HDPE is clearly shown in the micrographs. However, with the increase of the extent of grafting, the difference between the morphologies of the samples grafted in acetone and dichloromethane solutions became significant.

Figures 6(a,b) show the micrographs of the HDPE samples grafted with 550 and 3100 $\mu\text{g}/\text{cm}^2$ GMA, respectively. These samples were grafted in 1 mol/L GMA dichloromethane solution in air. The surfaces are quite similar. Some protuberances and cracks can be found on the surfaces. Surprisingly, the lamellar structure of HDPE can still be found in the micrographs of the HDPE samples grafted with such a high amount of GMA, though not so clearly as that of pristine HDPE [Fig. 4(a)]. If the grafted GMA were on the surface of HDPE, the thickness of the grafts is in μm , it is impossible for the grafts to be evenly distributed on the surface and keep the original morphology of HDPE. So, very possibly, the grafts were in the bulk of HDPE. When the grafted GMA is in the bulk of PE, it will increase the internal stress of HDPE, and the uneven distribution of internal stress will induce the deformation of HDPE. Possibly, that is the reason for the appearance of protuberances and cracks on the surfaces.

Significant difference can also be found in the scanning electron micrographs [Figs. 7(a,b)] of the cross section of the HDPE samples grafted with 3450 $\mu\text{g}/\text{cm}^2$ GMA (grafted in 1 mol/L GMA acetone solution in air) and 3000 $\mu\text{g}/\text{cm}^2$ GMA (grafted in 1 mol/L GMA dichloromethane solution in air). As shown in Figure 7(a), for the sample grafted in

acetone solution, a border between the grafted layer and the HDPE substrate can be found. The thickness of the grafted layer is about 40–50 μm . If the grafted GMA are evenly distributed on HDPE surface, then the thickness of the grafted layer can be calculated according to the extent of grafting. The calculated thickness is about 34.5 μm . It is close to but a little lower than that obtained from scanning electron micrograph, for the grafted GMA are not evenly distributed. On the contrary, for the sample grafted in dichloromethane solution, as shown in Figure 7(b), no grafted layer can be found.

The SEM analyses results suggest that the grafting of GMA carried out in acetone was mainly on HDPE surface and that carried out in dichloromethane was mainly in the bulk of HDPE. The possible reasons include:

First, dichloromethane has much better swelling ability to HDPE than acetone does. When acetone is used as the solvent, GMA monomer is difficult to enter the bulk of HDPE, so grafting can only occur on the surface if the grafting reaction is possible to occur. When dichloromethane is used as the solvent,

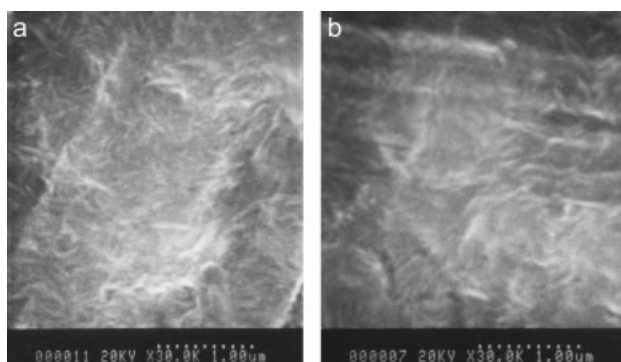


Figure 6 Scanning electron micrographs of HDPE grafted with different amount of GMA. Grafting carried out in 1 mol/L GMA dichloromethane solution in air. (a) 550 $\mu\text{g}/\text{cm}^2$; (b) 3100 $\mu\text{g}/\text{cm}^2$.

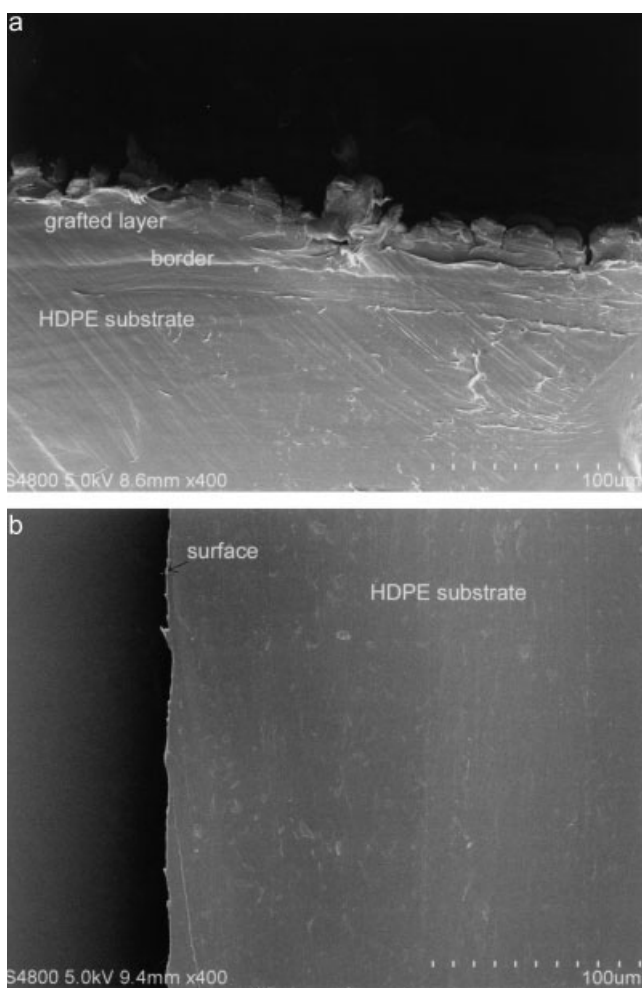


Figure 7 Scanning electron micrographs of the cross section of the HDPE samples grafted in different solvents. (a) Grafted in 1 mol/L GMA acetone solution in air, 3450 $\mu\text{g}/\text{cm}^2$; (b) grafted in 1 mol/L GMA dichloromethane solution in air, 3000 $\mu\text{g}/\text{cm}^2$.

GMA monomer is easy to enter the bulk of HDPE, and more and more GMA monomers enter the bulk of HDPE with the increasing swelling time. Therefore, the grafting is more possible to occur in the bulk of PE.

Second, acetone and dichloromethane are unstable under γ -irradiation and several kinds of free radicals can be formed. The free radicals can recombine to produce unreactive products or terminate the growing grafting chains or macromolecular free radicals, which can initiate the grafting. Chlorine free radical Cl can be formed from dichloromethane under γ -irradiation. Cl is a high reactive free radical. And there are much more Cl formed in the solution than in the bulk of PE. Possibly, the Cl formed in the solution is easy to move to PE surface to terminate the growing grafting chain; however, the Cl formed in the bulk of PE is not so easy to move to the growing grafting chain due to the steric hindrance of polyethylene chains. So, possibly, the macromolecular free

radicals and growing grafting chains formed on the HDPE surface are almost totally terminated by Cl, and thus no grafting can occur on the surface, but the macromolecular free radicals and growing grafting chains formed in the bulk of HDPE are just partly terminated by Cl, and thus grafting can still occur there. When acetone is used, several kinds of free radicals can also be formed, but these free radicals cannot terminate all the macromolecular free radicals and growing grafting chains formed on the surface; therefore, grafting can occur on PE surface.

As mentioned in the Introduction, we have tested the adhesion properties of the HDPE samples grafted with GMA. The grafted samples were bonded with epoxy resin and then tested. The samples grafted in acetone solution had stronger adhesion than the samples grafted in dichloromethane. The latter had almost no improvement in adhesion property. The apparent reason for the difference in the adhesion of the grafted samples is the different distribution of the grafted materials, i.e., on the surface or in the bulk of PE.

CONCLUSIONS

The radiation-induced grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) was carried out in acetone and dichloromethane solution in air and nitrogen atmosphere. The grafting is easier to occur in acetone solution than in dichloromethane solution, and easier in nitrogen than in air.

SEM investigations show that the morphologies of the PE samples grafted in acetone solution are quite different to those grafted in dichloromethane. The grafting of GMA carried out in acetone was mainly on HDPE surface and that carried out in dichloromethane was mainly in the bulk of HDPE.

The final property of the grafted polymeric materials is affected by many factors. A very important one is where the grafts are, it is crucial in many applications such as adhesion. This work demonstrates that the grafting of GMA onto HDPE can occur mainly on the surface or totally in the bulk of HDPE depending on the solvent used. Therefore, the selection of solvent is very important in the grafting of polymeric materials. Of course, where the grafting occurs can also be affected by the grafting method, atmosphere, additives, etc. Detailed study will provide more useful knowledge for industrial and other applications.

REFERENCES

1. Chapiro, A. *Radiat Phys Chem* 2002, 63, 207.
2. Mori, M.; Uyama, Y.; Ikada, Y. *J Polym Sci, Part A: Polym Chem* 1994, 32, 1683.
3. Liu, Y. X.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *J Polym Sci, Part A: Polym Chem* 2000, 38, 80.

4. Sun, Y.-J.; Hu, G.-H.; Lambla, M. *J Appl Polym Sci* 1995, 57, 1043.
5. Sun, Y.-J.; Hu, G.-H.; Lambla, M. *Angew Makromol Chem* 1995, 229, 1.
6. Cartier, H.; Hu, G.-H. *J Polym Sci, Part A: Polym Chem* 1998, 36, 2763.
7. Al-Malaika, S.; Kong, W. *J Appl Polym Sci* 2000, 79, 1401.
8. Al-Malaika, S.; Kong, W. *Polymer* 2005, 46, 209.
9. Pesneau, I.; Champagne, M. F.; Huneault, M. A. *J Appl Polym Sci* 2004, 91, 3180.
10. Zhang, L. F.; Guo, B. H.; Zhang, Z. M. *J Appl Polym Sci* 2002, 84, 929.
11. Pan, L. H.; Inoue, T.; Hayami, H.; Nishikawa, S. *Polymer* 2002, 43, 337.
12. Choi, S.-H.; Nho, Y. C. *Radiat Phys Chem* 2000, 58, 157.
13. Kim, M.; Saito, K. *Radiat Phys Chem* 2000, 57, 167.
14. Wei, Q.; Chionna, D.; Galoppini, E.; Pracella, M. *Macromol Chem Phys* 2003, 204, 1123.
15. Wei, Q.; Chionna, D.; Pracella, M. *Macromol Chem Phys* 2005, 206, 777.
16. Irwan, G. S.; Kuroda, S.; Kubota, H.; Kondo, T. *J Appl Polym Sci* 2004, 93, 994.
17. Chen, Y. S.; Liu, P. *J Appl Polym Sci* 2004, 93, 2014.
18. Ng, C. M.; Oei, H. P.; Wu, S. Y.; Zhang, M. C.; Kang, E. T.; Neoh, K. G. *Polym Eng Sci* 2000, 40, 1047.
19. Zou, X. P.; Kang, E. T.; Neoh, K. G. *Polym Eng Sci* 2001, 41, 1752.
20. Li, Z. R.; Wang, H. L. *J Appl Polym Sci* 2005, 96, 772.
21. Cardona, F.; George, G. A.; Hill, D. J. T.; Perera, S. *J Polym Sci, Part A: Polym Chem* 2002, 40, 3191.
22. Wang, H. L.; Brown, H. R. *J Adhes* 2003, 79, 955.
23. Kubota, H.; Koike, N.; Ogiwara, Y. *J Polym Sci, Part C: Polym Lett Ed* 1987, 25, 273.
24. Godovsky, Y. K.; Magonov, S. N. *Langmuir* 2000, 16, 3549.
25. Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* 1996, 29, 5797.