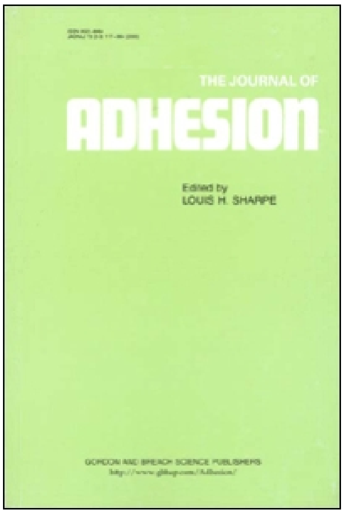

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Autoadhesion of high density polyethylene (HDPE) to HDPE by ultraviolet grafting of methacrylates and acrylates

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AUTOADHESION OF HIGH DENSITY POLYETHYLENE (HDPE) TO HDPE BY ULTRAVIOLET GRAFTING OF METHACRYLATES AND ACRYLATES

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A study has been made on the effect of the presence of grafted acrylic layers on the autoadhesion of polyethylene. Methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA), and butyl methacrylate (BMA) were grafted onto high density polyethylene (HDPE). The grafting reaction was faster at higher temperature and methacrylates graft more easily than acrylates. For methacrylates and acrylates, the grafted amount increases with increasing length of the pendant alkyl chain. The grafting temperature is a crucial factor affecting the adhesion of grafted PE samples. For the samples grafted at lower temperature (in a room temperature water bath), the adhesion is very low (less than 50 N/m), even for very thick grafted layers. But for the samples grafted at higher temperature, much higher adhesion can be obtained. The presence of homopolymer was another factor affecting the adhesion of PE samples. When homopolymer is removed from the surface of the grafted sample, higher adhesion can be obtained. For some samples, the highest peel strength of more than 1000 N/m has been obtained. The low adhesion of the samples grafted at low temperature is attributed to the high branching of grafted chains.

Keywords: Grafting; High density polyethylene (HDPE); Adhesion; Methacrylate; Acrylate

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INTRODUCTION

Polyethylene (PE) is one of the most widely employed polymer materials since it has many useful properties such as high chemical resistance, high impact strength, and availability at low cost. However, the adhesion between PE and most materials is poor, due to its chemical inertness and smooth surface, which prevent chemical as well as mechanical bonding [1, 2].

A large number of commercial techniques are used to treat polyethylene surfaces for improving adhesion. A commonly used surface treatment is surface modification by graft copolymerisation, including chemical graft polymerisation, glow or corona discharge-induced graft copolymerisation [3, 4], plasma-induced graft copolymerisation [5, 6], photoinduced graft copolymerisation [2, 7–10] and high-energy radiation-induced graft copolymerisation [11, 12].

Photoinduced grafting is a useful technique for the modification and functionalisation of polymeric materials due to its significant advantages: low cost of operation, mild reaction conditions, selective absorption of UV light without affecting the bulk polymer, and permanent alteration of the polymer surface chemistry. This area has been reviewed by a number of authors [13–15].

In most of the reported techniques for improving the adhesion of polyethylene by photografting, an adhesive is needed to bond the grafted samples. However, in recent years, some adhesive-free or auto-adhesion methods have been developed. Yang and Rånby [16–19] reported an innovative bulk surface photografting process, in which a drop of solution containing the monomer and a photoinitiator was sandwiched between two thin films. Most importantly, photolamination occurred simultaneously during the photografting process, resulting in good adhesion between the two films. But this method can only be used for thin and UV transparent films. Also, the adhesion obtained is not very large; the reported peel strength for the LDPE//LDPE laminate was 1050 N/m [20]. The HDPE surface is more difficult to graft than LDPE due to the linear chain structure of HDPE and its higher degree of crystallinity. The reported peel strength for a HDPE//HDPE laminate was just 290 N/m [18].

Yamada *et al.* [21, 22] and Yamada and Hirata [23] grafted hydrophilic monomers, such as methacrylic acid (MAA), acrylic acid (AA), 2-dimethylaminoethylmethacrylate (DMAEMA) and methacrylamide (MAAm) onto LDPE and HDPE. The grafted chains in the water-swollen grafted layers can become entangled with each other through their self-diffusion when the two grafted polymer plates are forced into contact, leading to bond formation by hot-pressing without any adhesives. However, the limitation of this method is that it can only be applied to water-soluble monomers, as the water plasticizer is required.

The main idea of the work described here is to graft amorphous polymers on the HDPE surface, then hot-press the two grafted surfaces together at a temperature above the T_g of the grafted polymer. Because of the diffusion and entanglement of grafted chains, good autoadhesion can be achieved. The joining mechanism of the grafted materials under hot pressing is shown in Figure 1.

In this article, the UV-induced grafting of methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), methyl acrylate (MA), and ethyl acrylate (EA) onto high density polyethylene (HDPE) has been performed at low and high temperature. The autoadhesion of the grafted samples was then measured.

EXPERIMENTAL TECHNIQUES

Materials

HDPE was supplied by Nova Chemicals Ltd. (Sarnia, Ontario, Canada). Its melt flow index (MFI) is 0.39 g/10 min, with a density of 0.9491 g/cm^3. HDPE film was cut into 2 cm × 3 cm (≈0.2 mm in thickness for the grafting study) and 2 cm × 10 cm or 2 cm × 14 cm (≈0.5 mm in thickness, for peel test) rectangular samples, and then subjected to Soxhlet extraction with acetone for 24 h to remove impurities and additives before use.

Monomers MMA, EMA, BMA, MA, and EA from Aldrich (New Castle, Australia) were used without purification; all are of AR grade. Photoinitiator benzophenone (BP) (from Aldrich, New Castle, Australia) (chemically pure grade) was used as received.

UV Equipment

The UV system with shutter assembly is supplied by Amba Lamps Australasia Proprietary Limited (Sydney, Australia). The input power

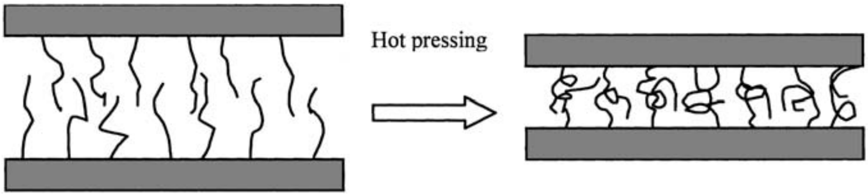

FIGURE 1 Joining mechanism of the grafted materials under hot pressing.

of the UV medium pressure mercury lamp is 2 kW. No filter was used to isolate UV light. The output UV intensity was measured by using UV Power Puck^{TM} from Electronic Instrumentation and Technology, Inc., Sterling, Virginia, USA). It measures the intensities of UVA (320–390 nm), UVB (280–320 nm), UVC (250–280 nm) and UVV (395–445 nm) simultaneously.

Grafting

Photografting was carried out in a cubic stainless steel container (length: 15 cm, width: 4.5 cm, height: 2 cm) specially designed for the grafting. Two pieces of HDPE sample are put in the vessel and then solution is added. The vessel is covered with a quartz plate or polyethylene foil and put in a water bath or directly on a ceramic plate. The reaction vessel was put at a fixed position 4 cm below the focal point of the UV lamp, where the UVC intensity is 0.024 W/cm^2.

Because the UV lamp produces a large amount of heat as well as UV light, it is not very easy to strictly control the reaction temperature. When the water bath and quartz plate are used together, the reaction temperature is in the range of 20–30°C and is referred to as low temperature. When the reaction vessel is put directly on the ceramic plate and no quartz plate is used to cover it, the reaction temperature increased from 30°C to 90°C during the grafting, with the heating rate depending on the amount of solvent present, and is referred to as high temperature.

After grafting, the grafted PE samples were Soxhlet extracted with acetone for at least 14 h to remove homopolymer and unreacted monomer and then dried at 50°C for 24 h or at room temperature for 5 h under reduced pressure.

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

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

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

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

Preparation of PE Film Samples Precoated with BP

PE film samples were dipped in chloroform solution containing 10% w/w BP for 14 h at room temperature, taken out, and dried. The amount of BP absorbed by the films was determined gravimetrically.

Microscopy Study of the Grafted Samples

A Leitz Orthoplan Research Microscope from Ernst Leitz GMBH (Wetzlar, Germany) was used. The samples for transmission microscopy were prepared according to the following procedure. Firstly, the grafted PE films were fixed in a plastic container, and then the container was filled with epoxy resin and hardener. After the epoxy cured, a thin cross section was cut (less than 100 μm). The two sides of the cross section were then polished and examined using polarised light.

Peel Tests

Two pieces of the pristine or grafted PE strips were hot pressed at 120°C (if not specially pointed out) and 5 MPa for 10 min. There was a little deformation (less than 10%) of the PE strips after hot pressing. However, the original width was used for calculation of peel strength.

Peel strength was measured at room temperature by a 180° T-peel test using an Instron Model 4302 (Buckinghamshire, England) with a cross-head speed of 50 mm/min. The average force after the initial peak load was taken as the peel strength, which was expressed in N/m. The values obtained were reproducible with about 20%.

RESULTS AND DISCUSSION

UV Grafting

Grafting of MMA

One M (mol/L) MMA in acetone solution with an added 1% BP (1% of monomer, mol/mol) was used for the grafting on PE films. One M (mol/L) MMA in acetone solution without BP was used for the grafting on PE films precoated with BP. As shown in Figure 2, these two grafting systems gave almost identical grafted amounts.

Grafting onto PE occurs by the extraction of a secondary H atom from the PE chain to form a radical that then initiates polymerisation of the monomer. Because there is no secondary or tertiary H atom in the structure of MMA, the BP in the excited triplet state is prone to extract a secondary hydrogen atom from the PE film or from the grafted layer rather than from a monomer molecule. Hence, grafting is much more likely than homopolymerisation. If there is no interaction between the excited triplet state BP and solvent or the solvent is stable under UV irradiation, there should be no significant difference no matter whether the photoinitiator is precoated on the PE or dissolved in the solution. It is interesting to note that

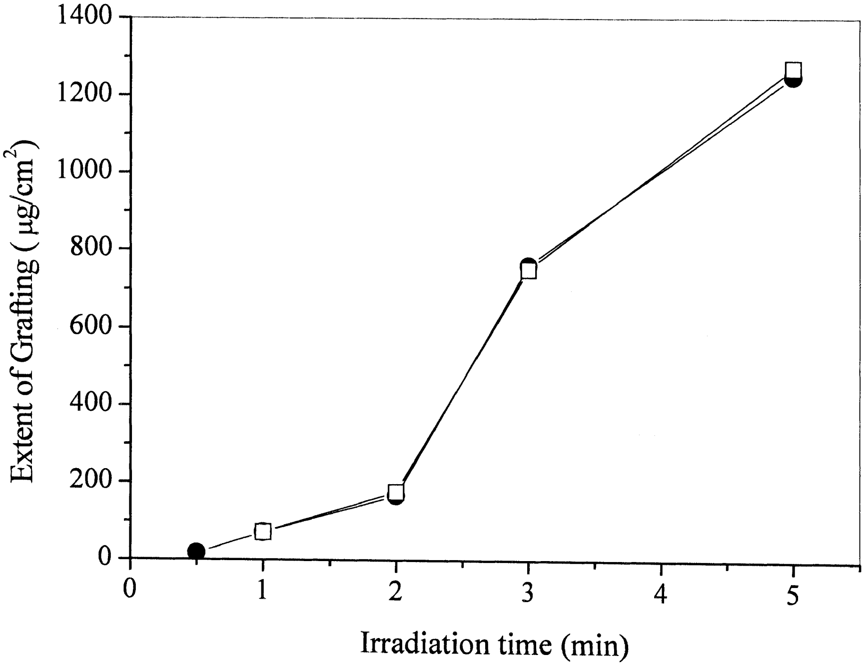

FIGURE 2 Grafting of MMA on PE films: 1% BP in acetone (●) and BP precoated on PE (□).

methacrylic acid (MAA) behaves quite differently from the MMA used here. For MAA, precoating the BP photoinitiator on PE gives much more grafting than adding the initiator to the solution. The reason for these different behaviors is unclear [24].

MMA has also been grafted onto PE when dissolved in petroleum ether and acetone, as shown in Figure 3. The extent of grafting of MMA in petroleum ether is higher than that in acetone for the same UV irradiation time. A possible reason for this result is that petroleum ether is a more powerful swelling agent for PE than acetone. Hence, much more PE is accessible to the excited BP.

Grafting of Different Monomers onto PE

EMA, MA, EA, and BMA have been grafted onto PE at low temperature in acetone solution; 1% BP (1% of monomer, mol/mol) was used in every solution. Figure 4 shows that the methacrylates (MMA, EMA, and BMA) are easier to graft onto PE than acrylates (MA and EA). For methacrylates and acrylates, the grafting becomes easier with increasing length of the pendant alkyl chain. The order of the grafting

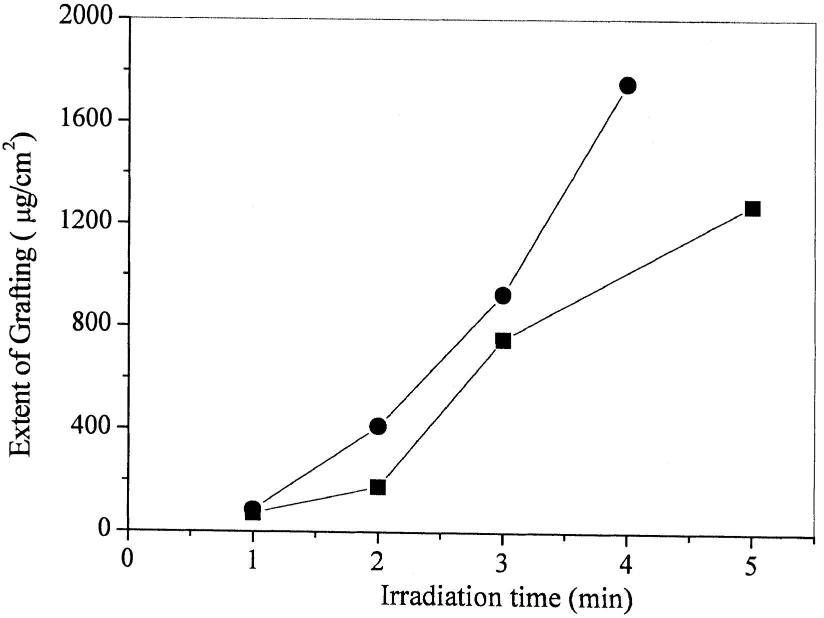

FIGURE 3 Grafting of MMA in acetone (■) and in petroleum ether (●).

reactivity for methacrylates is: BMA > EMA > MMA, and for acrylates is: EA > MA.

The bond strength of ethylenic hydrogens (443.5 kJ/mol) in the methacrylate and acrylate monomers is higher than that of primary (418.4 kJ/mol), secondary (401.7 kJ/mol), and tertiary (388.8 kJ/mol) hydrogens. Thus, BP is prone to abstract hydrogen from the PE substrate to initiate grafting rather than from the monomers to initiate homopolymerisation. Therefore, the difference in the grafting efficiency of these monomers is caused by either the different propagation rates of polymerisation of the grafted chains or by different efficiencies in initiating grafts on grafts. In terms of the monomer structure, these arguments give two possible reasons for the observed effect of side groups on grafting efficiency.

1. Because the pendant alkyl chain has a similar chemical structure to polyethylene, methacrylate or acrylate with a longer pendant alkyl chain has better solubility in the polyethylene, hence the grafting reaction occurs more easily on the PE surface, so there are more grafted chains. This is beneficial to adhesion.
2. Because there are secondary hydrogen atoms on the grafted chain, the photoinitiator can abstract them to initiate grafting reactions.

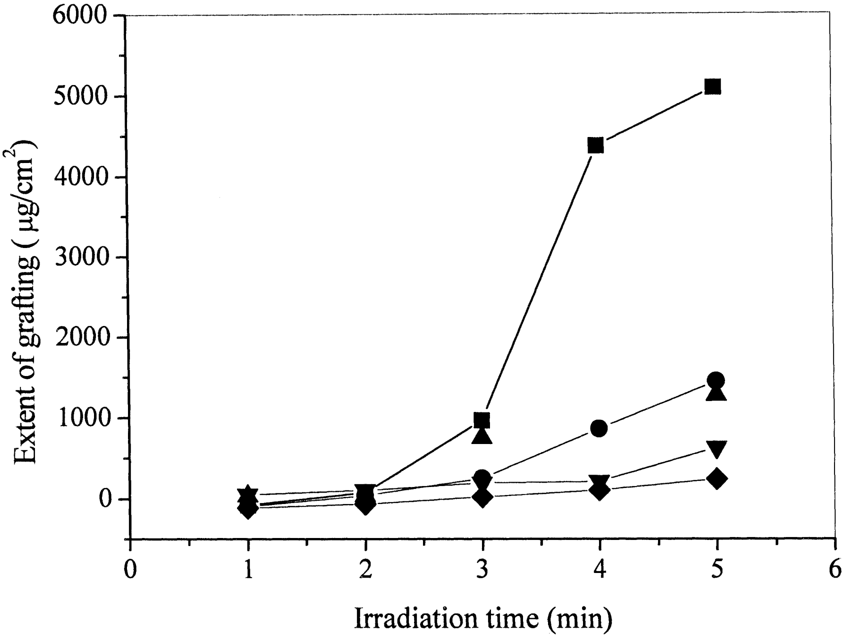

FIGURE 4 Grafting of BMA (■), EMA (●), MMA (▲), EA (▼), and MA (◆) onto PE.

For the grafted chain with longer pendant alkyl chains, there are more secondary hydrogen atoms, therefore, more grafting reactions can take place on the grafted chain to form a branched grafted chain. This branching is liable to affect adhesion as discussed below.

MA, EA, EMA, and BMA have also been grafted onto PE at high temperature. In all cases the higher temperature increased the grafting rate. As shown in Figure 5, when neither quartz plate nor water bath is used, the extent of grafting is much higher than that obtained using the quartz plate and water bath. However, when neither quartz plate nor water bath is used, the temperature increases very rapidly up to around 90°C, so the solution evaporates after 2 or 3 min.

Adhesion Tests

Peel Test of Reference PE Samples

The peel strength of an untreated PE sample was tested. As shown in Figure 6, the peel strength of a reference PE sample is very

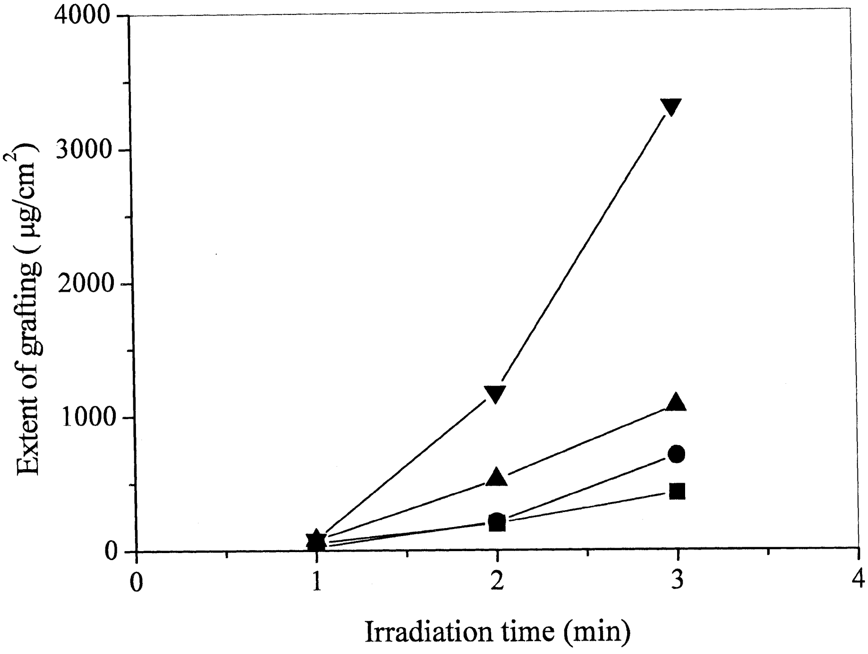

FIGURE 5 Grafting of MA (■), EA (●), EMA (▲), and BMA (▼) at higher temperature.

low, only about 5 N/m. Though the T_g of HDPE is very low (in the region of −140°C to −100°C), because of the high degree of crystallinity (70–90%) the polyethylene chains cannot interdiffuse. When two HDPE strips are hot-pressed at a temperature below the melting temperature of HDPE, there is almost no entanglement of polyethylene chains. Thus, the peel strength of the untreated HDPE sample is very low.

The selected temperature for hot pressing is 120°C. This temperature is between the melting temperature of HDPE (135°C) and the T_g of grafted PMMA (105°C). Though the T_g's of poly(ethyl methacrylate) (65°C), poly(butyl methacrylate) (21°C), poly(methyl acrylate) (3°C) and poly(ethyl acrylate) (−21°C) are much lower, 120°C is still used as the hot-pressing temperature to make the peel test values comparable as the PE properties, such as yield stress, that affect peel test results depend on thermal history. But for the grafted polymer with lower T_g, it may be possible to join the grafted PE samples at a lower temperature.

The failure in peel testing always occurred within the grafted copolymer as evidenced by the fact that the two fracture surfaces looked very similar and, as mentioned later, the samples could be rejoined.

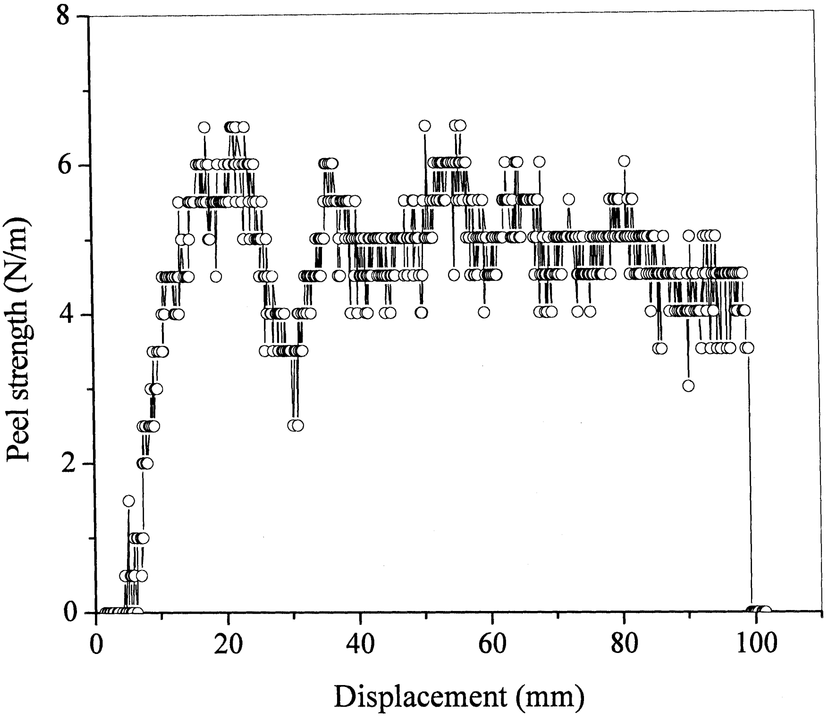

FIGURE 6 Peel test of reference PE sample.

Peel Test of PE Samples Grafted at Low Temperature

Figure 7 shows the peel test results for samples grafted with MMA in acetone and petroleum ether at low temperature. The extent of grafting is the average value of two grafted samples. For the PE samples grafted in acetone and petroleum ether the peel strength tends to increase with the extent of grafting. At the same grafting extent, the peel strength of the PE samples grafted in petroleum ether is higher than that in acetone. No matter if the grafting is carried out in acetone or petroleum ether, the adhesion obtained is still very weak, especially for the samples grafted in acetone, where the peel strength is just a little higher than that of the reference samples.

EMA, MA, EA, and BMA were grafted onto PE in the water bath with the reaction vessel covered with a quartz plate, joined in the press and then adhesion was measured. As shown in Table 1, the peel strengths of these samples grafted at low temperature are very low, no matter how thick the grafted layer.

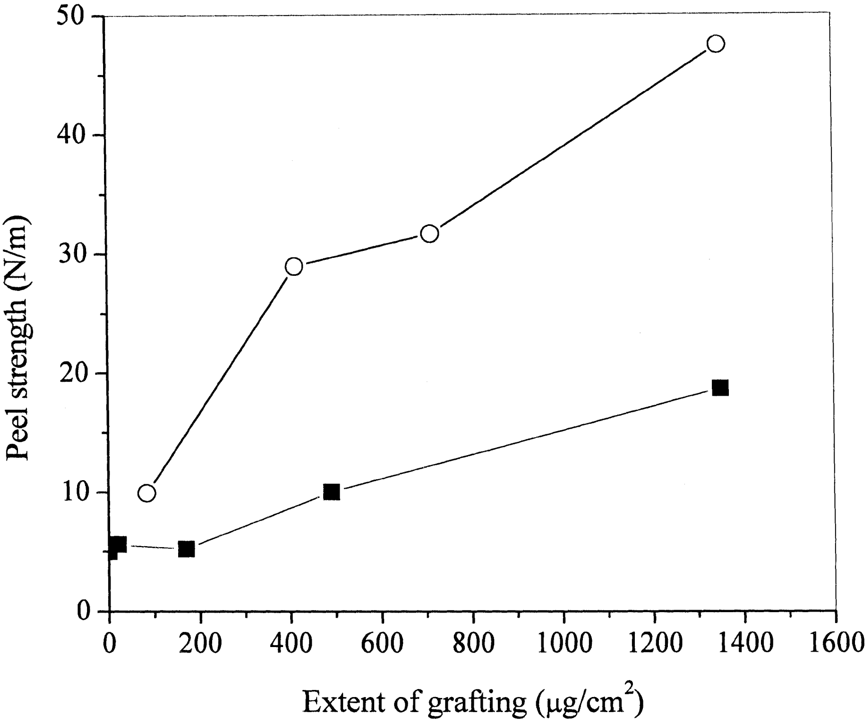

FIGURE 7 Peel strength of PE grafted by MMA in acetone (■) and petroleum ether (○) as a function of the extent of grafting.

There are at least three possible reasons for the poor adhesion of samples grafted at low temperature, as shown schematically in Figure 8.

1. Grafted chains are highly crosslinked.
2. Grafted chains are highly branched.
3. Grafted chains are buried in a deeper layer inside polyethylene rather than being on the surface.

TABLE 1 Peel Strength of PE Samples Grafted with EMA, MA, EA, and BMA at Low Temperature

Monomer	Extent of grafting (μg/cm^2)	Peel strength (N/m)
EMA	1428	6.0
MA	107	47.5
EA	627	75.0
BMA	5287	27.5

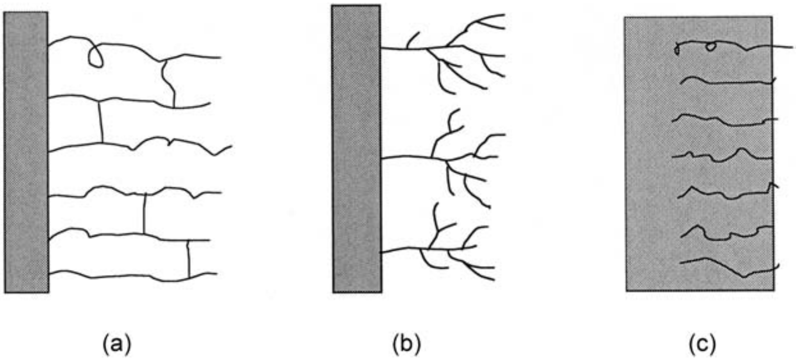

FIGURE 8 Illustrations of possible reasons for the poor adhesion of grafted chains: (a) highly crosslinked, (b) highly branched, and (c) buried inside of PE.

Transmission optical microscopy was used in an attempt to find the location of the grafted material, *i.e.*, is it on the surface or inside the PE? This question is relevant because wetting experiments have shown that some different water-soluble monomer/solvent systems tend to form grafts beneath the surface of the PE [25]. Figure 9 gives images of two different samples that were potted in epoxy and polished to a thin section. The polyethylene strip (around 0.2 mm thickness) is horizontal across the center of each of the images. The extra dark strip at the top surface is the grafted layer. It would appear, therefore, that all the grafted material is on the surface of PE. For the other grafted samples, similar results were obtained.

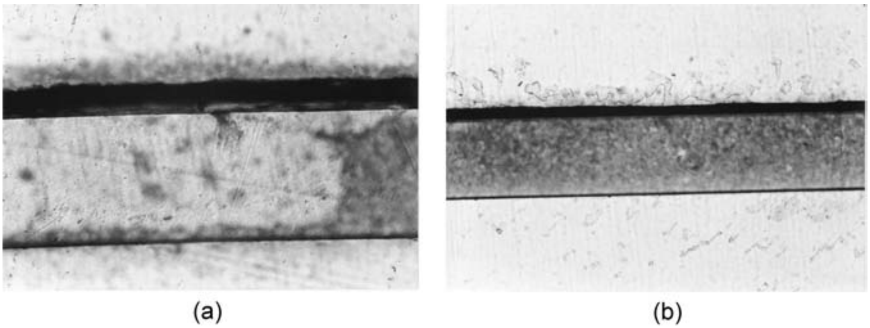

FIGURE 9 Optical microscopy of PE grafted with (a) 1293 $\mu g/cm^2$ EMA (image width = 0.55 mm) and (b) 1318 $\mu g/cm^2$ BMA (image width = 1.1 mm). The thick dark line is the grafted layer.

From the fact that the grafted material was on the surface of PE, it would appear likely that the poor adhesion of PE samples grafted at low temperature is caused by the microstructure of the grafted chains. However, it is not easy to discover if the grafted chains are highly crosslinked or branched. Instead, we tried to change the grafting conditions, as that may alter the microstructure of the grafted chains, and then test the adhesion of the grafted samples.

Peel Test of PE Samples Grafted at High Temperature

The PE samples grafted with MMA at high temperature gave much higher adhesion than those grafted at low temperature (as shown in Figure 7). For the PE sample grafted with 430 μg/cm^2 MMA, the peel strength is 279 N/m. For the sample grafted with 505 μg/cm^2 MMA, the peel strength is 450 N/m. These values are much higher than those obtained for low temperature grafting and about 90 times as high as those obtained with reference PE. Thus, grafting at high temperature significantly improved the adhesion of HDPE.

Figure 10 shows the peel test results of PE grafted with EMA at different grafting temperatures. When the samples are grafted at low temperature (using the quartz plate and water bath), the highest peel strength is just about 100 N/m. The peel strength tends to increase with the extent of grafting. However, when the amount of grafting is very high, the peel strength for low temperature grafted samples decreases to a value as low as that of the reference PE samples. As shown in Table 1, when the extent of grafting is 1428 μg/cm^2, the peel strength is only 6 N/m.

When there is no quartz plate, but the reaction vessel is still in the water bath, the peel strength of the grafted sample is higher than that of the sample grafted at low temperature at the same extent of grafting. When the extent of grafting is 1071 μg/cm^2, the peel strength is 458 N/m. This is much higher than the highest value obtained for the samples grafted at low temperature.

When there is no quartz plate and no water bath, the reaction temperature can become much higher. The adhesion of the samples grafted at high temperature is much higher than that at low temperature. For the PE sample grafted with 348 μg/cm^2 EMA, the peel strength is 795 N/m, and for the sample grafted with 812 μg/cm^2 EMA, the peel strength is 1085 N/m.

All the PE samples grafted at higher temperature have higher adhesion than those grafted at low temperature. Therefore, temperature is a very crucial factor affecting the grafting and the autoadhesion ability of grafted PE. More work will be done in the future to find out the optimal temperature range for the best adhesion of grafted samples.

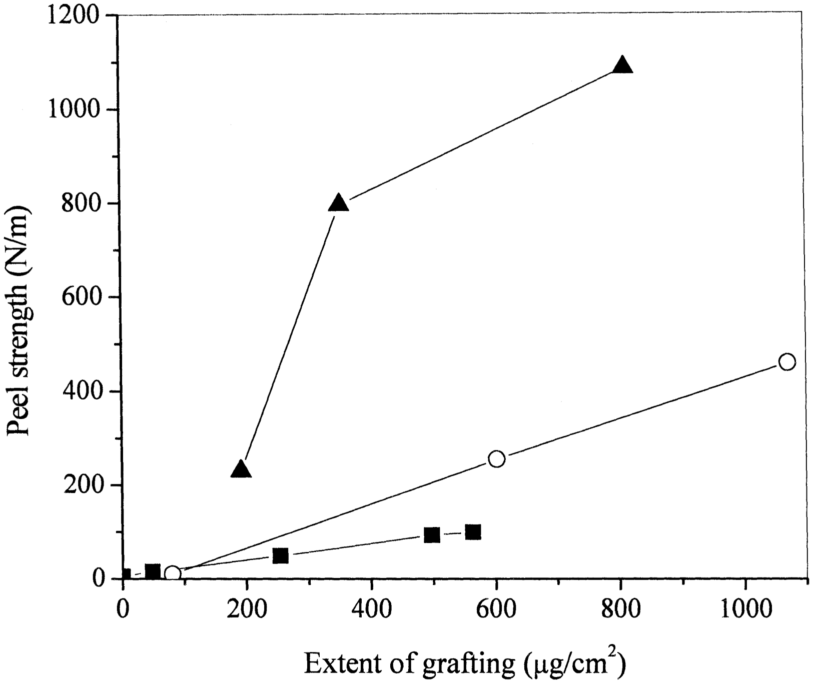

FIGURE 10 Peel strength of PE grafted with EMA at different temperatures as a function of the extent of grafting: ■, quartz plate and water bath; ○, water bath, no quartz plate; and ▲, no water bath, no quartz plate.

As is well known, for a given grafting system, the initiation rate of a photografting (photopolymerisation) reaction is mainly dominated by the incident intensity of the UV radiation [26]. For the experiments described here, all the samples were put at the same position with the same UV intensity. Thus, the initiation rate is similar at low or high temperature. Growth of a given amount of grafted polymer takes a longer time at low temperature than at high temperature; therefore, there are more initiation reactions and, consequently, the chains grafted at low temperature are shorter. Equivalently, the irradiation time for a given grafting extent is shorter at high temperature, so the propagation rate for the growth of the grafted chains must be faster and, therefore, the grafted chains are longer. The presence of longer chains is beneficial for the entanglement of grafted chains under hot pressing that is required to obtain good adhesion.

As has been discussed before, possibly some of the initiation reactions take place on the grafted chains, especially those with a long pendent alkyl group. At the higher reaction temperature, the swelling of the PE by the solvent and monomer is higher, so the number of grafting sites on the PE surface increases, increasing the density of grafted chains. This may be beneficial to adhesion. However, for the grafting carried out at low temperature, much of the initiation takes place on the grafted chains to form highly branched grafted chains that perhaps cannot interdiffuse and entangle. The short chain branching will increase the polymer's entanglement molecular weight.

Therefore, for a given amount of grafted polymer, there is much more initiation of grafted chains but less grafting actually takes place on the PE surface when the grafting is carried out at low temperature rather than at high temperature. Instead, the grafting is mainly on the pre-existing chains to form highly branched grafted chains when the grafting temperature is low. That is the reason for the very weak adhesion shown by the samples grafted at low temperature.

There is another possible reason for low adhesion of the samples grafted at low temperature: the grafted chains may be crosslinked. This is thought to be unlikely because, if the grafted chains are easy to crosslink, this should occur irrespective of the temperature, and there should be no adhesion even when the grafting is carried out at high temperature.

Effect of Homopolymer on the Adhesion of Grafted PE

The presence of homopolymer is also a very important factor affecting the adhesion of grafted PE. If the homopolymer is not removed from the surface of the grafted PE, the adhesion is much lower than that obtained after the homopolymer is removed. For the samples tested, if the homopolymer is not removed, the highest peel strength is only about 40 N/m. However, when the homopolymer is removed, the highest peel strength is more than 350 N/m.

When the homopolymer is not removed from the grafted PE surface, the surface is sticky to the touch, implying that the molecular weight of the homopolymer is very low as the T_g must be close to room temperature. As is well known, for low MW polymers there is almost no adhesion. After the removal of the homopolymer, the grafted chains can diffuse and entangle to give adhesion between the two grafted surfaces.

As shown in Figure 11, the adhesion of the grafted samples hot pressed at higher temperature (120°C) is higher than those hot pressed at lower temperature (110°C) when the hot-pressing time is the same. This is explained by the fact that, at higher hot-pressing temperatures, the diffusion of grafted chains is faster, so more entanglements of grafted chains occur within the fixed time period.

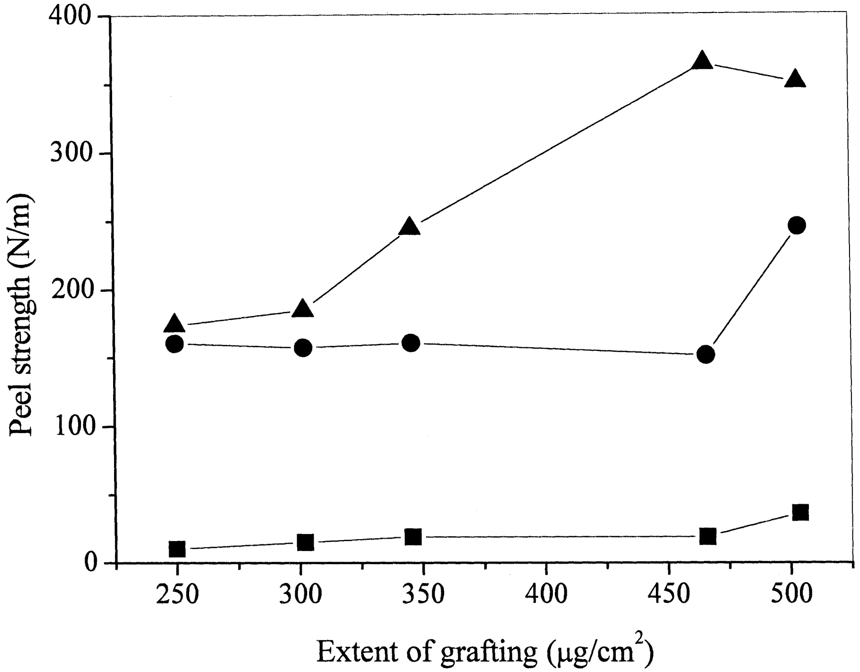

FIGURE 11 Peel test of sample with or without EMA homopolymer, grafted in the water bath (no quartz plate): ■, with homopolymer; ●, without homopolymer, hot pressed at 110°C; and ▲, without homopolymer, hot pressed at 120°C.

However, if the hot-pressing time is long enough, good adhesion can be achieved even at lower temperature (above the T_g of grafted polymer).

A secondary advantage of this method to cause autoadhesion is that the grafted samples can be hot pressed and peeled many times. However, the adhesion becomes weaker with the number of times of hot pressing and peeling, presumably because of the breaking of grafted chains during peeling.

CONCLUSIONS

A new method of joining high density polyethylene (HDPE) by hot pressing HDPE surfaces grafted with methacrylates or acrylates has been introduced. MMA, EMA, MA, EA, and BMA have been grafted onto HDPE.

The grafting temperature is the crucial factor affecting the adhesion of PE samples. For the samples grafted at low temperature (in a tap water bath), the adhesion is very low (less than 50 N/m), and independent of the thickness of the grafted layer. But for the samples grafted at higher temperature (without quartz plate and water bath), high adhesion can be obtained.

The presence of homopolymer is another factor affecting the adhesion of PE samples. When homopolymer is removed from the surface of the grafted samples, higher adhesion can be obtained.

The highest peel strength obtained was more than 1000 N/m.

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