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Effect of the orientation on the photooxidation behaviour of polymer films

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ABSTRACT

The effect of the orientation on the photooxidation of polymers is quite controversial. Both improvement of the photo-resistance along the oriented direction and worsening of the photooxidation kinetic have been reported. In this work the effect of the orientation has been investigated on films of PE, PP and PET with different degree of orientation and crystallinity. The results show that the photo-stability, measured from the decay of the elongation at break curve as a function of the irradiation time, improves in the more oriented direction, but this is more and more relevant with increasing the crystallinity degree. It has been hypothesized that the reinforcing action of the oriented crystalline fibers could be responsible for this behaviour. More crystalline fibers are present, more reinforcing action is shown and this can explain the remarkable effect of both orientation and crystallinity.

1. Introduction

The photooxidation of polymer systems depend on many factors: chemical nature of the polymers, irradiation conditions, permeability, properties and characteristics of the samples like crystallinity [1–3], orientation [4–11], compatibilization in the case of blends [12,13], and processing conditions during the preparation [14]. Among these factors the orientation has received less interest [4–11] because it is present only in a limited number of products (fibers, bioriented films for packaging, etc.) that usually are not subjected to UV radiations. Among the biaxially oriented films, only the films for greenhouses, are subjected to remarkable levels of photooxidation.

Moreover, orientation is in many cases accompanied by change of crystallinity and tacticity, so the effect of the orientation is not easy to separate from the effects of the other morphological parameters.

An improvement of the photo-resistance to natural weathering tests was found in [4] for uniaxially oriented polypropylene until a given orientation. Further orientation does not give any further improvement. Garton et al. [5] found that the elongation at break of highly oriented polypropylene monofilaments is much less affected by the UV irradiation than undrawn or less oriented filaments.

Other papers of Akay et al. [6,7] and Raab et al. [8] found similar results for biaxially oriented films of LDPE, HDPE and PP. Savchuk and Neverov [9] found that the orientation increases the resistance to photooxidation of polyethyleneterephthalate because of the increase of crystallinity during UV irradiation due to the reduction of the molecular weight. La Mantia et al. [10] showed that the kinetics of photooxidation was depressed on increasing crystallinity and orientation in the more oriented direction. This behaviour was attributed to the reinforcing action of the oriented crystalline fibers.

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All these papers agree that the orientation decreases the photo-sensibility of the investigated polymers and in particular show that the decrease of the mechanical properties is lower with respect to the isotropic or less oriented materials. On the contrary, Bellenger et al. [11] observed that the photooxidation rate of PVC films increases with the degree of orientation. The same result is reported in [6]. This result was explained [11] in terms of build-up, during stretching, of conformations which are especially reactive towards hydrogen abstraction by radicals. The authors, moreover, observe that PVC is an amorphous polymer while the other polymers investigated were semicrystalline and it is well known that orientation induces noticeable morphological changes in crystalline polymers which can influence the chemical kinetics. Finally, all these papers are mainly based on the investigation of the formation of oxygenated groups during photooxidation and only a very few papers report also mechanical properties [4,6,8].

Aim of this paper is to investigate the effect of the orientation on the mechanical properties of two photooxidized polyolefines biaxially oriented films and of a photooxidized biaxially oriented polyethylenetherephthalate film. These three polymers, low density polyethylene (LDPE), polypropylene (PP) and polyethylenetherephthalate (PET) have been chosen because show different values of the crystallinity and different types of a responses to the UV radiations. Indeed, the photooxidation of PP and PET is dominated by chain scission, while a competition between chain scission and cross-linking occurs during photooxidation of LDPE. These films show different values of crystallinity and different degrees of orientation along the two directions. The photooxidation behaviour has been investigated by measuring the change of the mechanical properties along the two directions with the irradiation time. Because the samples have been cut from the same films, all the bulk properties that can influence the photooxidation behaviour like thickness, crystallinity, permeability, new chemical groups, or the presence of photostabilizers are the same in both directions and then the change of the mechanical properties with the irradiation time can be attributed only to the effect of the orientation.

The results show that the photooxidation behaviour improves with the level orientation only in presence of a significant degree of crystallinity.

2. Experimental

Biaxially oriented LDPE film was produced by Agriplast (Vittoria, Italy) by film blowing using a low density polyethylene having a MFI of about 0.65 dg/10 min. The draw ratio in the machine direction was about 13 and the blow up ratio was about 2.6 and the thickness about 35 μm.

Biaxially oriented polyester film is a commercial film known as Nuroll PXE produced by Nuroll (Italy) with a thickness of 15 μm.

Biaxially oriented PP film is a commercial film produced by Taghleef Industries under the commercial name TSS and with a nominal thickness of 25 μm.

In order to measure the mechanical properties of the unoriented, isotropic samples, the films were kept at 100 °C for the PE film, at 120 °C for the PP film and at 220 °C for the PET film for a time enough to measure the same properties in the two directions. This means that all the orientation of the macromolecules into the two directions was eliminated.

2.1. Photooxidation

All samples were exposed to accelerated weathering in a Q-UV (U.S.A.) chamber containing eight UVB-313 (Q-Labs Corp., U.S.A) lamps. The exposure cycle conditions were: 8 h of light at T = 55 °C followed by 4 h condensation at T = 45 °C. The measured photon flux was about 2 mW/cm^2.

2.2. Characterization

Tensile properties were determined at room temperature and humidity, using an Instron (U.S.A.) dynamometer mod. 3365, according to ASTM test method D882. When the deformation was about 10%, the speed was increased from 1 mm/min up to 100 mm/min until break. The data reported are the average values obtained through at least ten tests per sample.

The calorimetric curves were recorded by differential scanning calorimetry, using a Perkin-Elmer DSC7, at heating and cooling rate of 10 °C/min for all the polymers.

3. Results and discussion

In Tables 1–3 the elastic modulus, E, tensile strength, TS, and elongation at break, EB, of the three films in the two directions are reported for the PE, PP and PET films respectively. O+ means more oriented direction and O− less oriented direction.

In the more oriented direction an increase of elastic modulus and tensile strength can be observed, accompanied by a reduction of the elongation at break. The difference between the values of the mechanical properties along the two directions is indicative of the different level of orientation between the two directions. Because the ratio between the elastic modulus in the two directions can be considered a parameter of the unbalancing of the orientation in the two directions, this means that PP film is much less balanced in the two directions with respect to the PET film and even more of the PE film. Indeed, for PE film this ratio is about 1.23, for the PP film is about 1.65 and for the PET film is about 1.26. Of course, the difference between