

The Influence of Implantation Conditions on the Surface Structure of Polypropylene

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SYNOPSIS

The influence of the fluence and the energy of implanted F⁺ ions on the surface structure of polypropylene was studied by measuring the contact angle and UV-visible spectra. With increasing ion fluence and energy, the polar component of the surface energy increases. At the same time, the number and the length of double-conjugated bindings in the polymer also increase. With higher ion energy, an increasing number of conjugations are observed but their length remains unchanged. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ion implantation is frequently used in the micro-electronic device technology for the modification of semiconductor properties by controlled introduction of dopands. In common implanter ion sources, cations are produced that, after some acceleration in the electrostatic field and after mass separation, strike the material surface with certain well-defined energy. Recently, the implantation technique has been used for enlargement of the electrical conductivity of some polymer and organic materials.¹ The thickness of the implanted layer varies from tenths up to several microns depending on the implantation energy.² For that reason, ion implantation can advantageously be used for the modification of the surface properties of polymers. For example, in Refs. 2 and 3, ion implantation has been successfully used for the enlargement of the surface polarity of polypropylene.

In this work, the changes of the polypropylene surface structure was studied as a function of the implantation fluence and energy.

EXPERIMENTAL

The present experiments were carried out on 6 μm-thick foils of oriented polypropylene (PP) with a

molecular mass, M_n , of 150,000 and density of 0.901 g cm⁻³. The PP was implanted with F⁺ ions from both sides to enlarge the expected changes in polymer optical properties. The ion current density was kept below 50 nA cm⁻² to prevent polymer thermal degradation.

After ion implantation, the surface free energy (γ_s) and its dispersal (γ_s^d) and polar (γ_s^p) components were determined on the basis of contact-angle measurement. The calculations were performed using the method described earlier^{2,3} using the following equation⁴:

$$\cos \theta = 2(\gamma_s^d \gamma_w^d)^{1/2} / \gamma_w + 2(\gamma_s^p \gamma_w^p)^{1/2} / \gamma_w - 1 \quad (1)$$

where θ is the contact angle and γ_w is the tension at the contact point of the liquid/vapor. The contact angle was measured by a reflexion goniometer, with hexan as the unpolar and water as the polar liquids. The UV-visible spectra were measured on a Specord spectrophotometer.

RESULTS AND DISCUSSION

The measured dispersal component of the PP surface energy has a constant value of $\gamma_s^d = 31.8$ mJ m⁻², which is close to the value $\gamma_s^d = 30.2$ mJ m⁻² reported earlier for some unspecified PP type.⁵ The influence of the fluence and the energy of the implanted F⁺ ions on the PP structure and the polar component of the PP surface energy was studied.

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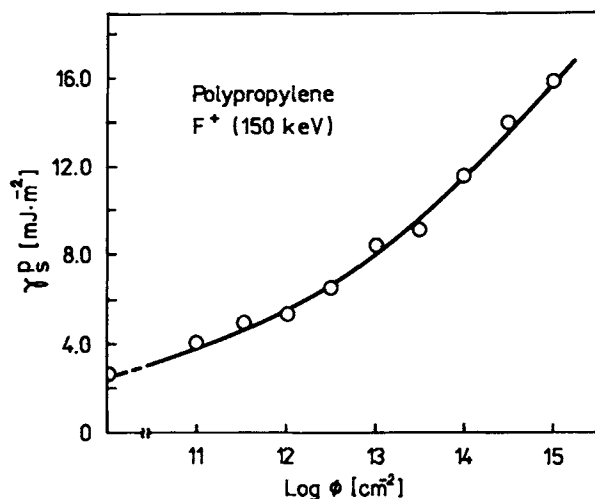


Figure 1 The dependence of the polar component of the PP free energy on the fluence of implanted F^+ ions.

The measured polar component of the PP free energy as a function of the F^+ ion fluence ϕ is shown in Figure 1. It can be seen that the polar component γ_s^p increases significantly with increasing ion fluence. It is also evident that the samples of PP, which belong to unpolar polymers,⁵ exhibit, before ion implantation, a nonzero polar component that is probably caused by the presence of a stabilizer and by a polymer orientation.

According to the results published earlier,² the fluorine implantation results in PP dehydrogenation, the generation of conjugated systems of double

bindings, and the oxidation in the rest atmosphere of the ion implanter. The oxidation was observed using the RBS technique and IR spectroscopy, but the concentration of the fluorine atoms in implanted PP was under the detection limits of both methods.

In this study, the changes in chemical composition and the structure of PP due to ion implantation were examined by measuring the UV-visible spectra. The measured UV spectra for different implanted ion fluences ϕ are shown in Figure 2. It is well known⁶ that the polymer absorbance in the UV-visible spectral region is connected with the presence and the length of the conjugated systems of double bonds in the polymer. Ranby and Rabek⁶ reported characteristic absorbance maxima for two to eight double bonds in a conjugated polymer system. On the basis of the present results (Fig. 2), it may be concluded that for the implantation to the fluence of $1 \times 10^{13} \text{ cm}^{-2}$ the two conjugated bonds in PP prevail. With increasing implanted fluence, the number of conjugated bonds increases. Therefore, for the fluence $1 \times 10^{14} \text{ cm}^{-2}$, four conjugations dominate, and for the fluence $5 \times 10^{14} \text{ cm}^{-2}$, the absorption maximum corresponds to seven to eight conjugations in the polymer chain. It appears from the results obtained that with increasing ion fluence the conjugated system of double bonds becomes longer, i.e., with increasing ion fluence, the PP dehydrogenation increases due to the effect that is often indicated as carbonization in the literature.¹

Another factor affecting ion behavior in the material is its energy. The influence of the ion energy

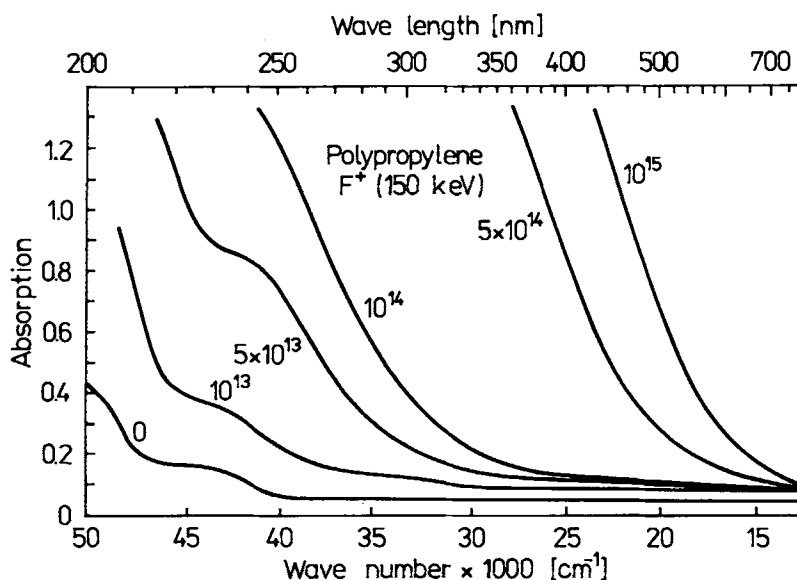


Figure 2 UV-visible spectra of the PP samples implanted with 150 keV F^+ ions to different fluences. The numbers are the ion fluences in cm^{-2} .

was examined at constant ion fluence of $5 \times 10^{13} \text{ cm}^{-2}$. The measured dependence of the polar component of the polymer free energy on the ion energy is shown in Figure 3. One can see that for lower implantation energy the polarity of the polymer surface increases rapidly, whereas for the implantation energies above 80 keV, the increase γ_s^p is slower. Generally, the thickness of the polymer layer degraded due to ion implantation is an increasing function of the ion energy. For example, the projected range and the range of straggling 150 keV F^+ ions in virgin PP, calculated using the TRIM 85 code, are 330 and 43 nm, respectively. As can be seen from Figure 3, the polar component of the surface free energy depends also on the thickness of the degraded layer.

The UV-visible spectra measured on PP implanted at different ion energies to constant ion fluence are shown in Figure 4. It is evident that the implantation energy does not affect the length of the conjugated double bonds in the chain and that for implantation energies used two conjugated double bonds dominate. An increase in the number of conjugations mostly with two double bonds with increasing implantation energy is due to dehydrogenation.

CONCLUSION

The changes of the polypropylene surface properties as a function of the energy and the fluence of implanted fluorine ions was studied. It was shown that the polar component of the PP surface energy as well as the number and the length of conjugated

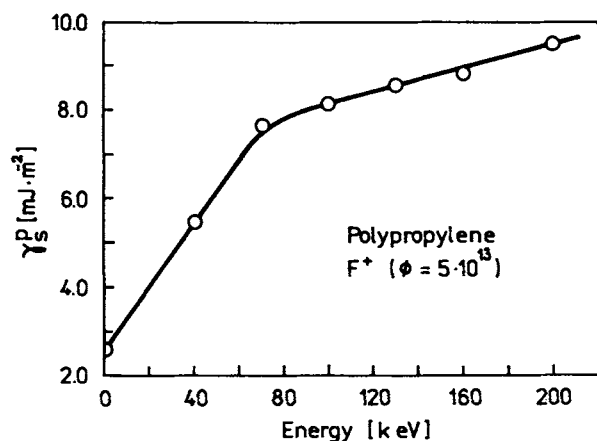


Figure 3 The dependence of the polar component of the PP free energy on the energy of implanted F^+ ions.

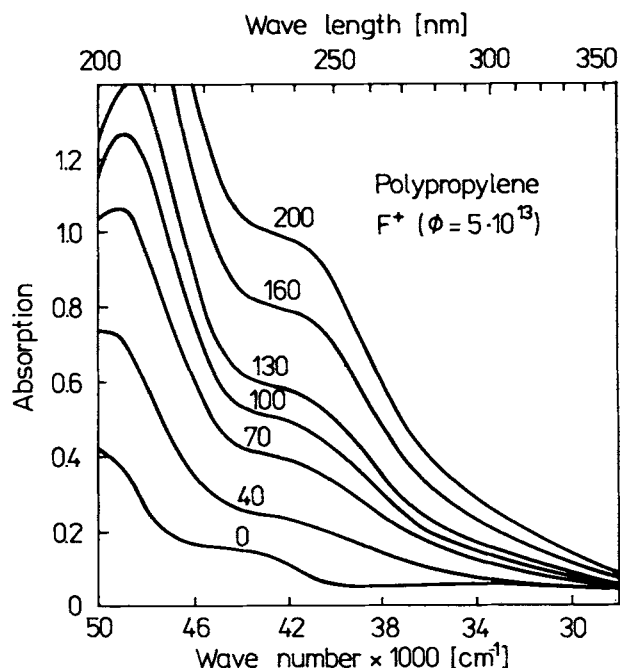


Figure 4 UV-visible spectra of the PP samples implanted with the fluence $5 \times 10^{13} \text{ cm}^{-2} F^+$ ions to different energies. The numbers are the ion energies in keV.

double bonds increase with increasing ion fluence. For lower implantation energies, the surface polarity increases with increasing ion energy. The ion energy affects the number of conjugations but not their length. The surface polarity depends also of the thickness of the polymer surface layer degraded as a result of ion implantation.

REFERENCES

1. A. J. Dann, M. R. Fahy, Ch. Jeynes, and M. R. Willis, *J. Phys. D*, **19**, L 217 (1986).
2. V. Švorčík, V. Rybka, K. Volka, V. Hnatowicz, J. Kvítek, and P. Seidl, *Jpn. J. Appl. Phys. B*, **31**, 291 (1992).
3. V. Švorčík, V. Rybka, P. Seidl, V. Hnatowicz, J. Kvítek, and K. Geryk, *Mater. Lett.*, **12**, 434 (1992).
4. A. J. Kinloch, *Adhesion and Adhesives*, Chapman and Hall, London, 1987.
5. D. G. Range, *Industrial Adhesion Problems*, Orbital Press, Oxford, 1985.
6. B. Ranby and J. F. Rabek, *Photodegradation, Photooxidation and Photostabilization of Polymers*, Wiley, London, 1975.

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