

## Surface properties of alternated aliphatic polyketones

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Surface properties of alternated aliphatic polyketones, C<sub>2</sub>/CO and C<sub>2</sub>/C<sub>3</sub>/CO (where C<sub>3</sub> is ≤ 11 mol%) have been studied by X-ray photoelectron spectroscopy and contact angle measurements. Core level photoemission spectra have been found similar to those of poly(vinyl alkyl ketones). Some lack of oxygen at the surface of powder polymers was attributed to contamination during synthesis. Contact angles were found intermediate between hydrophobic and hydrophilic polymers, with a large hysteresis likely caused by some surface degradation. Mild oxygen plasma treatments were found to increase very much the surface wettability, with a moderate increase of O/C atomic ratio. Aging was observed on plasma treated surfaces, with a partial hydrophobic recovery.

Surfaces were found to degrade easily under treatments like processing by injection or compression moulding and ion bombardment. © 1997 Elsevier Science Ltd. All rights reserved.

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### Introduction

Perfectly alternated copolymerization of hydrocarbon monomers with CO can be obtained in relatively mild conditions using catalysts based on transition metal compounds, mainly complexes of Pd(II) in the presence of a cocatalyst<sup>1,2</sup>. When the comonomers are ethylene and CO, white, highly crystalline powder polymers are obtained, having a melting temperature ( $T_m$ ) of 260°C. Because at such temperatures degradation phenomena are induced by processing, propylene is added as a third monomer, so obtaining a C<sub>2</sub>/C<sub>3</sub>/CO terpolymer. At a C<sub>3</sub> molar concentration of 5–10%,  $T_m$  decreases down to 200°C, without affecting the degradation temperature<sup>3</sup>. In this way, processability of the polymer becomes less critical.

In comparison with other thermoplastic polymers, mechanical properties of C<sub>2</sub>/C<sub>3</sub>/CO terpolymers are very interesting<sup>4</sup>. Other important properties, like chemical resistance and gas permeability<sup>5,6</sup>, show remarkable levels. Also for these reasons, commercialization of the polymer is going on<sup>7</sup>, under the trade name of Carilon®. Because no literature data are available on surface properties of aliphatic alternate polyketones, we made a study on this subject by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Some preliminary data on behaviour under cold plasma treatment are also described.

### Experimental

**Materials.** In order to avoid interference with additives, plain polymers have been examined. Both C<sub>2</sub>/CO and C<sub>2</sub>/C<sub>3</sub>/CO polymers have been synthesised, where C<sub>3</sub> ranges between 4 and 11 mol%. Synthesis was made following a published procedure<sup>8</sup> in a stirred stainless steel autoclave provided with temperature control and gas inlet valves. The gas mixture (C<sub>2</sub>/CO, 1/1, vol/vol) was fed to the reactor filled with methanol and containing the

appropriate amount of liquid propylene. Temperature was maintained near 75–80°C and pressure was fixed at 50–55 bar. The catalyst was formed *in situ* by mixing Pd (II) trifluoro acetate and 1,3-bis(diphenyl phosphine) propane (1/1, mol/mol), in the presence of trifluoroacetic acid.

Polymers were obtained as white powders, then washed with triphenylphosphine in order to decrease to residual Pd content under 10 ppm. Some properties of prepared polymers are reported in Table 1. Melting temperature,  $T_m$ , was measured by differential scanning calorimetry (DSC, second scan) using a Perkin Elmer DSC-7 system. Intrinsic viscosity,  $\eta$ , was determined by using a Brookfield viscosimeter<sup>9</sup>. C<sub>3</sub> amount in the terpolymers was determined by <sup>1</sup>H nuclear magnetic resonance (n.m.r.), using a Bruker 300 spectrometer and following a published method<sup>10</sup>. Crystallinity was measured by powder X-ray diffraction (XRD), by means of a Siemens diffractometer (Cu-K $\alpha$  radiation).

**Surface characterization.** All samples were analysed by XPS in powder form, so avoiding any contamination due to the processing procedure or to possible degradation phenomena. XPS was performed with a Physical Electronics PHI 5500 ESCA system. The spectrometer was equipped with an X-ray source (Al-K $\alpha$  radiation) operating at 14 kV and 200 W. Powder samples were pressed onto a clean In foil before analysis. The diameter of the primary beam on the specimen surface was 0.4 mm. Pressure in the analysis chamber was maintained in the 10<sup>-8</sup> Pa range. An electron take-off angle of 45° was generally adopted. An electron flood gun was switched on during measurements to compensate electrostatic charging effects.

After measuring the survey XPS spectra, C1s and O1s peaks were collected in high resolution conditions, as well as the valence band region (0–35 eV). Surface atomic concentrations were determined from peak intensities using the software and elemental sensitivity factors provided by the manufacturer.

Contact angle measurements were carried out by the

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**Table 2** Surface compositions from XPS data (at%)

Sample		C	O	Total contaminants	O/C
A	powder	79.1	20.9	0	0.26
	tablet	76.7	19.7	3.6 (Si,Cl,N,S,Na,Ca)	0.26
	calculated	75.0	25.0		0.333
B	powder	77.7	22.3	0	0.29
	calculated	75.2	24.8		0.33
C	powder	79.4	20.6	0	0.26
	calculated	75.3	24.7		0.328
D	moulded sheet	80.3	17.9	1.8 (Si,N,S)	0.22
	dip coated film	77.8	22.2	0	0.28
	calculated	75.4	24.6		0.326
E	powder	77.8	22.2	0	0.29
	calculated	75.5	24.5		0.325
F	powder	79.6	20.4	0	0.26
	calculated	75.6	24.4		0.324

**Table 3** Surface composition (at%) of oxygen plasma treated A copolymer. Plasma power 60 W

Treatment time (s)	C	O	Total contaminants	O/C
30	73.9	25.4	0.6 (Si, N, Na)	0.34
60	75.0	24.3	0.6 (Si, N, Na)	0.32
90	70.8	27.1	2.2 (Si, N, Na, Al)	0.38 (0.34) <sup>a</sup>
120	68.6	28.8	2.7 (Si, N, Na, S)	0.42 (0.32) <sup>a</sup>

<sup>a</sup> Without a possible contribution from oxygen bonded to silicon (assumed as SiO<sub>2</sub>)

can be concluded that only a minor influence can be attributed to sensitivity factors. As a consequence, some surface contamination with oxygen-poor carbon containing compounds are at the origin of oxygen shortage, likely occurring during preparation.

In *Table 2* surface composition results obtained on samples having different physical forms (tablets, molded sheets and dip coated films) are also reported. Any powder processing for obtaining extended solid surfaces causes several variations like contamination with a number of elements coming from materials used for processing and degradation of the polymer structure<sup>15</sup>. In fact, polyketone surfaces obtained by compression or injection molding exhibit surface O/C ratios around 0.22.

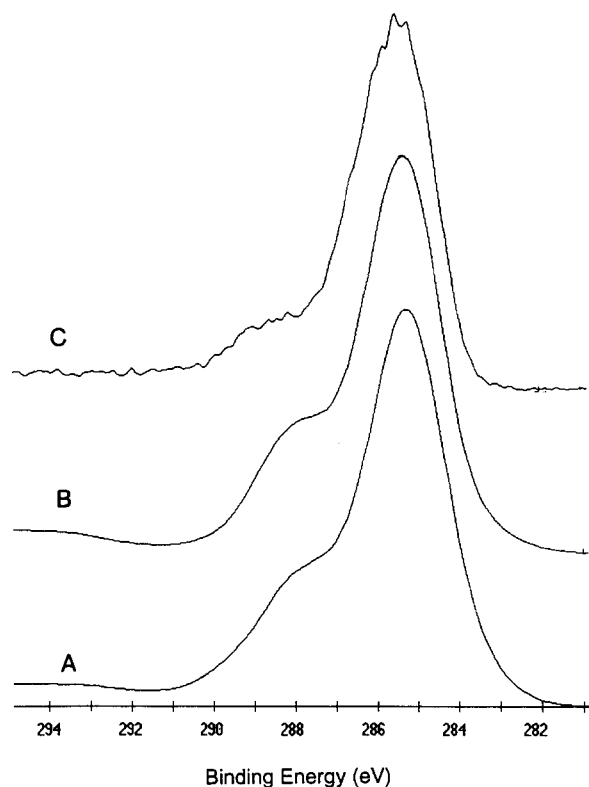
**Contact angle measurements.** Contact angles have been measured on cold compressed tablets, due to the necessity of obtaining a reasonably smooth surface, with dimensions of at least some millimetres. As prepared, ethylene/CO copolymer shows an advancing angle of 90° and a receding angle of 30°. Such values can be compared with those typical of some common polymers. Aliphatic polyketones fall reasonably in an intermediate position with respect to materials hardly wettable like fluoropolymers ( $\vartheta_a = 109^\circ$ )<sup>16,17</sup> and aliphatic polyolefins ( $\vartheta_a = 95-96^\circ$ )<sup>16,18,19</sup> and, on the other hand, polymers containing oxygenated functionalities, like PET ( $\vartheta_a = 82^\circ$ )<sup>16</sup>. The large hysteresis value measured on C<sub>2</sub>-CO is quite surprising, but, due to the difficulty to prepare proper surfaces of the material, it cannot be definitely assumed as an intrinsic property.

After 30 s of oxygen plasma treatment, both advancing and receding contact angles assume very low values, i.e.  $\vartheta_a = 17^\circ$  and  $\vartheta_r$  not measurable. Surface compositions after such treatments are reported in *Table 3*. The main effects of plasma treatments are a huge increase of wettability, an increase of oxygen concentration and an increase of surface contaminants, mainly Si. Considering that a fraction of observed oxygen is likely bonded to silicon, it appears

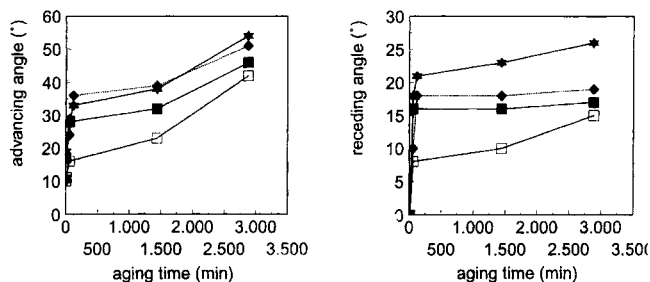
evident that further treatment after the first one of 30 s does not increase substantially the O/C content (corrected figures are also reported in *Table 3*). This is also in agreement to the observation that all C peaks after treatment assume an analogous profile. An example of a C1s peak profile after plasma treatment is reported in *Figure 3a*. The two main components appear broadened and overlapped.

**Aging behaviour.** Polymer surfaces rendered hydrophilic by a chemical or physical treatment show a peculiar behaviour based on the dynamic properties of macromolecules. This phenomenon, at the basis of which is the thermodynamic response of the modified layer to its interfacial tension against air atmosphere, is often called hydrophobic recovery, because it appears as an increase of contact angle values with time<sup>16</sup>. Hydrophobic recovery of a specific polymer is connected to its nature and can be complete, as for instance in the case of poly(propylene) (PP)<sup>20</sup>, or very partial, like in poly(ethylene) (PE)<sup>18</sup>. It has been observed for the most of polymers, like poly(styrene) (PS)<sup>19</sup>, polycarbonate (PC)<sup>20</sup>, poly(ethylene terephthalate) (PET)<sup>21</sup>, poly(dimethyl siloxane) (PDMS)<sup>22</sup>, poly(tetrafluoroethylene) (PTFE)<sup>23</sup> and poly(ether ether ketone) PEEK<sup>24</sup>. In order to determine if such behaviour is also followed by aliphatic polyketones, plasma treated C<sub>2</sub>/CO copolymers have been investigated, by measuring during aging in air at room temperature the evolution of contact angles. Results reported in *Figure 4* for both advancing and receding contact angles show clearly that also in this case hydrophobic recovery occurs, but, even if the time interval considered is too short for allowing a complete equilibration, it is definitely incomplete for both angles. Bearing in mind the behaviour of other polymers, it can be envisaged that, like for PE<sup>18</sup>, complete recovery is hindered by the occurrence of some crosslinking at the modified surface layer.

**Degradation.** Aliphatic polyketones are easily subjected



**Figure 3** C1s peak of polymer A after various treatments: (a) oxygen plasma treatment for 30 s; (b) compression moulding; (c) Ar<sup>+</sup> ion bombardment for 60 s



**Figure 4** Behaviour of advancing (left) and receding (right) contact angles with aging. Filled squares, 30 s plasma treated; filled rhombus, 60 s plasma treated; filled stars, 90 s plasma treated; open squares, 120 s plasma treated. Estimated errors:  $\pm 2^\circ$

to thermo-oxidative degradation, producing crosslinking, intramolecular cyclization and dehydration<sup>15</sup>. Processing by extrusion or injection moulding can cause extended degradation, rendering the polymer not further processable, when appropriate antioxidant additives are not used. Such attitudes are reflected also at their surfaces. *Figure 3b* shows the effect of compression moulding on the C1s peak, with extended loss and/or modification of CO groups, giving a final appearance similar by this point of view to that after plasma treatment (*Figure 3a*).

Also, ion bombardment induces strong degradative effects, as shown in *Figure 3c*. An Ar<sup>+</sup> flux at an energy of 1keV for 60 s is sufficient to cause a large loss of oxygen (O/C = 0.12). Because in thermal decomposition chain

scission between CO and olefin was found to be favoured with respect to breaking of CH<sub>2</sub>-CH<sub>2</sub> bonds, loss of CO is a likely consequence of such a mechanism<sup>15</sup>.

### Conclusions

Alternated aliphatic polyketones exhibit XPS spectra very similar to those of poly(vinyl alkyl ketones). Their wetting properties were found intermediate between hydrophobic and hydrophilic polymers. The large hysteresis of water contact angles was likely attributed to some surface degradation. Mild oxygen plasma treatments increase very much the surface wettability, with a moderate increase of O/C atomic ratio. Aging was observed on plasma treated surfaces, with a partial hydrophobic recovery.

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