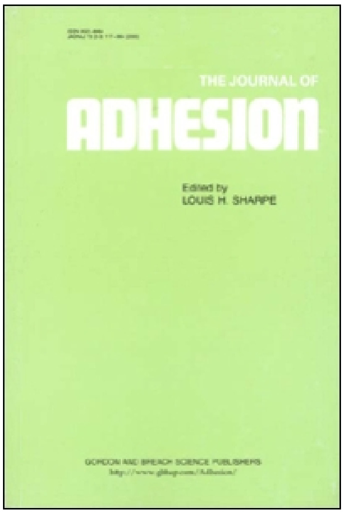
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Improving the Adhesion of Polyethylene by UV Grafting

Huiliang Wang[a]
[a] College of Chemistry, Beijing Normal University, Beijing, China

To cite this Article Wang, Huiliang(2006) 'Improving the Adhesion of Polyethylene by UV Grafting', The Journal of Adhesion, 82: 7, 731 — 745

To link to this Article: DOI: 10.1080/00218460600775815

URL: http://dx.doi.org/10.1080/00218460600775815

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 82:731–745, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460600775815

Improving the Adhesion of Polyethylene by UV Grafting

Huiliang Wang
College of Chemistry, Beijing Normal University, Beijing, China

This article briefly reviews the progress in ultraviolet (UV) or photoinitiated grafting for improving the adhesion property of polyethylene (PE). The first part involves the progress in the fundamental study of UV grafting, including the grafting methods, the photoinitiators, and the self-initiated grafting; the second part focuses on the progress in adhesion improvements of PE by UV grafting, including the auto-adhesion or adhesive free adhesion, the photolamination, and the grafting of reactive functional monomers. The factors affecting the adhesion of grafted PE are also discussed.

Keywords: Adhesion; Grafting; Polyethylene (PE)

Downloaded At: 20:41 21 January 2011

INTRODUCTION

Polyethylene (PE) is a high-tonnage commercial polymer that is produced in a vast range of grades. It has been widely used in many application fields because it has many good properties such as high chemical resistance, high impact strength, and flexibility, with low cost.

Because PE consists of just carbon and hydrogen atoms, it can only interact with other materials by van der Waals bonds; there is no possibility of hydrogen bonding or acid–base interactions. There are no solvents that can dissolve PE at room temperature. It follows also that the surface energy is low, and, without chemical modification of the surface, there is no chance of the strength of interaction with a second material that is required to give good adhesion. In addition, the smooth surface of PE and the presence of a weak boundary layer also prevent the strong adhesion of PE.

Received 9 October 2005; in final form 24 April 2006.

One of a collection of papers honoring Hugh R. Brown, who received *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*, in February 2006.

Address correspondence to Huiliang Wang, College of Chemistry, Beijing Normal University, Beijing 100875, China. E-mail: wanghl@bnu.edu.cn

To obtain a strong and durable adhesion, the surfaces of PE are often treated before bonding. In general, these treatments alter the surface region in one or more of the following ways: removal of a weak boundary layer, change in surface topography, change in chemical nature of the surface, or modification of the physical structure of the surface.

The surface modification methods are commonly categorized as two main groups [1]: 1) surface oxidation such as corona discharge, acid etching, and flame treatment, and 2) surface grafting, including chemical grafting, glow or corona discharge–induced grafting [2], plasma-induced grafting, photoinduced grafting [3], and high-energy radiation-induced grafting [4].

Photoinduced grafting is a useful technique for the modification and functionalization of polymeric materials because of its significant advantages: low cost of operation, mild reaction conditions, easy and controllable introduction of graft chains without affecting the bulk polymer, and long-term stability of the grafted chains. It has been reviewed by many authors [5–7].

This article focuses on the progress in the ultraviolet (UV) grafting modification of PE for adhesion improvement, mainly on the work done by Brown and Wang.

Downloaded At: 20:41 21 January 2011

FUNDAMENTAL STUDY OF UV GRAFTING

Grafting Methods

Photografting methods can be divided into two main categories.

One-Step or Simultaneous Method

Vapor process [8,9], liquid process [10], and continuous process [11–13] are the main traditional one-step processes.

Although the grafting efficiency (GE) (i.e., the amount of grafted polymer of total polymer formed) in the vapor process is high, its grafting rate is slow because of the vapor-phase transfer. It requires minutes or longer times of UV irradiation for complete coverage of the substrate with grafted chains. The grafting rate in the liquid process is also slow, and the grafting efficiency is low as a result of the high homopolymerization conversion ratio. In the continuous process, the grafting reaction is fast because of the efficient liquid transfer of initiator and monomer in the surface layer on the substrate. Complete coverage with grafted chains requires only 5–10 s of UV irradiation. The grafting efficiency is high, normally about 70–80%. The continuous process can be applied to the surface modification of polymeric

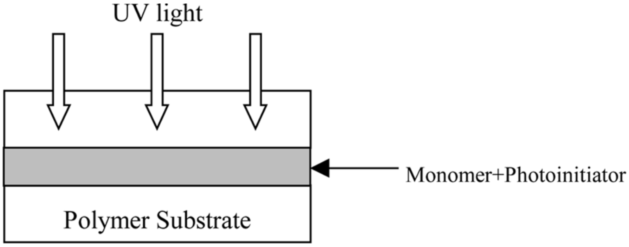


FIGURE 1 Cross section of bulk surface photografting device.

films. These grafting methods are not convenient in industrial applications, because they can only be applied in inert gas (usually in N_2) atmosphere because of the strong inhibition effect of oxygen.

Yang and Ranby [14–18] have developed a bulk (no solvent) surface photografting process, in which a thin layer of an acrylic monomer containing dissolved photoinitiator was sandwiched between the two thin films and then photografted and photopolymerized (Figure 1). Photolamination occurred simultaneously during the photografting process, resulting in good adhesion of the two films. This method can also be used to study the photoinitiation efficiencies of photoinitiators and the grafting and polymerization reactivities of monomers.

Brown and Wang [19] have developed a new one-step UV grafting process. A thin layer of monomer solution containing dissolved photoinitiator was directly coated on polymer substrate and then photopolymerized and photografted. This grafting method is similar to the UV curing of coatings, but the crucial difference between them is that the main reaction in our method is photografting but in curing is photopolymerization.

These two new grafting methods can be applied in air because of the quick consumption of oxygen dissolved in the monomer solution; therefore, the methods may be more industrially applicable.

Downloaded At: 20:41 21 January 2011

Two-Step Method

The two-step grafting method usually involves coating or applying photoinitiator onto polymer surface, and then monomer solution is applied and UV irradiated.

The grafting density and graft polymer chain length are the important microstructure factors affecting the final properties of the graft polymer; however, they are difficult to control in conventional grafting methods. Ma *et al.* developed a novel two-step UV-induced living graft polymerization method [20,21]. In the first step, a surface initiator is formed on a substrate under UV irradiation in the presence of

Downloaded At: 20:41 21 January 2011

benzophenone (BP) solutions; in the second step, the monomers are grafted to the substrate by a living polymerization initiated by the surface photoinitiator. Grafting density and graft polymer chain length can be controlled by choosing the reaction conditions in the first step and in the subsequent step(s) independently. This method may have some potential industrial applications.

Aliphatic Ketones as Photoinitiators for UV Grafting

Benzophenone and its derivatives are the most commonly used photoinitiators for surface photografting [10,14,22,23]. When benzophenone (BP) absorbs a UV photon, it is excited to the short-lifetime singlet state and relaxes to a more stable triplet state. Benzophenone in the triplet state can abstract a hydrogen atom from a polymer substrate with C–H bond(s) and create an active site for surface graft polymerization.

Benzophenone and most of its derivatives are not water soluble; therefore they can only be used in organic solvents, which increases costs and induces environmental problems. This limits the industrial applications of UV grafting. The usage of water-soluble photoinitiators possibly can solve the problems. In recent years, some water-soluble photoinitiators such as (4-benzoyl benzyl) tri-methylammonium chloride, a water-soluble derivative of benzophenone, and anthraquinone-2-sulfonate sodium salt have been developed and used by Geuskens *et al.* to initiate the photografting of acrylamide (AAm) onto the surface of various hydrocarbon polymers or copolymers [24,25]. However, the development of water-soluble photoinitiators seems to be difficult and slow.

The simplest aliphatic ketone (acetone) is one of the most common solvents. It is very cheap in comparison with aromatic ketones and, more important, it is miscible with water. If it can be used as a photoinitiator for UV grafting, it would become the most desirable one for water-borne grafting systems. However, aliphatic ketones, including acetone, are not used as photoinitiators because of their low photoinitiation efficiencies. Yang and Rånby [26] studied the photoinitiation efficiencies of many aromatic and aliphatic ketones and found that the photoinitiation efficiencies of aliphatic ketones were much lower than those of aromatic ketones. Allmer *et al.* [8] reported that acetone could act as both solvent and photoinitiator in the photografting of acrylic acid (AA) onto polyethylene film in a vapor process. Recently, Zhao *et al.* [27] reported the acetone-initiated photografting of methacrylic acid (MAA) onto low-density polyethylene (LDPE) film in a mainly water solvent. Wang and Brown [28,29] reported the

Downloaded At: 20:41 21 January 2011

acetone-initiated photografting of MAA and AA onto high-density polyethylene (HDPE) and the significant difference in the wettabilities between HDPE samples grafted in organic solvents and in acetone/water mixed solvents where acetone acts as solvent and photoinitiator.

Other aliphatic ketones, such as butanone, heptanone, and pentanone, have very similar chemical structures to that of acetone. However, they become less soluble in water with the increasing length of alkyl chain and, hence, cannot be used to initiate photografting carried out in water. These ketones cannot initiate photografting when they are used alone or with organic solvents, either. However, Wang and Brown [30] found that the aliphatic ketones (butanone, pentanone, and heptanone) were able to initiate the photografting of MAA onto HDPE when they were in suitable ketone/water/alcohol mixed solvents. When the volume ratio of ketone was fixed, the grafting of MAA onto HDPE became easier and faster with the increase of the volume ratio of water. The aliphatic ketones have similar, or even higher, photoinitiation efficiencies than aromatic ketones when they are in proper mixed solvents. For example, the extent of grafting of HDPE could reach 4000 $\mu g/cm^2$ after 5 min of UV irradiation in a 1-mol/L MAA solution when 5% butanone/92% H_2O/3% ethanol (volume ratio) was used as the mixed solvent. In fact, when there was only 1% butanone in the mixed solvent, it still had very high photoinitiation efficiency. We also found that aliphatic ketone/water/alcohol mixed system could initiate the grafting of AA and AAm onto HDPE and LDPE.

We discussed the photoinitiation mechanism of aliphatic ketones in the mixed solvents. Very possibly, the hydrogen bond formed between aliphatic ketone and water makes the energy of the excited state of ketone higher and the lifetime of the excited state longer; therefore, self-initiation of aliphatic ketone can take place.

This finding is important because 1) it has broadened the range of photoinitiators for UV grafting from traditional aromatic ketones (mostly benzophenone and its derivatives) to aliphatic ketones; 2) it may have many potential industrial applications, for the significant advantages of aliphatic ketones are their applicability in water-borne systems, their low cost, and their easy recovery; and 3) it may also have some theoretical values for research.

Self-Initiated Grafting

Most acrylic monomers and some other monomers can be polymerized by self-initiation. In recent years, some work has been done on self-initiated grafting. Deng and Yang found that maleic anhydride

(MAH) [31] and styrene [32] could be photografted onto LDPE films in the absence of a photoinitiator.

Wang and Brown [33] found that AA, glycidyl acrylate (GA), and several other acrylic monomers could be photopolymerized and photografted onto HDPE and polypropylene (PP) by self-initiation during photolamination. The self-initiated grafting is different from that initiated by a photoinitiator. Most of the grafting, for two sheets being grafted, takes place on the upper HDPE surface. The adhesion of the sample photolaminated by acrylic monomer without photoinitiator is much weaker than that with photoinitiator. The self-initiation mechanism of these acrylic monomers is possibly by an excitation of the monomer to a triplet state (T_3) with enough energy to abstract hydrogen from the polymer substrate and initiate the grafting.

Yang [34] recently found that methyl methacrylate (MMA) could be photografted readily on an LDPE film surface under UV irradiation when N,N-dimethylformamide (DMF) was used as the solvent without additional photoinitiator. The possible reaction mechanism was based on the photosensitivity of DMF, which induced this photografting polymerization.

These findings may be useful in developing a photoinitiator-free grafting or photopolymerization system.

Downloaded At: 20:41 21 January 2011

ADHESION STUDY

Autoadhesion or Adhesive-Free Adhesion

In most of the reported techniques for improving the adhesion of PE 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.

Uyama, Ikada, *et al.* [35,36] grafted nonionic and ionic water-soluble monomers onto HDPE films by the combination of plasma pretreatment and photoirradiation. 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. The adhesion strength depends on the graft density and the ionic nature of the grafted chains. The surface with larger graft density generally exhibited stronger adhesion when the water present at the interface was dried up. Substantial interaction occurred almost instantaneously upon contact when one surface was grafted with an anionic polymer and the other grafted with a cationic polymer. A lap shear adhesion strength of 90 N/cm^2 was achieved. The interaction

Downloaded At: 20:41 21 January 2011

between similarly charged surfaces was weak in the presence of water, probably because of the electrostatic repulsion operating between the charged groups. Kang *et al.* [37,38] modified the surfaces of LDPE, polytetrafluoroethylene (PTFE), *etc.*, by graft copolymerization with N,N-dimethylacrylamide (DMAA), the Na salt of styrenesulfonic acid (NaSS), 3-dimethyl (methacryloylethyl)ammonium propanesulfonate (DMAPS), and AA. Two grafted surfaces exhibited adhesive-free adhesion or auto-adhesion when brought into contact in the presence of water and subsequently dried. Lap shear adhesion strengths in excess of $90\,\mathrm{N/cm^2}$ were readily achieved between films grafted with the amphoteric DMAPS. Yamada *et al.* [39,40] grafted hydrophilic monomers, such as MAA, AA, 2-dimethylaminoethylmethacrylate (DMAEMA), and methacrylamide (MAAm) onto LDPE and HDPE. The auto-adhesion strength increased with an increase in the wettability and water absorptivity of the grafted plates as well as the temperature and load on heat pressing. For all grafted plates, substrate breaking at auto-adhesion strength measurements was observed for grafted amounts two to three times as much as those at adhesive strength measurements. The substrate breakings for the HDPE and PP plates photografted with AA and DMAEMA, when adhesive strengths were measured, were observed at lower grafted amounts compared with those photografted with MAA.

Previous works on auto-adhesion of PE were done with water-soluble monomers, and water was required as a pasticizer in forming adhesion. Hence, the limitations of this method are that it can only be applied to water-soluble monomers and the bonded polymeric items cannot be used in water or humid environments. To overcome the limitations, Wang and Brown [41] tried to graft some hydrophobic monomers, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), methyl acrylate (MA), and ethyl acrylate (EA), onto an HDPE surface. The grafted polymers are amorphous, and when two grafted surfaces are hot-pressed at a temperature above the glass transition temperature (T_g) of the grafted polymer but below the melting temperature (T_m) of HDPE, good auto-adhesion can be achieved because of the interdiffusion and entanglement of grafted chains. The joining mechanism of the grafted materials under hot-pressing is shown in Figure 2.

The UV-induced grafting of the monomers onto HDPE has been performed at low and high temperature. The grafting temperature is a crucial factor affecting the grafting and the adhesion of grafted PE samples. The grafting reaction was faster at higher temperature, methacrylates grafted more easily than acrylates, and the grafted amount increased with increasing length of the pendant alkyl chain.

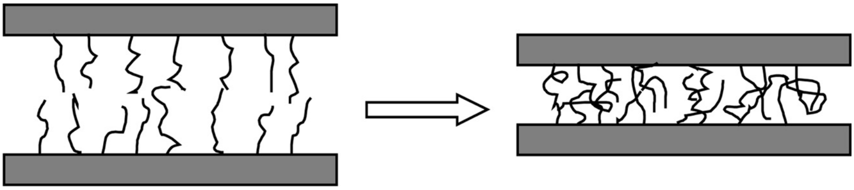


FIGURE 2 Joining mechanism of the grafted materials under hot pressing.

For the samples grafted at lower temperature, the adhesion was very low (less than 50 N/m), even for very thick grafted layers. For the samples grafted at higher temperature, much higher adhesion could be achieved. The presence of homopolymer in the grafted layer decreased the adhesion of PE samples. Higher adhesion could be obtained for the samples washed with organic solvents to remove homopolymers. The adhesion strength also increased with hot-pressing temperature. The highest peel strength (180° T-peel test) of more than 1000 N/m has been obtained.

To achieve strong auto-adhesion of grafted materials, high grafting density is essential. In addition, the grafted chains must be long, because only long grafted chains can interdiffuse and become entangled easily in hot-pressing. Possibly, the grafting density is higher and the grafted chains are longer when the grafting is carried out at high temperature; thus, strong auto-adhesion can be obtained. The low adhesion of the samples grafted at low temperature is attributed to the low grafting density and the short, highly branched grafted chains.

Downloaded At: 20:41 21 January 2011

Photolamination

The bulk surface photografting process developed by Yang and Rånby [14–18] can be used to photolaminate polymer films, and good adhesion can be obtained. This technique can be applied to a wide variety of plastic films, and it gives laminates of high mechanical strength and high and selective barrier properties to different gases and vapors. T-peel tests showed most of the laminates broke inside the substrates rather than the interface failing. The reported apparent peel strength at break for a laminate where both films were 0.188-mm-thick LDPE films was 1050 N/m [42], and for a laminate of two HDPE films 0.04 mm thick was only 290 N/m [16].

Wang, Kang, *et al.* [43,44] reported the photolamination of ozone-pretreated LDPE films *via* UV-induced graft copolymerization with AAm, NaSS, DMAPS, AA, DMAA, and DMAEMA under atmospheric conditions and in the complete absence of an added initiator or oxygen scavenger. The photolamination strengths depend on UV illumination time, monomer concentration, and the chemical nature of the monomer being graft copolymerized. Lap shear photolamination strength of about 90 N/cm^2 could be readily achieved in the LDPE/DMAPS (aq)/LDPE assembly after UV illumination. The failure mode of the photolaminated surfaces was either cohesive or adhesional in nature, depending on the type of monomer used in the photolamination assembly.

In the previous work on photolamination of polymeric films, LDPE rather than HDPE was the commonly used PE grade. HDPE has a surface that is more difficult to graft than the LDPE because of the linear chain structure of HDPE and its higher crystallinity. Wang and Brown [45] found that HDPE could be photolaminated very easily by bulk photografting AA, with very strong adhesion obtained after a short time of UV irradiation and with the adhesion failure mode being PE breakage. In our experiments, much higher apparent peel strengths at break have been obtained because the strips were much thicker. For 0.5-mm HDPE sheets, the peel strength at break was about 5000 N/m; for 1-mm HDPE sheets, it was 9000 N/m; and for 2-mm HDPE sheets, it was about 15000 N/m. Thicker HDPE sheets need longer irradiation time to give strong adhesion. Very good adhesion could be obtained for the HDPE samples photolaminated by AA even when the polymerization conversion and grafting conversion were very low. There was no adhesion at all for the samples photolaminated by MAA or hydroxyethyl methacrylate (HEMA), even when the polymerization conversion and grafting conversion were rather high.

The monomers previously used were usually water-soluble, and acrylic acid was the most effective one. It is likely that the adhesion of polymeric films photolaminated by a water-soluble monomer will become weaker when soaked in water for some time or even when held in a humid atmosphere for a long time. Therefore, we [45] studied the use of a mixture of water-soluble and water-insoluble monomers to form less water-soluble grafted copolymers and, hence to improve the water resistance of photolaminated films. When glycidyl acrylate (GA) was employed alone between the HDPE sheets, the peel strength of the photolaminated HDPE was only about 320 N/m, but when GA or HEMA were cografted together with AA, very good adhesion could be obtained and the water resistance of photolaminated samples was improved.

Yang and Rånby [16] suggested that the lamination method involved the formation of hyperbranched graft macromolecules and a

Downloaded At: 20:41 21 January 2011

cross-linked macromolecular network obtained by adding multifunctional monomers. We [45] have done some work to understand the true adhesion mechanism of photolamination by bulk photografting. The PE sheets joined by acrylic acid could be separated in water and then rejoined to give good adhesion, showing that the main adhesion mechanism is the entanglement of grafted chains, rather than covalent bonds formed by the cross-linking between the grafted chains attached to the two sides (forming a continuous network). We propose that the stronger adhesion is given by a less branched grafted chain structure that permits much more chain entanglement.

The photolamination method has an unavoidable drawback; *i.e.*, it can only be applied to thin and UV transparent films. High-energy irradiation such as gamma irradiation can penetrate thick polymeric materials, no matter whether they are transparent or not. Therefore, if we use high-energy irradiation as the radiation source, then the shortcoming of photolamination can be overcome. Li and Wang [46] developed a new lamination method called *radiation lamination* to laminate polymeric materials by high-energy irradiation-induced bulk grafting. In contrast to the photolamination method, no adhesion could be obtained when AA was used as the monomer to laminate HDPE under γ-irradiation. However, when glycidyl methacrylate (GMA) or the mixture of GMA and AA was used as the monomer(s), very strong adhesion of HDPE could be obtained by γ-radiation lamination.

Downloaded At: 20:41 21 January 2011

Grafting Reactive Functional Monomers

Except for the auto-adhesion and photolamination methods, an adhesive is always necessary for bonding the grafted items. The adhesives can be divided into two categories: reactive and nonreactive. The non-reactive ones can only interact with the grafted polymer chains by van der Waals forces. The reactive ones, can also form chemical bonds with the grafted polymer with a reactive functional group in addition to the van der Waals forces (Figure 3). Chemical bonds are usually much stronger than van der Waals forces; hence, theoretically, the adhesion of samples grafted with reactive monomers and then bonded with a reactive adhesive should be much better than that of samples grafted with nonreactive monomers. Epoxies are among the most widely used two-part reactive adhesives. To graft a monomer, which can react with either of the two parts, onto polymeric materials is possible to obtain good adhesion. The studies based on this idea have been previously carried out by many researchers [43,47,48], but the adhesion of grafted PE was not good enough. When Yamada *et al.* [49,50]

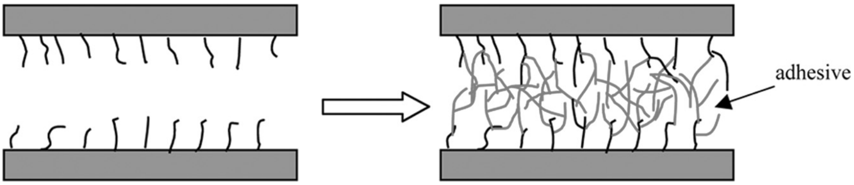


FIGURE 3 Graft reactive multifunctional monomers on PE and then bonded with adhesive.

grafted MAA, AA, methacrylamide (MAAm), and AAm onto PE and then bonded the grafted PE with an epoxy adhesive, the tensile shear adhesive strength increased from 70 psi (0.48 MPa) (pristine PE) to 240 psi (1.65 MPa) (grafted PE). Although the adhesion strength increased more than three times, it was still not satisfactory because the adhesion of untreated PE is too low. In addition, the grafting processes were usually quite complicated, which impedes their industrial applications.

Wang and Brown [19] improved the previous grafting methods and developed a new grafting process. We grafted monomers with an epoxide functional group onto HDPE, and very strong adhesion was obtained. As shown in Figure 4, the adhesion strength of the HDPE samples grafted for 30 s and then bonded with epoxy resin Araldite K106 (Ciba Speciality Chemicals Pty. Ltd., Melbourne, Australia)

Downloaded At: 20:41 21 January 2011

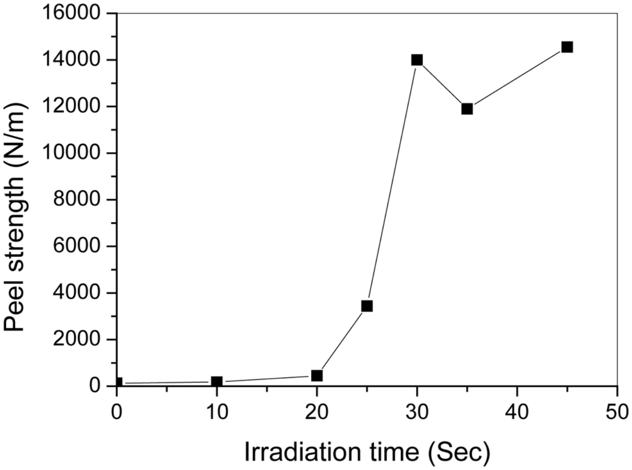


FIGURE 4 Peel strength of grafted PE samples bonded with epoxy resin Araldite K106 as a function of UV irradiation time.

was larger than the mechanical strength of HDPE itself. The HDPE sample (2 mm thick and 2 cm wide) broke in 180° T-peel test and the apparent peel strength at break was more than 14000 N/m.

The bonded HDPE samples had very good long-term stability in NaOH solution (pH 14), outdoor weathering, temperature cycling, *etc*.

This technology has many advantages, such as easy and fast processing, low monomer consumption and low cost, and high practicality, over other methods. This technique can also be used for the surface modification of other polymeric materials and for other purposes.

Factors Affecting the Adhesion of Grafted PE

The surface properties of grafted polymer have no direct relation with the amount of grafts, but do with the grafting density, the microstructure, and the morphology of grafted chains. No good adhesion could be obtained in the former work even when the same monomers as we [19] used were grafted onto PE. In our work, we also found that when the same amount of the same monomer was grafted onto PE at different conditions, the adhesion of the grafted PE samples was quite different. Some had very strong adhesion, but some had very weak or even no adhesion. This implies that the microstructure of grafted chains has a decisive effect on the final property of the grafted surface.

For the surface-grafting modification intended to improve the adhesion of polymeric materials, the crucial factors affecting the adhesion property of grafted polymers are possibly the grafting density and the length and branching of the grafted chain. The adhesion is proportional to the grafting density. By one calculation, one grafted chain on per 1-nm^2 area is necessary for obtaining strong adhesion. Long, less-branched grafted chains are easier to diffuse into and to become entangled with an adhesive, and they more easily react with adhesive if they both are chemically reactive.

However, unfortunately, there is still not a direct method to characterize the microstructure of grafted polymers. Wang and Brown [51] studied the initial stage of the grafting of GMA, carried out in different solvents, with atomic force microscopy (AFM). A highly branched (or superbranched) microstructure (Figure 5a) was believed to be the main structure of the grafted polymer chains obtained in the grafting carried out in the solvents. This is, very possibly, the true reason for the poor adhesion of the grafted samples. On the contrary, to obtain good adhesion, the grafted polymer should have a microstructure, as shown in Figure 5b, of high grafting density and long, less branched grafted chains.

Downloaded At: 20:41 21 January 2011

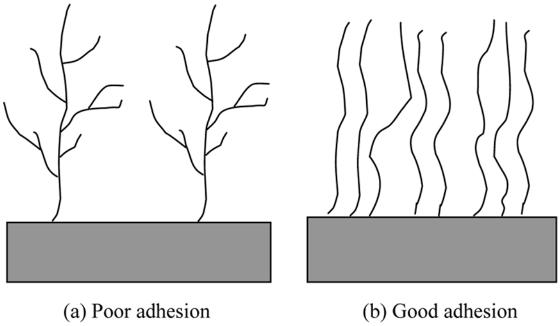


FIGURE 5 Proposed microstructures of the grafted chains.

Downloaded At: 20:41 21 January 2011

CONCLUSIONS

UV or photoinitiated grafting has become a powerful technique for the modification and functionalization of polymeric materials because of its significant advantages. The fundamental study of UV grafting and its applications in many fields has drawn a lot of attention. This article reviews some of the recent progresses in both areas.

In recent years, some new and more industrially applicable UV grafting methods have been developed. Some water-soluble photoinitiators or photo initiating systems (*e.g.*, a aliphatic ketone/water/alcohol mixed system) were developed or discovered and used in UV grafting. Therefore, it is possible to develop more environmentally friendly UV grafting methods. Some monomers such as maleic anhydride, styrene, and some (meth)acrylates were found to be photograftable onto polymer substrates by self-initiation.

Improvement of the adhesion properties of polyolefins, especially polyethylene (PE), is one of UV grafting's most important applications. An adhesive is usually necessary for bonding the grafted samples in most of the previously reported techniques. However, in recent years, some adhesive-free or auto-adhesion methods with hydrophilic and hydrophobic monomers have been developed. The auto-adhesion comes from the entanglement and/or the electrostatic attraction (when ionic monomers are used) of the grafted chains through their self-diffusion, when the two grafted polymer plates are forced into contact and hot-pressed without an adhesive. Photolamination of PE and other polymer substrates by bulk surface photografting is a convenient way to obtain strong adhesion for thin films and thicker sheets. We grafted monomers with an epoxide functional group onto HDPE and obtained very strong adhesion with a new grafting process.

The grafting density, the microstructure, and the morphology, *inter alia*, of grafted chains affect the final adhesion properties of the grafted polymer substrate. Very possibly, to obtain good adhesion, the grafted polymer should have a microstructure of high grafting density and long, less-branched grafted chains.

REFERENCES

[1] Bergbreiter, D. E., *Prog. Polym. Sci.* **19**(3), 529–560 (1994).

[2] Lei, J. X., Liao, X., and Gao, J., *J. Adhes. Sci. Technol.* **15**(8), 993–999 (2001).

[3] Wu, J. Z., Kang, E. T., Neoh, K. G., Wu, P. L., and Liaw, D. J., *J. Appl. Polym. Sci.* **80**(9), 1526–1534 (2001).

[4] Bucio, E., Cedillo, G., Burillo, G., and Ogawa, T., *Polym. Bull. (Berlin, Ger.)* **46**(1), 115–121 (2001).

[5] Chan, C. M., *Polymer Surface Modification and Characterization* (Hanser Publishers, Munich/Vienna/New York, 1994).

[6] Bhattacharya, A. and Misra, B. N., *Prog. Polym. Sci.* **29**(8), 767–814 (2004).

[7] Kato, K., Uchida, E., Kang, E. T., Uyama, Y., and Ikada, Y., *Prog. Polym. Sci.* **28**(2), 209–259 (2003).

[8] Allmer, K., Hult, A., and Ranby, B., *J. Polym. Sci. Pol. Chem.* **26**(8), 2099–2111 (1988).

[9] Gao, J., Lei, J. X., Su, Z. J., Zhang, B. S., and Wang, J., *Polym. J.* **33**(2), 147–149 (2001).

[10] Decker, C. and Zahouily, K., *Macromol. Symp.* **129**, 99–108 (1998).

[11] Zhang, P. Y. and Ranby, B., *J. Appl. Polym. Sci.* **40**(9–10), 1647–1661 (1990).

[12] Zhang, P. Y. and Ranby, B., *J. Appl. Polym. Sci.* **43**, 621–636 (1991).

[13] Zhang, P. Y. and Ranby, B., *J. Appl. Polym. Sci.* **41**(7–8), 1459–1467 (1990).

[14] Yang, W. T. and Ranby, B., *J. Appl. Polym. Sci.* **62**(3), 533–540 (1996).

[15] Yang, W. T. and Ranby, B., *J. Appl. Polym. Sci.* **62**(3), 545–555 (1996).

[16] Yang, W. T. and Ranby, B., *J. Appl. Polym. Sci.* **63**(13), 1723–1732 (1997).

[17] Ranby, B., Yang, W. T., and Tretinnikov, O., *Nucl. Instrum. Meth. Phys. Res., B* **151**(1–4), 301–305 (1999).

[18] Ranby, B., *Int. J. Adhes. Adhes.* **19**(5), 337–343 (1999).

[19] Brown, H. R. and Wang, H. L., Australiasia Patents Application No. 2004904655 (2004).

[20] Ma, H. M., Davis, R. H., and Bowman, C. N., *Macromolecules* **33**(2), 331–335 (2000).

[21] Ma, H., Davis, R. H., and Bowman, C. N., *Polymer* **42**(20), 8333–8338 (2001).

[22] Lei, J. X., Gao, J., Zhou, R., Zhang, B. S., and Wang, J., *Polym. Int.* **49**(11), 1492–1495 (2000).

[23] Kubota, H., *J. Appl. Polym. Sci.* **48**(10), 1717–1721 (1993).

[24] Ruckert, D. and Geuskens, G., *Europ. Polym. J.* **32**(2), 201–208 (1996).

[25] Geuskens, G., Etoc, A., and Di Michele, P., *Europ. Polym. J.* **36**(2), 265–271 (2000).

[26] Yang, W. T. and Ranby, B., *Europ. Polym. J.* **35**(8), 1557–1568 (1999).

[27] Zhao, L. Q., Irwan, G. S., Kondo, T., and Kubota, H., *Europ. Polym. J.* **36**(8), 1591–1595 (2000).

[28] Wang, H. L. and Brown, H. R., *J. Polym. Sci. Pol. Chem.* **42**(2), 253–262 (2004).

[29] Wang, H. L. and Brown, H. R., *J. Polym. Sci. Pol. Chem.* **42**(2), 263–270 (2004).

[30] Wang, H. L. and Brown, H. R., *Macromol. Rapid Commun.* **25**(13), 1257–1262 (2004).

Downloaded At: 20:41 21 January 2011

[31] Deng, J. P. and Yang, W. T., *J. Polym. Sci. Pol. Chem.* **39**(19), 3246–3249 (2001).

[32] Deng, J. P., Yang, W. T., and Ranby, B., *Macromol. Rapid Commun.* **22**(7), 535–538 (2001).

[33] Wang, H. L. and Brown, H. R., *Macromol. Rapid Commun.* **25**(11), 1095–1099 (2004).

[34] Yang, P., Deng, J. P., Yang, W. T., and Yang, P., *Macromol. Chem. Phys.* **205**(8), 1096–1102 (2004).

[35] Chen, K. S., Uyama, Y., and Ikada, Y., *Langmuir* **10**(4), 1319–1322 (1994).

[36] Zhang, J. F., Uchida, E., Uyama, Y., and Ikada, Y., *Langmuir* **11**(5), 1688–1692 (1995).

[37] Kang, E. T., Neoh, K. G., Li, Z. F., Tan, K. L., and Liaw, D. J., *Polymer* **39**(12), 2429–2436 (1998).

[38] Kang, E. T., Shi, J. L., Neoh, K. G., Tan, K. L., and Liaw, D. J., *J. Polym. Sci. Pol. Chem.* **36**(17), 3107–3114 (1998).

[39] Yamada, K. and Hirata, M., *Polymer Preprints* **42**(2), 757–758 (2001).

[40] Yamada, K., Kimura, J., and Hirata, M., *J. Appl. Polym. Sci.* **87**(14), 2244–2252 (2003).

[41] Wang, H. L. and Brown, H. R., *J. Adhes.* **79**(10), 955–971 (2003).

[42] Ranby, B., *Int. J. Adhes. Adhes.* **19**(5), 337–343 (1999).

[43] Wang, T., Lim, W. P., Kang, E. T., Neoh, K. G., Fuh, J. Y. H., Lu, L., and Nee, A. Y. C., *J. Adhes. Sci. Technol.* **11**(9), 1211–1227 (1997).

[44] Wang, T., Kang, E. T., Neoh, K. G., Tan, K. L., and Liaw, D. J., *Langmuir* **14**(4), 921–927 (1998).

[45] Wang, H. L. and Brown, H. R., *J. Appl. Polym. Sci.* **97**(3), 1097–1106 (2005).

[46] Li, Z. R. and Wang, I. L., *J. Appl. Polym. Sci.* **96**(3), 772–779 (2005).

[47] Feng, Z. and Ranby, B., *Angew. Makromol. Chem.* **195**, 17–33 (1992).

[48] Wang, T., Kang, E. T., Neoh, K. G., Tan, K. L., Cui, C. Q., and Lim, T. B., *J. Adhes. Sci. Technol.* **11**(5), 679–693 (1997).

[49] Yamada, K., Kimura, T., Tsutaya, H., and Hirata, M., *J. Appl. Polym. Sci.* **44**(6), 993–1001 (1992).

[50] Yamada, K., Tsutaya, H., Tatekawa, S., and Hirata, M., *J. Appl. Polym. Sci.* **46**(6), 1065–1085 (1992).

[51] Wang, H. L. and Brown, H. R., *Macromolecules*, to be submitted.

Downloaded At: 20:41 21 January 2011