# Peroxide-Initiated Grafting of Acrylamide on to Polyethylene Surfaces

K. KILDAL,* K. OLAFSEN,† and A. STORI

Senter for Industriforskning, Box 124 Blindern, N-0314 OSLO 3, Norway

## SYNOPSIS

Acrylamide has been grafted onto the surface of a polyethylene film with the aid of a peroxide initiator (tert-butyl peroxyneodecanoate). The peroxide was first swollen into the film from cyclohexane solution; the film was then dried under reduced pressure at room temperature. Excess initiator, adsorbed on the surface, was washed off with acetone. The grafting reaction was carried out by placing the film in a boiling solution of the monomer in water. After grafting, the film was extracted with water to remove monomers and homopolymer. The grafted films were characterized by infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), gravimetric measurements, and contact angle measurements. The graft yield was found to increase with reaction time up to about 5–15 min and thereafter level off. The presence of air was found to retard the grafting reaction. Increase in monomer concentration gave an almost continuous increase in graft yield, but high concentrations were not necessary to cover the surface of the film with polyacrylamide. This grafting has been found to function, but the process requires further development to reduce the total grafting time before it can be used commercially.

## INTRODUCTION

Polyolefins have relatively inert, hydrophobic surfaces. There is therefore much interest in the modification of such surfaces to create more hydrophilic and/or functionalized surfaces. Modified polymer surfaces have a number of applications, e.g., adhesion improvement for lacquers, inks, and adhesives,[1] better adhesion to inorganic substances such as aluminum,[2] and for biocompatibility.[3]

Several different methods may be used for surface modification, e.g., oxidation by chromic acid, flame, or corona discharge,[1] plasma treatment,[4] and surface grafting of polar monomers.[5-11] This paper describes a novel method for surface grafting on polyethylene.

Surface grafting may proceed by a free radical mechanism where the free radicals abstract hydrogen atoms from the polymer. Macroradicals are then formed, and these radicals can act as grafting sites for vinyl functional monomers. Free radicals can be generated by several different methods, e.g., UV[5] or γ-radiation,[6] Ce^{4+} ions,[7] or peroxide initiators. To our knowledge, only a few articles have previously been published where peroxides have been used to initiate surface grafting.[8-11] Our aim has been to study peroxide-initiated grafting as an alternative to the other methods mentioned and to find a reaction process that gives high graft yields without large amounts of homopolymer formed on the surface or in the reaction bath. One advantage with peroxide-initiated grafting is that no special equipment is needed: Only heating is necessary to facilitate a grafting reaction. Our intention has also been to study how different reaction parameters as reaction time, monomer concentration, absence of inert atmosphere, etc., influences the grafting reaction and yield. With knowledge about what parameters are important for the graft yield, the reaction may be optimized.

## EXPERIMENTAL

### Materials

The film used was a low-density polyethylene (PE, L 400 from Statoil, Norway, thickness 125 $\mu$m). The

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* Current address: NIOM-Scandinavian Institute of Dental Materials, Kirkeveien 71 B, N-1344 Haslum, Norway.

† To whom correspondence should be addressed.

film did not contain any stabilizer. Before use, the film samples were cleaned in an ultrasonic bath in a mixture of 50/50 water and ethanol, washed with distilled water, and dried at atmospheric pressure. Solvents used were cyclohexane P.A., acetone P.A. from Merck A.G., 96% ethanol from A/S Vinmonopolet, and distilled water. The monomer used was acrylamide, 97%, from Janssen Chimica. The peroxide initiator was *tert*-butyl peroxyneodecanoate (Trigonox 23-C 75 from Akzo Chemie). Solvents, monomer, and peroxide initiator were used as received without further purification.

## Graft Polymerization

After cleaning and drying, the film samples were immersed in a solution of 4 wt % peroxide initiator in cyclohexane at room temperature. The immersion time was 1 h. After swelling the initiator into the film samples, they were dried under reduced pressure at room temperature. The film surface was then washed with acetone to remove excess initiator adsorbed on the surface. To carry out the graft polymerization, the film samples were transferred to the reaction vessel and boiled under reflux in an aqueous monomer solution. Unreacted monomer and homopolymer were removed by Soxhlet extraction with water as the solvent. Finally (after drying the film samples), surface analyses were carried out.

## Surface Analysis

XPS measurements were conducted with a Vacuum Generators Microlab 3 spectrometer. IR measurements were made with a Nicolet 5 SX FTIR spectrometer using ATR equipment with a KRS-5 prism (from Spectratec). Contact angle measurements were made with a NRC contact angle goniometer model 100-00 from Ramé-Hart at ambient humidity and temperature. The scanning electron microscope used was a Jeol JSM-840.

## Gravimetric Measurements

Grafted polymer on PE films was quantified by weighing the film before reaction and after polymerization (after extraction and drying). The homopolymer generated in solution was quantified gravimetrically after precipitation with acetone. The graft yield ($\Delta M$) and monomer conversion ($MC$) were calculated according to the following equations:

$$\Delta M = (M_2 - M_1)/M_1 \cdot 100$$

$$MC = (M_3 - M_4)/M_3 \cdot 100$$

where $M_1$ is PE film mass before grafting, $M_2$ is PE film mass after grafting, $M_3$ is monomer mass, and $M_4$ is homopolymer mass.

## RESULTS AND DISCUSSION

### The Reaction Principle

An organic peroxide is thermally unstable. At elevated temperatures, the oxygen–oxygen bond of the peroxide is homolytically cleaved to form radicals. The radicals formed may abstract hydrogen atoms from the polymer, and macroradicals are thereby formed. The hydrogen abstraction will preferably take place at tertiary carbon atoms (branch points in PE).[12] These macroradicals may act as grafting sites for vinyl monomers. In addition, different types of side reactions can occur, i.e., cross-linking of the polymer, degradation of the polymer, reaction of the radicals with oxygen (this will be discussed later), and transfer of radical to monomer—hence, homopolymerization. The peroxide used in these studies is a peroxy ester with a half-life of 76 s at the reaction temperature of 100°C.[13]

### Solvent Effect on Grafting

Our aim in this study was to modify the surface of PE without modifying the bulk material. It is therefore important to localize the initiator and the monomer such that grafting occurs only in the outermost surface layer of the polymer. This concept is discussed in a paper by Tazuke et al.[14] Tazuke et al. performed photografting with the monomer solution in contact with the polymer surface. They concluded that if the interaction between the solvent and the polymer film was small, grafting would preferentially occur on the film surface. If the interaction between the solvent and the polymer film is strong, grafting will preferentially occur below the surface. In our case, the solvent is water, with very small interactions with the PE. In addition, the water-insoluble peroxide is preswelled into the polymer and the monomer is in an aqueous solution. Grafting should therefore preferentially take place on the surface of the polymer. A similar technique has recently been used for grafting acrylic acid onto PET.[11]

With acrylamide, the monomer and the grafted chains are water-soluble. This is advantageous because it will assist the growing of the grafted chains outside the PE surface. Homopolymerization can occur by chain transfer from grafted chain to monomer or by migration of radical fragments from the peroxide in the film into the solution. Migration of

initiator fragments out into the solution is expected to be minimal because of low solubility of initiator in water. The degree and depth of cross-linking of the PE is determined by the solvent, concentration of peroxide, and time of swelling of the peroxide.

### Effect of Extraction Time

As mentioned earlier, the grafted films were extracted with water in order to remove unreacted monomer and homopolymer. The effect of extraction time was followed by IR measurements. It was found that the signal from polyacrylamide stayed at an approximately constant level for films extracted from 1 to 24 h. The IR spectra of film before extraction showed a larger signal from polyacrylamide, with additional signals from unreacted monomer. These results show that not all polyacrylamide can be removed from the film surface by extraction with hot water. Although this is not conclusive evidence for covalently bonded polyacrylamide to the PE film surface, we take these results as a strong indication for a successful grafting reaction. The results also indicate that unreacted monomer and homopolymer can be removed from the film's surface with 1 h of extraction. All films used in this study were extracted for at least 3 h.

### Effect of Reaction Time on Graft Yield

In Figure 1, the contact angle and nitrogen content on the surface (nitrogen from acrylamide as measured by XPS) as a function of reaction time for films grafted in 3 wt % acrylamide solution are shown. The trend is that the contact angle decreases rapidly up to 5 min reaction time (from 90° to 30°)

and thereafter holds this value up to 60 min reaction time. The nitrogen content on the surface shows the same trend as for contact angle measurements, i.e., rapid increase in grafting yield up to 5 min and thereafter a leveling off. An XPS spectra was also taken of a pure polyacrylamide film. The measured nitrogen content on the surface of this film was 17 atom %. The nitrogen content on the surface of the grafted films levels off around 16 atom %, indicating a PE surface almost completely covered by grafted polyacrylamide.

The effect of reaction time was also studied by IR measurements. The absorbance (peak height) from polyacrylamide (Abs. 1670) relative to IR absorbance from PE (Abs. 1470) was studied. These measurements showed a saturation tendency of the relative absorbance after about 5 min reaction time. This is the same as was observed by XPS measurements.

The results from the gravimetric studies from this experiment is shown in Figure 2 where $\Delta M$ is plotted as a function of reaction time. It is interesting to note that $\Delta M$ levels off after around 5–15 min reaction time.

The results from XPS, IR, and contact-angle measurements indicate that the graft yield levels off after around 5 min reaction time. In addition, the XPS and IR measurements indicate an almost total coverage of the surface. The results from the gravimetric studies show a leveling-off after a little longer reaction time (between 5 and 15 min). This is because, unlike XPS and IR, the gravimetric technique is not surface-sensitive, i.e., an increase in graft yield can be observed even if the surface is completely covered by polyacrylamide. The leveling-off can be explained by the exhaustion of the per-
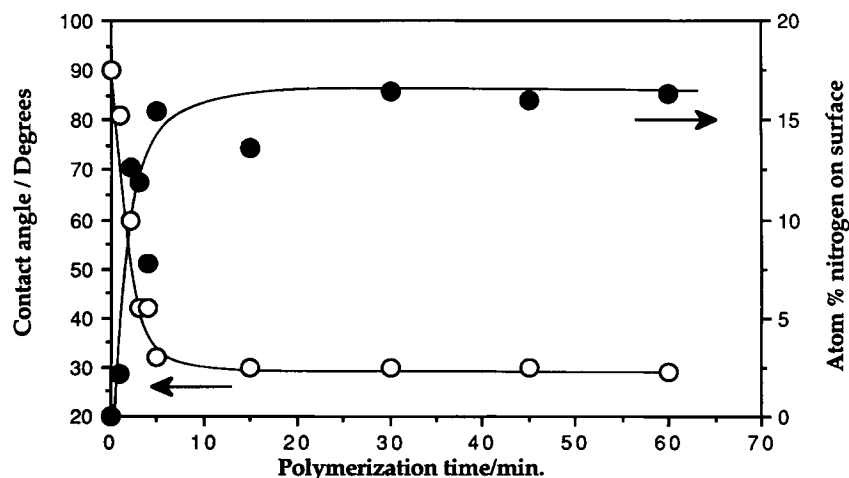


**Figure 1** Contact angle and atom % nitrogen as a function of polymerization time for a film suspended in 3 wt % aqueous solution of acrylamide at 100°C.
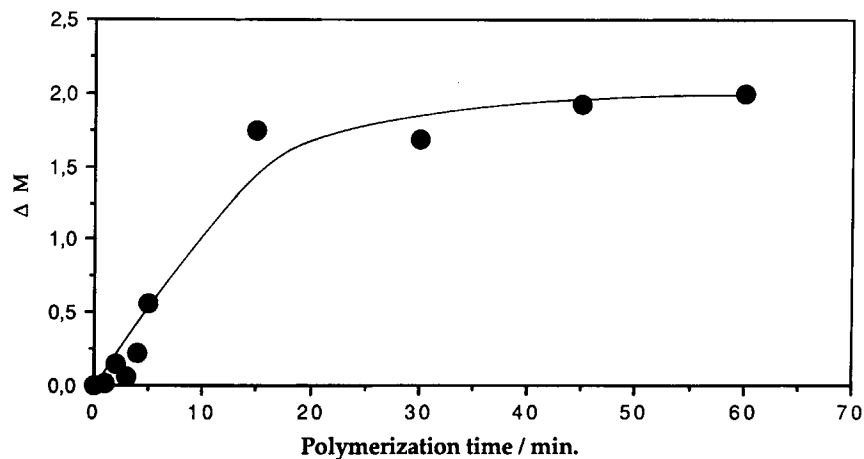
**Figure 2** Graft yield ($\Delta M$) as a function of polymerization time for a film suspended in 3 wt % aqueous solution of acrylamide at 100°C.

oxide supply. Ten minutes corresponds to approximately eight times the half-life of the peroxide; thus, no new grafting sites are generated.

### Effect of Oxygen on Graft Yield

It is well known that oxygen can act as a radical scavenger and thereby retard the graft polymerization reaction.[14] An experiment was therefore performed to study the effect of oxygen on graft yield. The experiment was performed in the same way as described above except that air was used in place of nitrogen. The contact angle, IR, and XPS measurements indicate that no grafting reaction occurs up to 5 min reaction time; the graft yield thereafter increases rapidly up to 15 min reaction time and then levels off.

### Effect of Monomer Concentration

Figure 3 shows the contact angle and nitrogen content on the surface as measured by XPS for grafting reactions with different monomer concentrations. The reaction time was 3 min. The results from XPS and contact angle measurements show an increase in graft yield up to 5% monomer and, thereafter, a leveling-off. Relative IR absorbance measurements showed a continuous increase over the whole concentration range, possibly a slight leveling-off tendency at the highest concentrations.

Figure 4 shows the weight increase of grafted films as a function of monomer concentration. The reaction conditions were as described above. The results from these measurements support the results from IR analysis, i.e., a continuous increase in graft yield with increasing monomer concentration. The
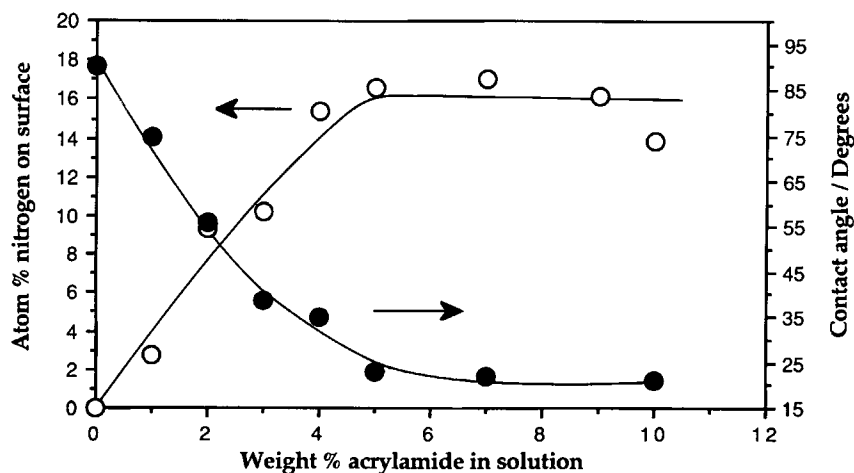


**Figure 3** Contact angle and atom % nitrogen as a function of acrylamide concentration in aqueous solution for films reacted 3 min at 100°C.
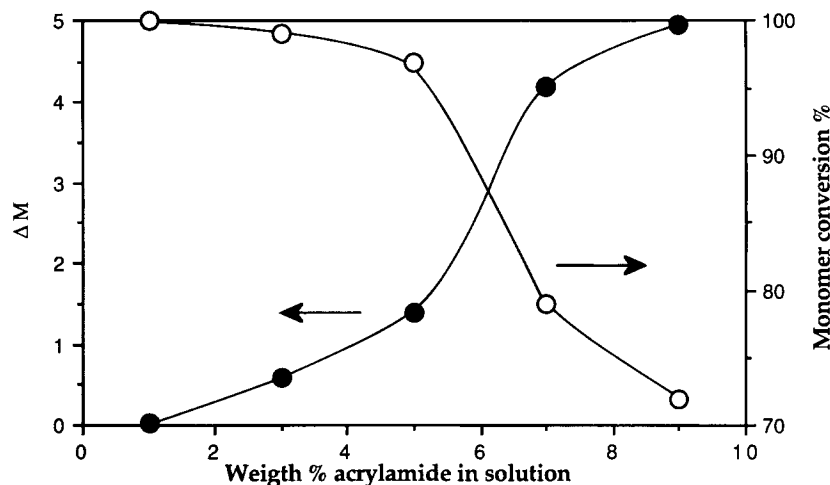
**Figure 4**  Monomer conversion and graft yield ($\Delta M$) as a function of acrylamide concentration in aqueous solution for films reacted 3 min at 100°C.

resolution of this gravimetric technique makes it unsuited for the study of the initial stages of the reaction. The conclusion from these results is that from a monomer concentration of 5% and higher the PE surface is almost completely covered by polyacrylamide although the graft yield increases over the whole concentration range. The results also indicate that the thickness of the grafted layer is above the depth of analysis for XPS ($\sim$ 50 Å).

In connection with the variation in monomer concentration, the reaction mixture was analyzed to establish the amount of homopolymer formed. As can be seen from Figure 4, low levels of homopolymer are formed at monomer concentrations up to 5%; at higher monomer concentrations, a marked increase in homopolymerization is observed. Homopolymerization is unwanted for our purpose. However, as shown already, high monomer concentrations are not needed to achieve a PE surface covered by polyacrylamide.

### Homogeneity of Grafted Surfaces

Figure 5(a) and (b) show scanning electron micrographs (SEM) of an untreated PE surface and a film surface reacted for 3 min in 9 wt % acrylamide, respectively. The second micrograph is typical for all the grafted samples. All display an apparently homogeneous surface.

## CONCLUDING REMARKS

A method using peroxides to achieve grafting of acrylamide onto a PE surface has been studied. This
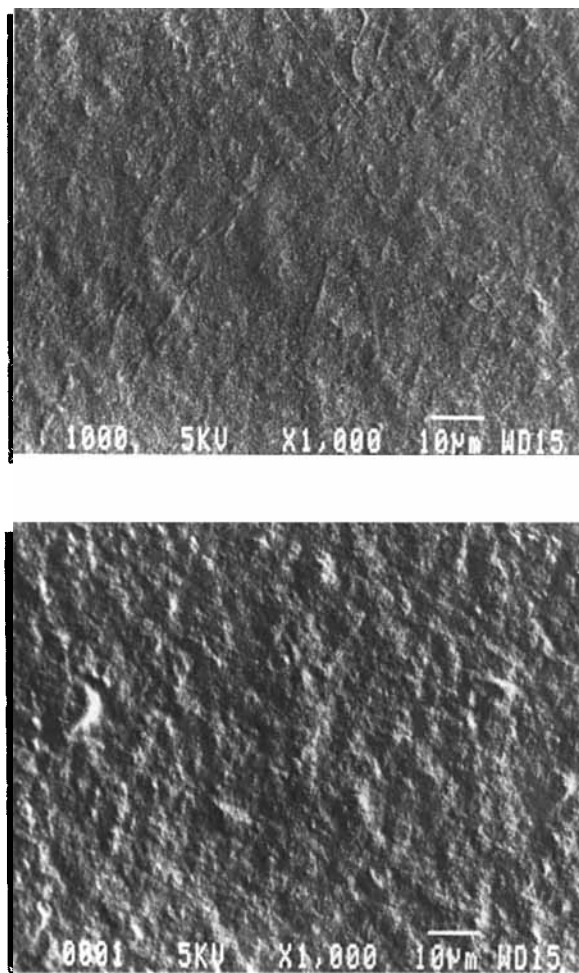




**Figure 5**  (a) SEM micrograph of an untreaded PE surface. (b) SEM micrograph of a PE surface grafted in 9 wt % aqueous solution of acrylamide for 3 min.

surface modification technique has been shown to function but the process is too protracted for all but special low-volume production. The method is relatively simple and high levels of grafting are obtained after only a few minutes' reaction time. It should be possible to further simplify the reaction procedure by finding a peroxide with a shorter half-life, by decreasing the swelling time of the initiator into the film surface, etc. When using relatively low monomer concentrations, only negligible amounts of homopolymer are formed. As a consequence of the use of water as a solvent and the hydrophobic nature of the PE substrate, grafting is limited to the outermost surface of the polymer. Relatively high graft yields are observed even though water does not wet the PE surface.

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