NITROGEN PLASMA TREATMENT OF ISOTACTIC POLYPROPYLENE : CHEMICAL SURFACE AND BULK CRYSTALLINE STRUCTURE MODIFICATIONS

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The increasing use of polymers in various fields requires, concerning specific applications, improvement of their surface properties such as wettability and adhesion. Among different techniques for polymer surfaces processing, cold plasma treatment is developed as it modifies the chemical and sometimes morphological structure of a material within a thin layer without changing its bulk characteristics (for example viscoelasticity). We have chosen nitrogen as plasma gas because it seems to scarecely degrade polypropylene, but creates free radicals and functional groups on the polypropylene surface. This study also shows a sharp increase of the polypropylene surface energy during nitrogen plasma treatment, mainly caused by the formation of functional groups such as amines acting as electron donors. In some discharge conditions, competitive reactions of crosslinking and degradation appear, the first ones being predominant. It also leads to bulk crystalline structure modification of the material. This unexpected effect of plasma treatment results in a polypropylene crystallization of paracrystalline or "smectic" form into the α-crystalline form.

Introduction

A polymer when treated into a plasma undergoes chemical reactions, which are the direct or indirect consequences of surface interactions with plasma reactive species (ions, neutral excited or not, radicals, free electrons and radiations) whose effects are activation (creation of radicals), functionalization, crosslinking and degradation.

During a plasma treatment, all these phenomena take place simultaneously, the importance of each highly depends on gas and polymer natures.

Experimental part

The microwave plasma apparatus and the process are described in [1]. Two standard conditions of treatment were chosen :

conditions A: D_{N2} = 20 sccm, P= 60 W, p = 0,3 mbar, d = 10 cm,
conditions B: D_{N2} = 20 sccm, P= 100 W, p = 0,3 mbar, d = 4 cm,

Sample surface energies were estimated from the contact angles of distilled water, formamide and tricresylphosphate using Good's method [2]. The different melting points and phase transitions are measured with a DSC Perkin Elmer equipment.

Results and Discussion

We have chosen nitrogen as plasma gas because it seems to weakly degrade polypropylene [1] as shown by scanning electron microscopy pictures. A nitrogen plasma creates radicals, amines and a slight oxidation on the polymer surface (all of them displayed by SIMS and XPS). Amino groups and radicals were respectively titrated using an aromatic disulfonate (Ponceau 2R) and diphenylpicrylhydrazyl (DPPH) reagents [1]. Following these studies [1], two conditions were chosen as representative of two types of modified surfaces :

- one (conditions A) corresponds to a treatment with functionalization as preponderant reaction, a maximum of amino groups was found,

- and the other (conditions B) leads to a surface with the highest radicals concentration. The surface and bulk structure characteristics of the two samples are compared.

Surface functionalization

In previous study [1], functionalization was shown to lead mostly to amino groups formation. Therefore, polypropylene surface contains functionnal groups acting as electron-donating groups. Amino groups characterization has been confirmed by surface tension determination based on Good's theory [2] which takes into account the electron-donating or electron-accepting effects. This concept gives an approach on the acid-base character of the surface which in many applications in the adhesion domain is the key point.

In the case of treatment in conditions A (Fig. 1a), contact angle measurements based on this model emphasizes for short durations polypropylene functionalization through electron-donating groups such as amino groups already detected by XPS analysis [1]. A longer duration leads to a slight surface tension decrease certainly due to the crosslinking preponderance for such conditions whose effect weakens the surperficial groups mobility. Treatment in conditions B (Fig. 1b) with duration longer than 3 mn generates an increase of surface tension and of its electron-donating component, more important than functionalization study predicted. This effect reflects the surface postoxidation after plasma treatment as for such conditions, the surface contains a high concentration of radicals, these latter being then oxidized in order to form electron-donating groups.

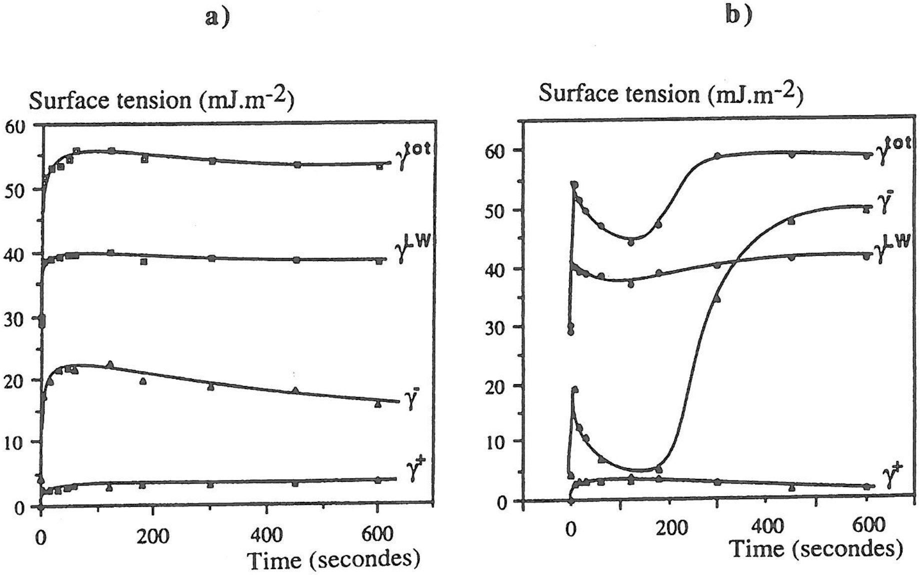

Fig. 1 : Dependence of surface energies on treatment time in conditions A and B

Substrat morphology

In order to realize a complete characterization of the modified surface, the ^{13}C solid state NMR analysis has been undertaken. If the solid state NMR is not enough sensitive to give evidence of functionalization (no peak corresponding to amino groups is detected), ^{13}C solid state NMR spectrum of sample treated in conditions B presents two peaks for each methyl and methylene groups (Fig. 2) which are characteristic of a phase transition in the bulk of polymer film. This phase transition corresponds to transformation of paracrystalline phase, called "smectic" of the initial material to an α crystalline form [3].

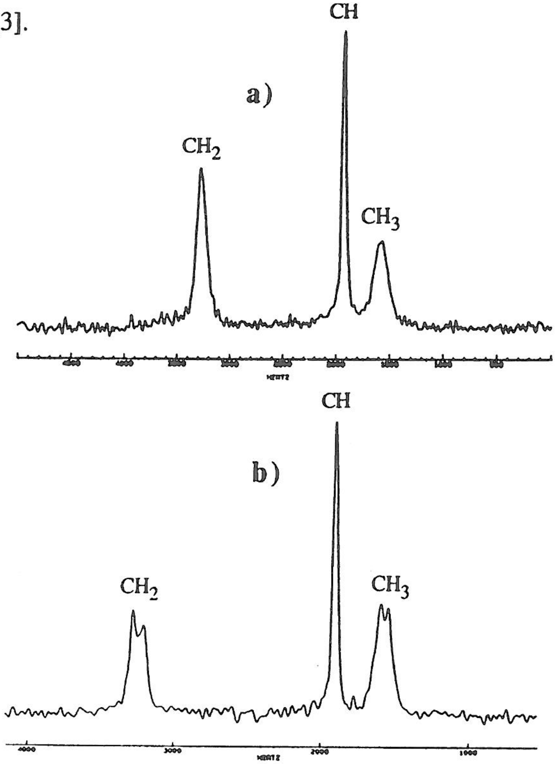

Fig. 2 : ^{13}C NMR spectra of (a) virgin (b) plasma modified PP in conditions B

The phase transition of sample treated in conditions B was confirmed by X-ray diffraction [4] (Fig. 3), but the transition is not complete. Peaks at 2 Θ = 14.01, 17.11, 18.53, 21.14, 24.22, 25.33, 28.22° are assigned to α form, and peak at 2 Θ = 15.83° to "smectic" phase. The calculated proportion of α form versus crystalline phases is around 0.4.

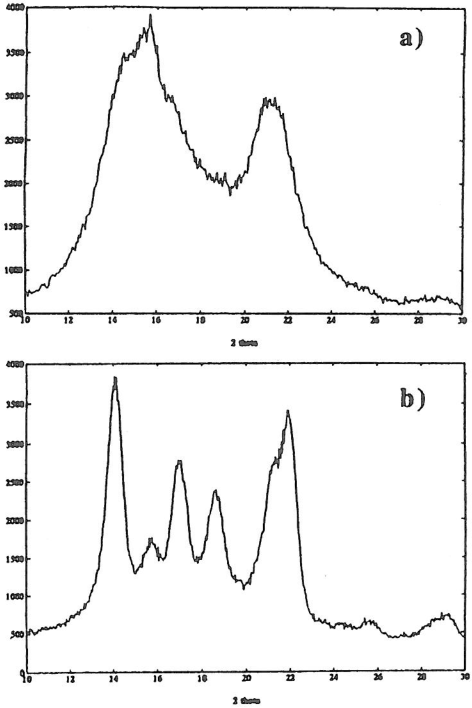

Fig. 3 : X-ray diffraction patterns of (a) virgin (b) plasma modified PP in conditions B.

Furthermore, some absorption bands in transmission FTIR spectroscopy are representative of the regular network or in opposite manner to the disorder [5,6]. The determination of the ratio between two absorption bands associated to the 3_1 helices order or disorder (respectively at $\nu = 998$ and 973 cm^{-1}) indicates an order development which translates the α modification induced by plasma treatment. This ratio increases from 0,79 to 0,95 for treated sample in conditions B, so the order degree increases also with this kind of plasma treatment.

Thermal diagram of the same sample does not present the endothermal peak of the α transition around 70°C but shows a shoulder on the fusion peak at 137°C assigned to the presence of spherulites [7].

The correlation between FTIR analysis and X-ray measurements allows to calculate the relative amounts of α, “smectic” and amorphous phases which are respectively 0%, 56%, 44% for virgin polypropylene and 50%, 23%, 27% for modified samples. These results suggest that a crystallization of the amorphous phase to paracrystalline form occurs in addition to crystalline transformation. The α conversion involves a substantial rearrangement of the chain structure [8]. This transition would require either lateral movement of segments of the chains or a rewinding of 3_1 helices to give the ordered left- and right-hand chain structure characteristic of the α form. The needed energy for this arrangement may be provided by a thermal effect but may also correspond to an energy transfert from the different plasma reactive species (ions and VUV radiations) to the polymer surface. Further experiments avoiding thermal effects are in progress.

These same analysis carried out on the sample treated in conditions A are characteristic of the polypropylene paracrystalline form which corresponds to the blank sample.

Conclusion

This study gives evidence of the different competitive reactions taking place on polypropylene surface (functionalization, activation and crosslinking). Specific conditions could also lead to a crystalline bulk structure modification For example, isotactic polypropylene will undergo a modification from a smectic phase to an α form.

Références

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