

Grafting of Acrylic Acid onto Corona-Treated Polyethylene Surfaces

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SYNOPSIS

Peroxides formed on the surface by corona treatment of low-density polyethylene film can be used to initiate grafting of polar vinyl monomers such as acrylic acid. Different types of peroxides are probably formed on the surface, but at least hydroperoxides could be detected by XPS analysis. The grafting reaction was carried out directly after corona treatment, by placing the corona-treated film above a solution of acrylic acid heated to 100°C. The grafting reaction takes place in a vapor phase of the monomer. After extracting the reacted films with hot methanol and drying, surface analysis by XPS, IR, and contact angle measurements were carried out. Effect of degree of corona treatment and reaction time have been studied. The conclusion from this work is that acrylic acid in vapor phase can successfully be grafted onto corona-treated polyethylene film by this method. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

There is much interest in the modification of polyolefin surfaces. Such surfaces are inert and hydrophobic and need to be made more hydrophilic to, e.g., improve printability, paintability, or adhesion to adhesives or inorganic substances. Traditionally, surface oxidation with flame or corona treatment has been used extensively for industrial purposes. The advantage with these kind of treatments is that they can be carried out with high speed in continuous industrial processes. On the other hand, the disadvantage with corona and flame treatment is the limited control of the process.

The surface grafting of polar monomers gives better possibilities for controlling which chemical groups are introduced on a surface. Among several methods, peroxides can be used to initiate surface grafting.¹⁻³ In a recent work⁴ we demonstrated that acrylamide could be grafted onto a polyethylene surface with the aid of an organic peroxide swelled into the surface. Iwata et al.⁵ showed that it was

possible to use the peroxides formed on a polyethylene surface during corona treatment to initiate grafting of acrylamide in aqueous solution. Several studies have shown that grafting of polymer surfaces with the monomer in vapor phase could be performed successfully with UV initiation^{6,7} and argon gas plasma.⁸

The present method for surface grafting has several advantages compared with the method described in our recent work.⁴ The main advantage is the avoidance of time-consuming swelling of the peroxide into the film prior to grafting. The peroxides formed by corona treatment are probably formed only on the outermost surface of the polymer film, limiting the grafting only to the surface.

EXPERIMENTAL

Materials

The polymer film used for these studies was a low-density polyethylene quality from Statoil, Norway (L 400 without stabilizer, thickness 125 μm). Before corona treatment 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. The monomer used was acrylic acid 99%, stabilized with 220 ppm MeHQ

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Journal of Applied Polymer Science, Vol. 46, 1673-1676 (1992)

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CCC 0021-8995/92/091673-04

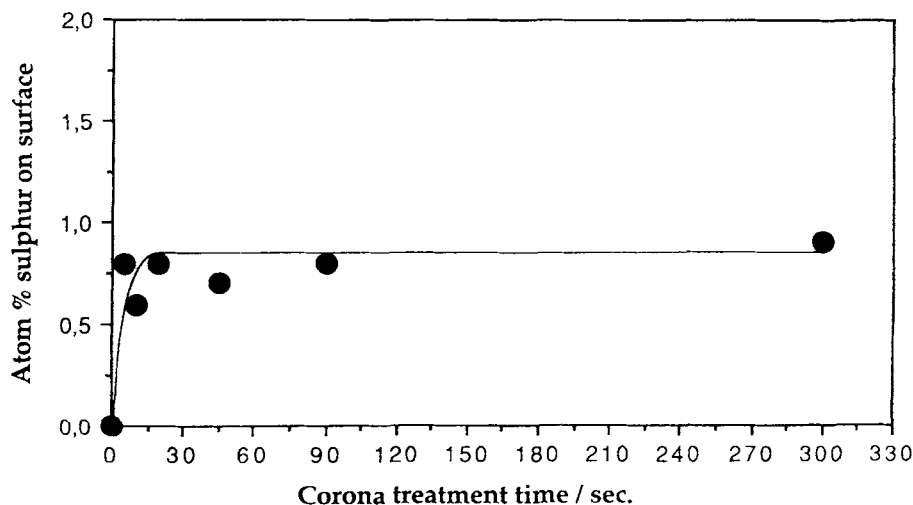


Figure 1 Atom percent sulfur on surface as a function of corona treatment time for films reacted with SO_2 .

from Janssen Chimica. Solvents used were methanol P.A. from Merck A.G., ethanol 96% from A/S Vinmonopolet, and distilled water. Sulfur dioxide (SO_2) 98.98% was from Messer Griesheim. Monomer, solvents, and SO_2 were used as received without further purification.

Corona Treatment

The corona treatment apparatus used for these experiments was a Viktor 30 K 500 with a gap potential of 15 kV. The polyethylene film was fastened around motor-driven rollers of diameter 63 mm. All experiments were carried out with a constant rate of 150

rpm. The treatment time was varied from 5 s to 60 min. All runs were performed at ambient temperature and atmosphere.

Derivatization of Hydroperoxide Groups for XPS Analysis

Derivatization of hydroperoxide groups on the film surface after corona treatment was carried out according to the method described by Gerenser et al.⁹ Film samples were exposed to an atmosphere of SO_2 for 5 min followed by 30 s washing with distilled water. The time between corona treatment and the derivatization was 2 min.

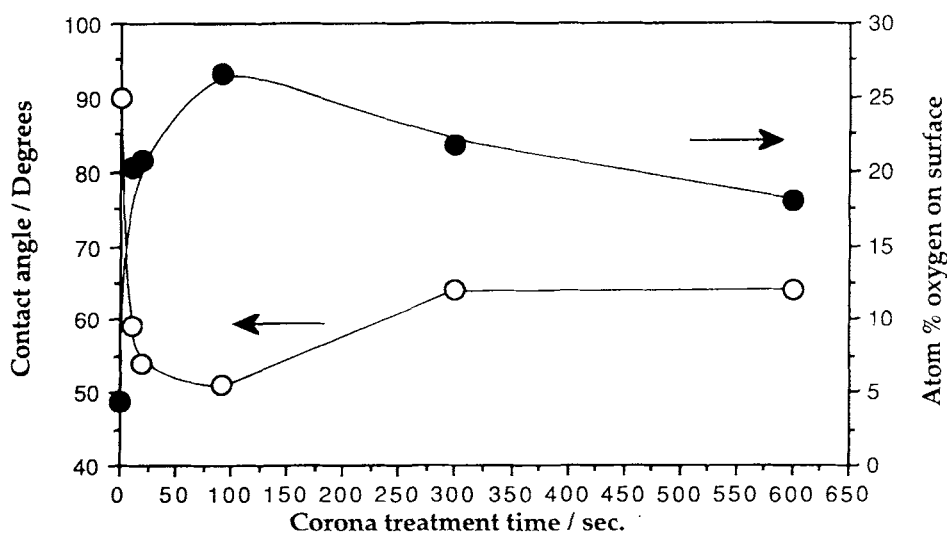


Figure 2 Contact angle and atom percent oxygen on surface as a function of corona treatment time for films reacted 10 min in acrylic acid vapor.

Graft Polymerization

The film samples were placed in the vapor phase above a 50/50 mixture of water and acrylic acid at 95°C. Oxygen was eliminated from the reaction vessel with aid of a nitrogen purge. At the end of the polymerization the film samples were extracted with methanol for 24 h in a Soxhlet extractor.

Surface Analysis

XPS measurements were conducted with a Vacuum Generators Microlab 3 spectrometer. IR measurements were carried out with a Perkin-Elmer 1725 X together with an Attenuated Total Reflection

(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, Inc., at ambient humidity and temperature.

RESULTS AND DISCUSSION

Derivatization of Hydroperoxide Groups

Figure 1 shows the atom percent sulfur after derivatization of a polyethylene (PE) surface, as measured by XPS, as a function of corona treatment time. The sulfur content on the surface stays nearly

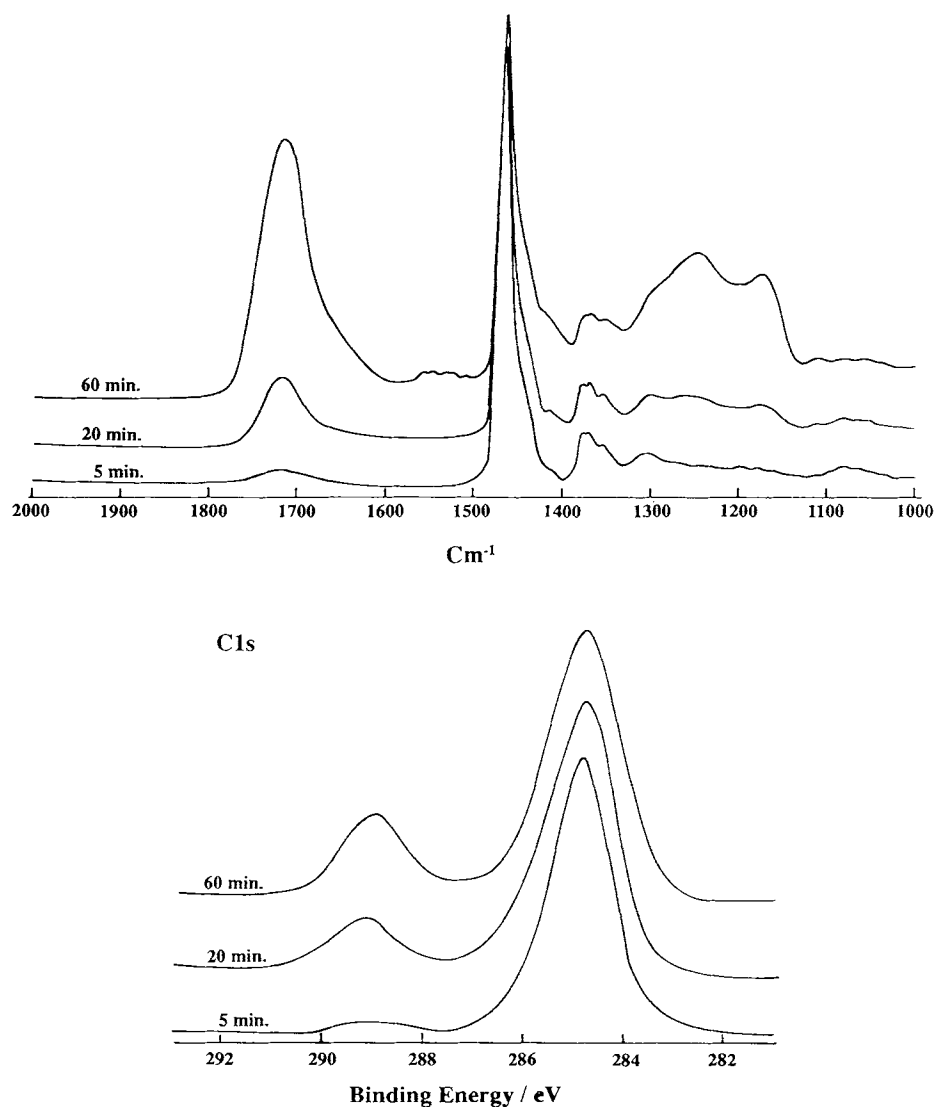


Figure 3 (a) IR spectra of films reacted different times in acrylic acid vapor. The corona treatment time was 90 s. (b) XPS spectra of films reacted different times in acrylic acid vapor. The corona treatment time was 90 s.

constant up to a treatment time of 5 min, indicating that the amount of hydroperoxides on the surface is constant. A constant hydroperoxide level is not unexpected as oxidation to hydroperoxide is just the first step in the oxidation process.¹⁰ Further exposure to the corona converts the hydroperoxide to carbonyl/carboxylic acids. Hydroperoxides are just one of the possible types of peroxides on the surface,^{5,10} but other peroxide groups are difficult to identify and quantify by XPS methods. Identification and quantification of hydroperoxides gives an indication of the kinetics for peroxide formation, and these results indicate a very fast buildup of the concentration of active hydroperoxides.

Effect of Corona Treatment Time on Graft Yield

In this experiment the corona treatment time was varied from 0 to 10 min with a constant reaction time in acrylic acid vapor of 10 min. The contact angle and atom percent oxygen as a function of corona treatment time is shown in Figure 2. Both contact angle and XPS indicates that the graft yield reaches a maximum around a treatment time of 90 s and thereafter falls off to a lower level. A maximum in graft amount and thereafter a leveling off was also observed by Iwata et al.⁵ for grafting of acrylamide in liquid phase. The same authors also observed that the total amount of peroxides on the surface showed a maximum around the same corona treatment time as the maximum graft yield.

Effect of Reaction Time in Monomer Vapor on Graft Yield

Figures 3(a) and (b) show the IR and XPS spectra of film surfaces reacted different times with acrylic acid vapor with a constant corona treatment time of 90 s. The IR spectra show a continuous increase in signals from acrylic acid as a function of reaction time. The XPS spectra show a continuous increase in the C1s3 peak indicating an increase in the graft yield of acrylic acid. This observed increase in graft

yield up to a reaction time of 60 min indicate that peroxides with a long half-life at 95°C must exist on the surface.

CONCLUSION

This study has shown that acrylic acid in the vapor phase can successfully be grafted on to corona-treated polyethylene. The method is relatively simple and relatively high graft yields can be achieved after only a few minutes total reaction time.

This work has been funded by the Royal Norwegian Council for Scientific and Industrial Research (NTNF) under grant MT.50.03.21711, and supported by Statoil, Norsk Hydro, and Raufoss A/S. Thanks are due to Jens Anton Horst for performing the XPS measurements and to Keith Redford for useful comments and discussion.

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Received June 19, 1991

Accepted February 18, 1992