Modification of Polyolefin Surfaces by Plasma-Induced Grafting

K. JOHNSEN,* S. KIRKHORN,† K. OLAFSEN,‡ K. REDFORD, and A. STORI

SINTEF Materials Technology, P.O. Box 124 Blindern, N-0314 Oslo, Norway

SYNOPSIS

Polar monomers have been grafted onto polyolefin surfaces with the aid of inert gas plasma. In the first stage, an inert gas plasma (argon plasma) was used to generate free radicals on the polyolefin surface. In the second stage, the plasma generator was turned off and a vinyl monomer introduced as a vapor. Monomer was surface grafted by free radical polymerization. After cleaning and drying, the samples were analyzed by XPS, IR, and contact angle. LD–PE was successfully grafted with acrylic acid, glycidyl methacrylate, methyl acrylate, and 2-hydroxy ethylacrylate. The grafting of acrylic acid was studied in more detail, and the rate of grafting was observed to increase with increasing monomer pressure and to decrease with time. The increasing of grafting temperature was found to reduce the degree of grafting. This last factor can be explained by the reduced concentration of monomer at the polymer surface or by a deactivation of surface radicals. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Nonmodified polyolefin surfaces are difficult to paint or print on without prior surface treatment. A number of methods are employed to modify polyolefin surfaces. These methods include: corona treatment,[1] flame treatment,[2] and cold oxygen plasma.[3] All three methods serve to add polar groups to the surface by oxidation. They add a poorly defined mixture of hydroxyl, ketone, aldehyde, acid, peroxide, and ester groups to the surface of the polymer.

It would be of interest to study the interactions of a lacquer system to a polyolefin surface with a better defined surface chemistry, preferably a surface with primarily one chemical group. Such a surface may be generated by the surface grafting of a polar monomer. Grafting has been reported initiated by peroxides[4,5] (either by swelling organic peroxides into the polyolefin surface or by peroxides generated with corona treatment), UV initiation,[6] or γ-irradiation.[7] In the present work, the use of inert gas plasma (argon) has been used to generate free radical sites for the grafting of polar vinyl monomers. The use of inert gas plasma to graft monomers on to a polymer surface from the vapor phase has been described earlier in the literature.[8-11] The use of inert gas plasma for generating free radicals and later exposure to oxygen or direct exposure to oxygen plasma (for formation of peroxide groups for initiating grafting from liquid phase monomer) has also been described in the literature.[12,13]

This article deals with the surface generation of radicals by inert gas plasma and the grafting of monomers from the vapor phase. Inert gas plasma was chosen in favor of corona or UV, as it enables the treatment of difficult geometries. The inside of a bottle can be easily activated by plasma but would prove difficult by the alternative techniques. Vapor phase grafting was chosen over liquid or solution grafting, as it offers the simplification that the same chamber can be used for the plasma generation of radicals and the grafting. Although plasma-induced grafting using monomer in the vapor phase at the present probably is not an industrial method, it may have a potential for further development.

* Current address: JOTUN A/S, P.O. Box 2021, N-3235 Sandefjord, Norway.

† Current address: Statoil Fou, N-7004 Trondheim, Norway.

‡ To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Stabilizer-free low-density polyethylene 125 μm film, PE L400 Borealis, Norway, was used. The films were cleaned both before and after grafting by immersion in an ultrasonic bath filled with a 50:50 mixture of water and ethanol (A/S Vinmonopolet, Norway). The samples grafted with methyl acrylate were cleaned with acetone. The monomers used were acrylic acid 99%, N-ethyl-2-methylallylamine 98%, glycidyl methacrylate 97%, 2-hydroxy ethylacrylate 97%, and methyl acrylate 99%, all from Aldrich Chemie, and diallyllamine from Fluka. Monomers were degassed using an ultrasonic bath for 15 min, and by being subjected to a vacuum (0.02 Torr) for 15 min. Argon gas for inert plasma treatment 99.997% Ar from Norsk Hydro.

Equipment

The plasma-induced grafting was carried out using a commercial radio frequency (13.56 MHz) plasma reactor (PS 0150 from Himont Plasma Science, USA) with a volume of 28.4 L. XPS measurements were conducted with a Vacuum Generators Micro-lab 3 spectrometer. IR measurements were made with a Perkin–Elmer 1725 X spectrometer using ATR equipment with a KRS-5 prism (from Spectratec). Contact angle measurements between sample and distilled water were carried out using a sessile drop on a horizontal surface with a NRC contact angle goniometer model 100-00 from Ramé–Hart at ambient humidity and temperature. A minimum of six parallel measurements were performed for each sample, with reproducibility typically between 1 and 3°.

Plasma-Induced Grafting

Before plasma treatment the plasma chamber was evacuated to a pressure of 0.02 Torr. The argon plasma treatment was carried out with an argon flow rate of 7.2 sccm (standard cm^3 per minute) and a power of 25 W for 5 min. After the plasma treatment was completed, the chamber was again evacuated to 0.02 Torr, and the valve between plasma chamber and vacuum pump closed. The monomer was introduced into the chamber through a needle valve. In some experiments the monomer was introduced until a defined pressure was obtained then the needle valve was closed. In other experiments the needle valve was open during the whole grafting period.

After the grafting reaction was completed the chamber was again evacuated to 0.02 Torr before air was introduced into the chamber. To remove unreacted monomer and homopolymer, the samples were cleaned in an ultrasonic bath (as described above) and dried under vacuum (at least 2 h) before surface analysis. The samples were kept in aluminium foil, precleaned with oxygen plasma, when not in use.

RESULTS AND DISCUSSION

Grafting of Monomers with Different Polar Groups

In order to generate surfaces with different chemical groups the following monomers were evaluated for grafting onto a polyethylene surface: acrylic acid (acid), N-ethyl-2-methylallylamine and diallyllamine (amine), glycidyl methacrylate (epoxy), 2-hydroxy ethylacrylate (hydroxyl), and methyl acrylate (ester). The grafting reactions were performed at room temperature for 15 min. In these reactions the valve between monomer reservoir and plasma chamber was open during the whole grafting period.

Figure 1 shows the IR spectra of the original LD–PE and LD–PE grafted with the various monomers. Considering the intensities of the carbonyl absorptions, acrylic acid, glycidyl methacrylate, and methyl acrylate have been successfully grafted on to the PE surface. A small amount of 2-hydroxy ethylacrylate was grafted on to the PE surface when the monomer was heated to 60°C with 60 min reaction time (the temperature in the reaction chamber was 25°C). For the monomers containing amino groups, no significant changes in the IR spectra relative to the original LD–PE film were detected.

Table I shows the boiling point for the different monomers and the monomer pressure in the plasma chamber after 15 min grafting reaction. For acrylic acid and methyl acrylate the boiling points are relatively low, and the final monomer pressure was above 5 Torr (5 Torr is the upper detection limit for pressure measurement in the plasma chamber) and a high graft yield is observed. For glycidyl methacrylate and 2-hydroxy ethylacrylate the boiling points are higher, and the observed graft yields are lower. For 2-hydroxy ethylacrylate it was not possible to achieve grafting without heating the monomer to increase the monomer pressure in the plasma chamber. Despite having low boiling points and providing vapor pressures above 5 Torr no grafting could be observed using the amino group containing mono-
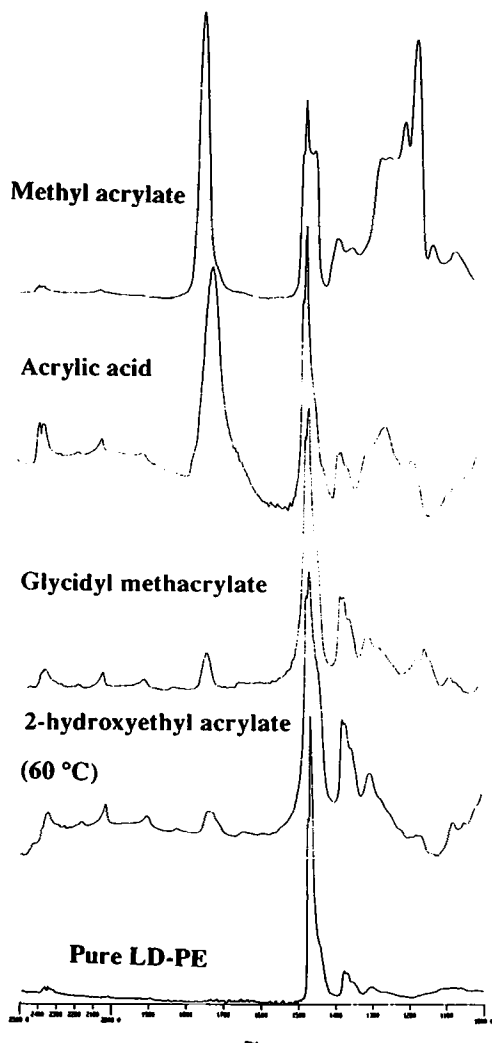
The results presented above show that vapor phase grafting at 25°C can be achieved on an inert gas plasma-activated surface given a monomer containing a suitably reactive unsaturation and providing a high enough vapor pressure. The grafting efficiency would be expected to be a function of the reactivity and partial pressure of the monomer.

Surface Analysis of Samples Grafted with Acrylic Acid and Reference Samples

Acrylic acid was chosen for a more detailed study of the factors influencing grafting yield. Figure 2(a) shows the details of the deconvoluted carbon peak from the XPS analysis of a sample treated for 5 min with Ar plasma. The carbon peak is deconvoluted into four peaks, C1s (carbon bonded to carbon or hydrogen), C1s1 (carbon bonded with single bond to oxygen), C1s2 (carbon bonded with one double bond to oxygen), and C1s3 (carbon bonded with one single and one double bond to oxygen). The C1s3 signal should represent carboxylic acid on the polyethylene surface. In this case, the quantification of the four peaks gave 78% C1s, 8% C1s1, 2% C1s2, and 2% C1s3, i.e., a variety of oxidised groups. Figure 2(b) shows an XPS spectra of a sample grafted with acrylic acid for 45 min. The monomer temperature was 45°C, and the valve was open throughout the experiment. In this case, the quantification gave 11% C1s3. The C1s3 peak can be used to represent the amount of acrylic acid grafted onto a LD–PE surface. There may be a contribution to the C1s1 from peroxide groups generated by the termination of radicals by oxygen on the addition of air after the polymerization reaction. Peroxide formed by termination of polymer radicals should not alter the size of the C1s3 peak used for the identification of poly(acrylic acid), but will have a small effect on the total oxygen values. The uncertainty in the C1s3 quantification is estimated to be ±1 atom %.

Figure 1 ATR-IR spectra of pure LD–PE and LD–PE grafted with different monomers.

mers N-ethyl-2-methylallyllamine and diallyllamine with a reaction time of 15 min. The lack of reactivity for the two amines could be attributed to the allylic nature of the unsaturation.[14]

Table I Boiling Points and Pressure after 15 Minutes in Plasma Chamber for the Monomers Used in This Study

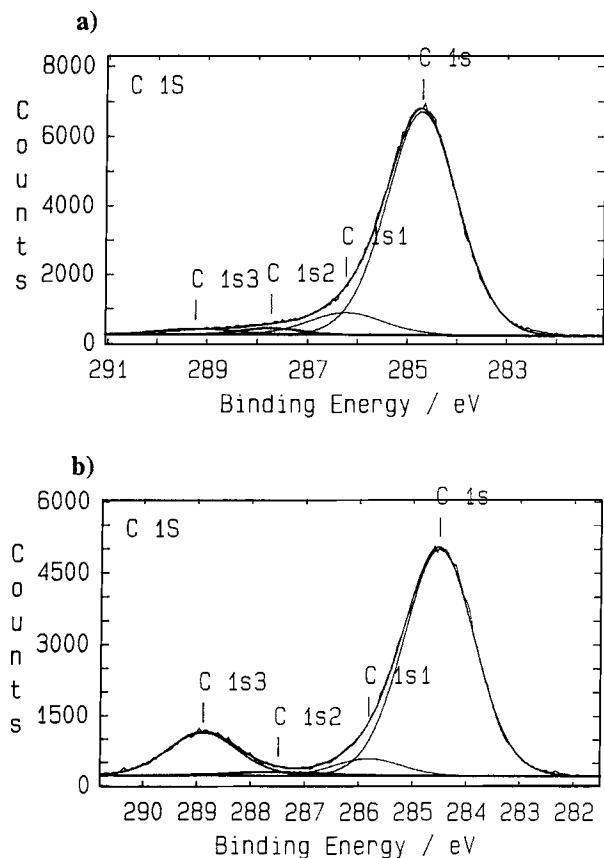| Monomer	Boiling Point (°C)	Pressure in Plasma Chamber after 15 min/Torr
Acrylic acid	141	>5
Glycidyl methacrylate	189	0.15
2-hydroxy ethylacryalate	91/12 mmHg	1.2 (monomer at 60°C)
Methyl acrylate	80	>5
N-Ethyl-2-methylallyllamine	105	>5
Diallyllamine	112	>5

a)

b)

Figure 2 (a) Deconvoluted carbon peak from XPS analysis of LD–PE sample treated 5 min with Ar plasma. (b) Deconvoluted carbon peak from XPS analysis of LD–PE sample grafted 45 min with acrylic acid with increasing monomer pressure with monomer at 45°C and plasma chamber at 25°C.

Figure 3 shows the IR spectra and XPS analyses of the reference samples. Analysis of the original LD–PE sample by XPS and IR showed no signs of oxidation. The sample treated with argon plasma for 5 min without a following grafting reaction has an IR spectrum similar to untreated LD–PE. XPS analysis shows 2 atom % Cls3, indicating a degree of surface oxidation. This oxidation is the result of the reaction between radicals generated on the polymer surface by argon plasma and atmospheric oxygen. Oxidation occurs as soon as the plasma chamber is filled with air. The fact that no oxidation can be detected by IR analysis indicates that only the outermost layer of the polymer is oxidized.

Three samples were reacted with acrylic acid (15 min reaction with continuously increasing monomer pressure in the plasma chamber). The first sample was a film without plasma treatment exposed to acrylic acid. In this case, no reaction on the surface

could be detected either with XPS or IR analysis. This observation indicates that acrylic acid is not physically adsorbed on the PE sample. The second sample was treated with argon plasma, thereafter exposed to air at 1 atmosphere before reducing the pressure to 0.02 Torr and introducing acrylic acid. In this case, a small peak from acrylic acid could be detected by IR analysis, while XPS did not show any higher amount of Cls3 than for the argon-only plasma-treated sample (2 atom %). This may be interpreted as being a surface oxidation by air and a grafting below the surface. (ATR IR has an analysis depth in the order of μm, while XPS has an analysis depth in the order of Ångström.) For comparison, using plasma-induced grafting of acrylic acid performed with first argon plasma without exposure to air, the XPS analysis showed 5 atom % Cls3. The third sample consisted of plasma-induced grafting of acrylic acid in the ordinary way except that air was not removed from the monomer before reaction.
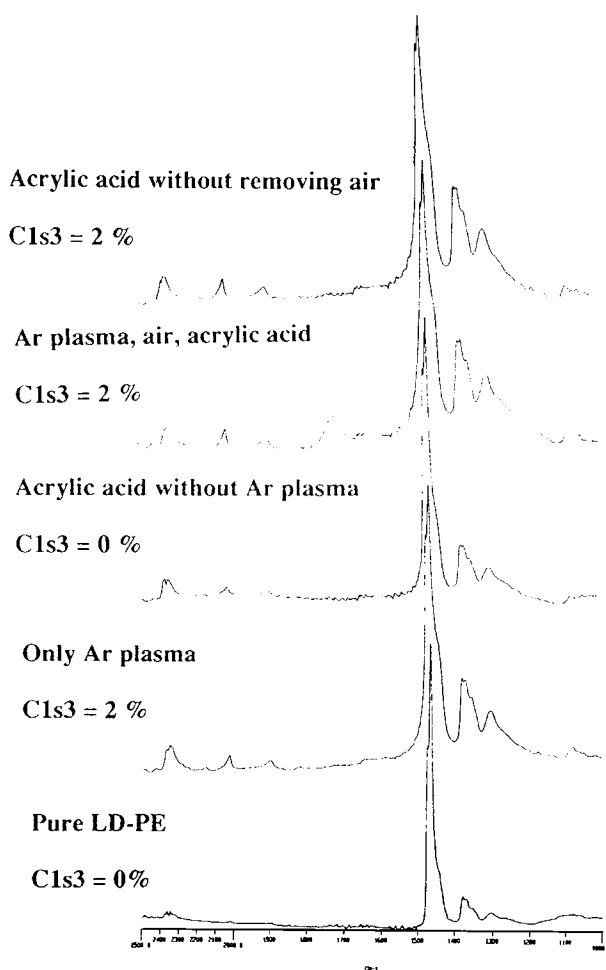

Figure 3 ATR-IR spectra and XPS analysis (Cls3) of reference samples.
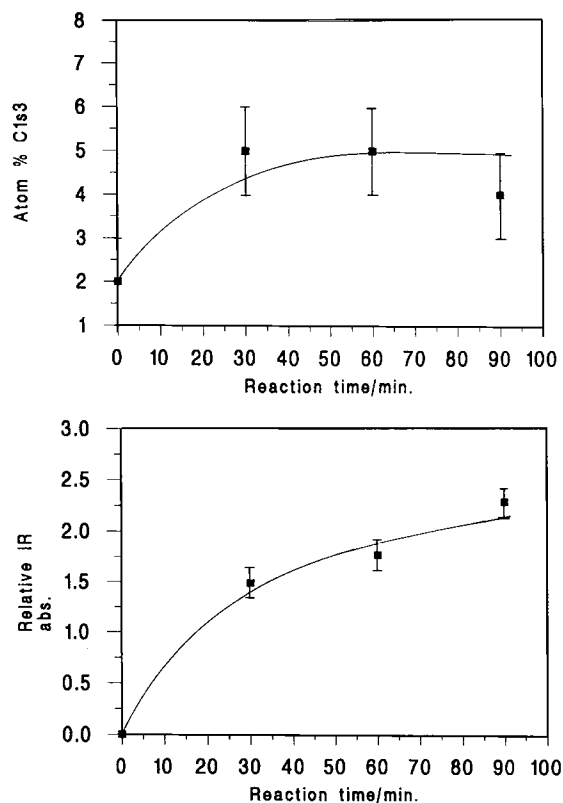
Figure 4 ATR-IR analysis and XPS analysis (C1s3) of LD–PE as a function of grafting time with acrylic acid. Monomer pressure 3 Torr with monomer and plasma chamber at 25°C.

In this case, neither XPS nor IR analysis showed any signs of grafted acrylic acid. The results indicate that oxygen in air reacts more easily with free radicals at the polymer surface than acrylic acid, and effectively inhibits the grafting.[15]

This series of experiments shows that the brief exposure to oxygen effectively inhibits the grafting at the very surface. Radicals are lost by combination with oxygen. Below the outer surface radicals survive and can still promote grafting.

Effect of Reaction Time and Monomer Pressure on Graft Yield

The experiments described initially were performed with an unlimited supply of monomer vapor. Pressure was permitted to rise until the system was saturated. For the experiments described below, the grafting yield is studied as a function of time at both constant monomer pressure and increasing monomer pressure.

Figure 4 shows the time development of the C1s3 peak and the relative IR absorption (carbonyl signal

from acrylic acid vs. PE signal at 1475 cm^{-1}) as a function of time for grafting of acrylic acid with a monomer pressure of 3 Torr (reaction temperature and monomer supply temperature 25°C). The time to attain a monomer pressure of 3 Torr in the chamber was 10 min. XPS analyses indicate a relatively constant degree of grafting between 30 and 90 min reaction time; IR analyses indicate an increase in grafting up to 90 min, but the rate of grafting decreases with time. The results at zero reaction time are values for an argon plasma-treated sample having had no contact with the monomer. These samples contain the oxidized surface resulting from the reaction with atmospheric oxygen.

The effect of reaction time with acrylic acid was also studied in the case where the monomer valve was open during the experiment. The monomer reservoir temperature was 45°C. A pressure of 5 Torr was attained after 4 min. Above this pressure it was not possible to follow pressure development. The reaction temperature in the chamber was 25°C. Figure 5 shows the time development of the C1s3 peak and relative IR absorption for this experiment.
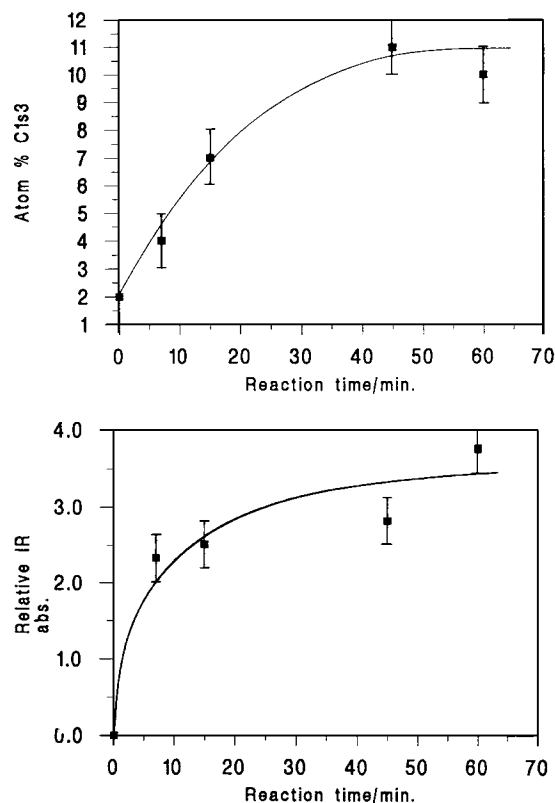

Figure 5 ATR-IR analysis and XPS analysis (C1s3) of LD–PE as function of grafting time with acrylic acid. Increasing monomer pressure with monomer at 45°C and plasma chamber at 25°C.
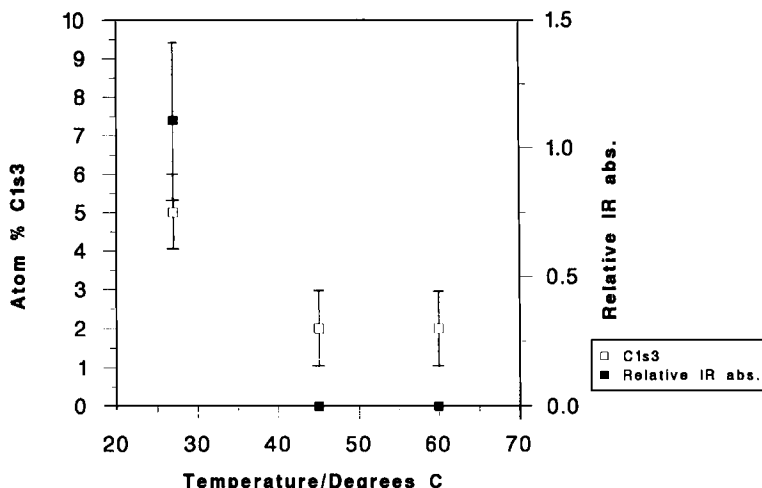
Figure 6 ATR-IR analysis and XPS analysis (C1s3) of LD–PE grafted with acrylic acid as a function of temperature.

Compared with the previous experiment (at 3 Torr), the surface analyses from this experiment indicate a faster rate of grafting, and the grafting continues throughout the experiment. Comparison of the two experiments indicates that the degree of grafting is more pressure (concentration) dependent than time dependent.

Effect of Temperature on Graft Yield

To study the effect of temperature on the reaction, grafting experiments were performed with acrylic acid with a reactor temperature of 27, 43, and 57°C. The grafting was performed with continuously increasing monomer pressure (monomer at room temperature) and 15 min reaction time. Figure 6 shows atom % C1s3 and relative IR absorbencies for these experiments. The results show no sign of grafting at the temperatures 43 and 57°C. The graft yield of acrylic acid, therefore, seems to decrease with increasing temperature.

The decrease in graft yield for plasma-induced grafting with increasing temperature has been reported in the literature. Hirotsu and Isayama[12] reported a slightly lower degree of grafting of acrylic acid in liquid phase onto plasma pretreated polypropylene when the temperature was raised from 50 to 60°C. Hirotsu[16] reported a decrease in graft yield of acrylamide on polypropylene when the polypropylene sample was heated to 90°C (comparison with a room temperature sample) before grafting but after plasma treatment. This observation was explained by deactivation of the free radicals in the polypropylene surface at elevated temperature.

An alternative explanation for the observed temperature dependence of graft yield can be the monomer's condensation on the sample surface. At 27°C the monomer may condense to a thin liquid film on the sample surface, resulting in a high monomer concentration. At elevated grafting temperature there will be a tendency for distillation of monomer away from the sample, i.e., a much lower effective monomer concentration.

Time Development of Contact Angle for Acrylic Acid-Grafted Samples

The time development of contact angle for LD–PE samples grafted with acrylic acid is shown in Figure 7. The samples were grafted for 7 min with the
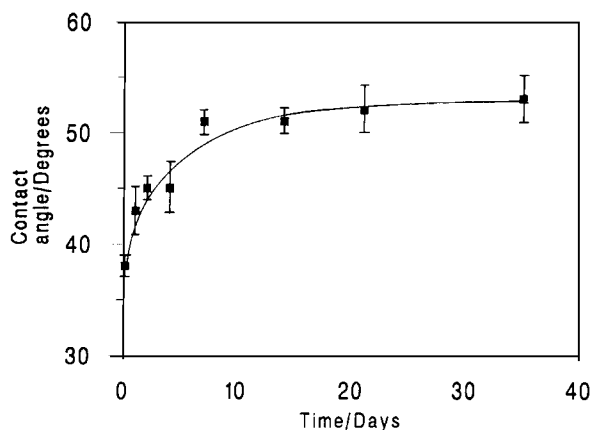

Figure 7 Contact angle between water and LD–PE grafted with acrylic acid as a function of storage time in vacuum.

monomer supply at 45°C and reactor at 25°C with continuously increasing monomer pressure. After cleaning and drying, the samples were placed in aluminium foil under vacuum. The figure shows that the contact angle increases from 38° 2 h after treatment to around 50° after 7 days. From 7 up to 35 days the contact angle lies approximately constant just above 50°. For untreated LD–PE the contact angle was measured to 91.5 ± 0.5°. These observations indicate some reorganization in the surface up to 7 days, and a relatively stable surface thereafter (during the time interval studied).

The time development of contact angle for plasma-treated polyolefins has been reported earlier. Hsiue and Wang[13] studied the time development of the contact angle for PE film grafted with acrylic acid. The grafting was performed in the liquid phase on PE samples treated with Ar plasma and subsequent exposure to oxygen. A contact angle stable at around 50° up to 28 days was reported. In this case, the samples were stored in air at room temperature. These results are comparable to the ones obtained in the present study except that we observed a lower initial contact angle. The contact angle of plasma-induced grafted polyolefins seems to be more stable than for oxygen plasma-treated polyolefins. Occhiello et al.[3] reported that the advancing contact angle against water for oxygen plasma-treated polypropylene changed from an initial 24° to 95° after 30 days for samples stored in air.

CONCLUSION

This article has shown that using plasma-induced grafting with first argon plasma and thereafter performing the grafting with the monomer in the vapor phase, it is possible to graft monomers with different polar groups onto a LD–PE surface. The yield of monomer grafting seems to depend on both the reactivity of the monomer and the pressure of monomer in the reaction chamber. With the grafting of acrylic acid at 25°C and relatively low pressures, the grafting rate decreased significantly after the first 15 min. With a continuously increasing monomer pressure the high rate of grafting was maintained for up to 90 min. The graft yield of acrylic acid was observed to decrease with increasing reaction temperature. This could be attributed to a deactivation of radicals or a decrease in effective monomer concentration. The contact angle against

water for samples grafted with acrylic acid stored under vacuum increased up to 7 days but were thereafter stable at slightly above 50° for up to 30 days. Although the method, as described, is too slow to be of direct industrial application, it does provide a means for producing well-defined polar surfaces on polyolefins for further study.

REFERENCES

1. J. M. Lane and D. J. Hourston, *Prog. Org. Coat.*, **21**, 269 (1993).
2. D. Briggs, D. M. Brewis, and M. B. Konieczko, *J. Mater. Sci.*, **14**, 1344 (1979).
3. E. Occhiello, M. Morra, G. Morini, F. Garbassi, and P. Humphrey, *J. Appl. Polym. Sci.*, **42**, 551 (1991).
4. K. Kildal, K. Olafsen, and A. Stori, *J. Appl. Polym. Sci.*, **44**, 1893 (1992).
5. K. Olafsen, A. Stori, and D. A. Tellefsen, *J. Appl. Polym. Sci.*, **46**, 1673 (1992).
6. Z. P. Yao and B. Rånby, *J. Appl. Polym. Sci.*, **40**, 1647 (1990).
7. I. K. Mehta, S. Kumar, G. S. Chauhan, and B. N. Misra, *J. Appl. Polym. Sci.*, **41**, 1171 (1990).
8. Y. L. Hsieh and W. Meiping, *J. Appl. Polym. Sci.*, **43**, 2067 (1991).
9. T. Hirotsu and I. Munetoshi, *Proc. Jpn. Symp. Plasma Chem.*, **1**, 291 (1988).
10. J. Meichsner and H. U. Poll, *Acta Polym.*, **32**, 203 (1981).
11. N. Inagaki, S. Tasaka, and Y. Horikawa, *Polym. Bull.*, **26**, 283 (1991).
12. G. H. Hsiue and C. C. Wang, *J. Polym. Sci. Part A.*, **31**, 3327 (1993).
13. C. C. Wang and G. H. Hsiue, *J. Polym. Sci. Part A.*, **31**, 1307 (1993).
14. G. Odian, *Principles of Polymerization*, Wiley, New York, 1991.
15. S. Tazuke, T. Matoba, H. Kimura, and T. Okada, ACS Symposium Series 121, American Chemical Society, Washington, DC, 1980.
16. T. Hirotsu, *Adv. Low-Temp. Plasma Chem., Technol. Appl.*, **3**, 9 (1991).