The Role of the Disposition of the Recycled Polymer on the Properties of Films for Greenhouses Coverage

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ABSTRACT: Multilayer films, by using postconsumer materials in the central layer, i.e., multilayer composition: virgin polyethylene/postconsumer polymer/virgin polyethylene, allows to get a film for greenhouses coverage with good mechanical properties and photo-oxidation resistance, similar to that of the films made from virgin material and certainly better than the photo-oxidation resistance of the film made melt blending the virgin polyethylene and the postconsumer polymer. Moreover, the disposition of the postconsumer polymer containing oxygenated groups only in the central layer determines a significant slowdown of the photo-oxidation process of the multilayer film although faster than of the pristine vPE film. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1986–1991, 2011

Key words: multilayer film; postconsumer polymer; photo-oxidation; mechanical behaviour

INTRODUCTION

The mechanical recycling of postconsumer polymeric materials coming from the agricultural applications is an important and somewhat easy strategy to solve the problem of the relevant amount of these plastics waste. Unfortunately, the final properties of the postconsumer materials are generally worse than those of the virgin ones, due to some degradation achieved during the use of these items and during the reprocessing transformation.[1–3]

The most used polymer in numerous agricultural applications, i.e., for greenhouse covering, mulching and packaging is the polyethylene, and then the postconsumer polyethylene represents an important source at industrial level of postconsumer materials. Moreover, EVA copolymer is an another important polymers especially for films for greenhouses coverage because of its relevant optical properties.

The greenhouses films undergo relevant degradation during their use and during melt reprocessing. Indeed the synergistic effect of oxygen, temperature, and UV radiation during the lifetime cause relevant damages in the chemical structure and morphology and, consequently, in the mechanical and optical properties of the postconsumer material, while the combined effect of temperature and stress gives rise more degradation.[4–10]

Different strategies have been adopted to decrease the negative effect of the degradation on the final properties of postconsumer plastics, like stabilization,[11–18] regradation,[19–21] etc.

The use of the recycled polymer in the middle of a multilayer structure[22] is a possible way to minimize the effect of the worsening of the properties in these secondary plastics.

In a previous article,[23] we have demonstrated that a film for covering greenhouses with a multilayer structure where a layer of recycled polyethylene is between two external layers of virgin polyethylene gives rise to a film with good mechanical properties and good photoresistance.

The aim of this work is to deeply understand the properties and the photo-oxidation behavior of these multilayer films, through accurate mechanical and spectroscopical characterizations. The multilayer film shows excellent photo-oxidation resistance, similar to the photo-oxidation resistance of the pristine polyethylene film and significantly better than the photo-oxidation resistance of the melt blended film between virgin and recycled materials.

EXPERIMENTAL

Materials

The compositions of all the films used in this work are reported in Table I. vF is a film made of virgin

TABLE I
Composition of All the Investigated films

Code sample	Composition
vF	Virgin polyethylene film added with suitable thermal and UV stabilizing systems: Hindered Amine Light Stabilizer at 0.2 % wt/wt and Benzophenone at 0.3 % wt/wt.
rF	Film composition: PE and EVA.
vF/rF blend	Film composition: 50 wt % virgin PE and 50 wt % postconsumer greenhouse film, rF, blended during processing. Stabilizing additives: Hindered Amine Light Stabilizer at 0.2 % wt/wt and Benzophenone at 0.3% wt/wt were added during the film-blowing.
Multilayer vF/rF/vF	Multilayer film composition: external layer 25% vF central layer 50% rF external layer 25% vF Stabilizing additives: Hindered Amine Light Stabilizer at 0.2% wt/wt and Benzophenone at 0.3% wt/wt were added during the film-blowing.

polyethylene and rF is a recycled material coming from a mixture of postconsumer films for greenhouses coverage.

Processing and characterization

All films were prepared in an industrial single screw extruder equipped with a film-blowing head from Agriplast s.p.a. (Sicily-Italy). The thermal profile was 120-140-160-170-180°C and the screw speed 100 rpm. The thicknesses of all films were about 160 microns.

Tensile properties were determined at room temperature and humidity using an Instron machine mod. 3365 according to ASTM test method D882. The specimens were cut from films in machine and transverse direction, and were tested at two strain rates: for modulus measurement purposes, the speed was 1 mm/min until a deformation of 10%, therefore increased to 500 mm/min until break. The data reported are the average values obtained by analyzing the results of 10 tests per sample, the reproducibility being ± 7%.

All polymer films were analysed using Spectrum One by Perkin Elmer with the Spectrum software. Carbonyl (peak measured between 1650 and 1850 cm^{-1}) and hydroxyl concentrations (peak measured between 3200 and 3600 cm^{-1}) were determined from peak absorption area index (peak area absorbance of the group compared to that of a reference peak area measured between 1979 and 2110 cm^{-1}). Measurements were obtained from the average of triplicate samples.

All the films were photo-oxidized in a QU-V chamber mounting eight UV-B lamps. The weathering conditions were 8 h of light at $T = 55$°C and 4 h of condensation at $T = 35$°C.

RESULTS AND DISCUSSION

Characterization of the greenhouse multilayer film

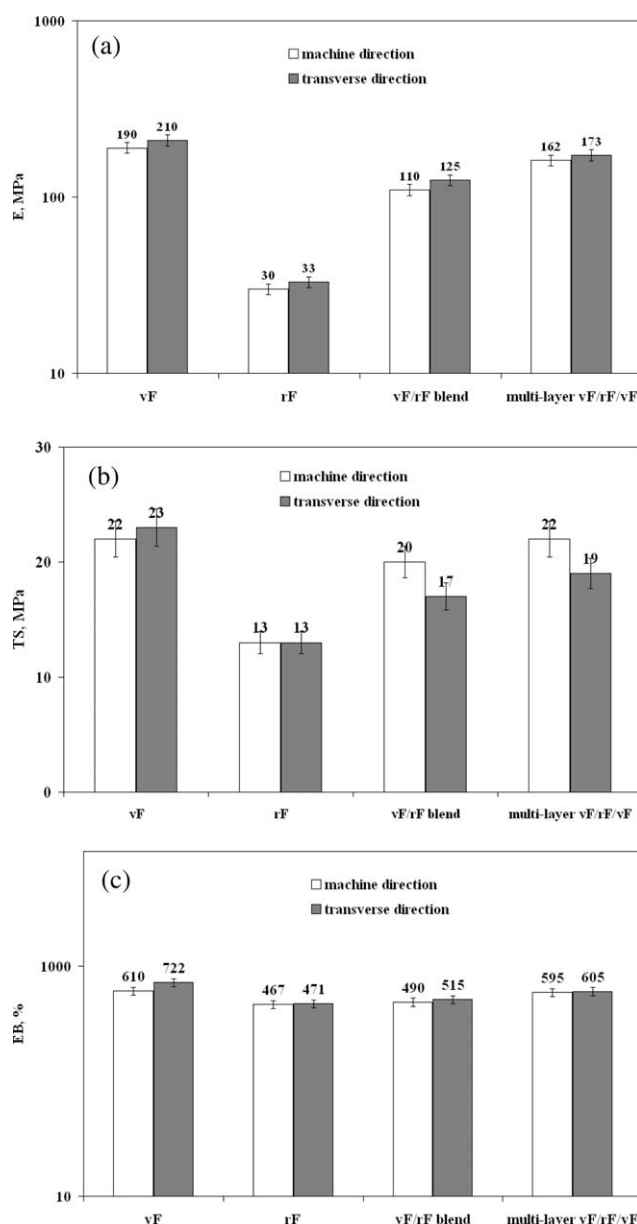In Figure 1(a–c), the main mechanical properties, in particular, elastic modulus, tensile strength, and

Figure 1 Elastic modulus, E, (a); tensile strength, TS, (b); and elongation at break, EB, (c) in machine (MD) and transverse (TD) directions of all the investigated films.
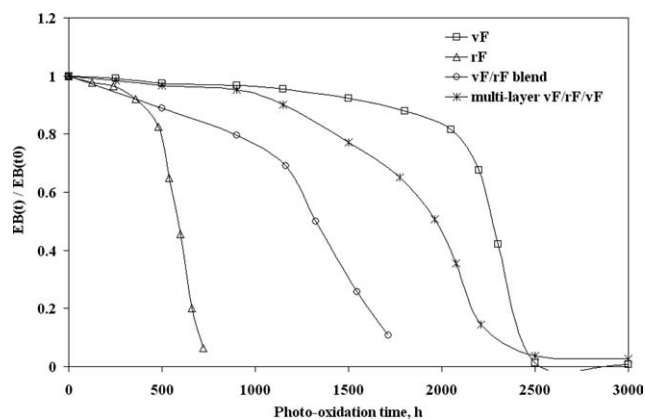
Figure 2 Dimensionless elongation at break of all the investigated films as a function of the photo-oxidation time.

Figure 3 Dimensionless tensile strength of all the investigated films as a function of the photo-oxidation time.

elongation at break of all investigated films in both machine and transverse directions are reported. The low values of the elastic modulus and of the tensile strength for the film made from postconsumer films for greenhouses depend on the fact that the postconsumer material is a mixture of PE and EVA copolymer. For the same reason the values of the mechanical properties of the film made from the blend of virgin and postconsumer polymer are lower than those of the virgin film.

The properties of the multilayer film, with the same amount of virgin and postconsumer material than the blend already discussed, are intermediate between the properties of the virgin film and those of the film made of the blend. This means that this disposition of the postconsumer material in the middle of two virgin layers and not in the bulk decreases the negative effect of the bad properties of the recycled polymer.

Resistance to the artificial photo-oxidation of the multilayer film

To monitor the resistance to the photo-oxidation, the accelerated artificial aging test was carried out for all the investigated films.

In Figures 2 and 3, the dimensionless mechanical properties, in particular elongation at break and tensile strength are reported, partly taken from Ref. 23. All the dimensionless mechanical properties are calculated as the values at a given exposure time divided by the values before the photo-oxidation, i.e., at time, $t_{(0)}$.

The elongation at break is the most sensitive parameter to the structural and morphological variations of the polymers. The postconsumer film, rF, shows the faster decay of the elongation at break and, in particular, after about 700 h of artificial irradiation the film becomes fragile. The presence of photo-oxidation products, like carbonyl groups, per-
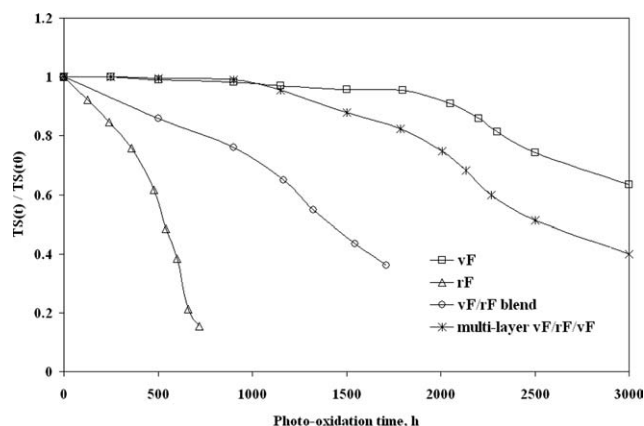
oxides and hydro-peroxides formed during the outdoor exposure accelerates the photo-oxidation of the postconsumer polymer film. The vF/rF blend film is much more resistant than the rF film because the blend contains less initial photo-oxidation products and the fragility appears after 1700 h of irradiation. The multilayer vF/rF/vF film shows a better photo-oxidation resistance because the postconsumer material is located in the central layer and is not directly involved, at least at low irradiation time, in the photo-oxidative reactions during the artificial weathering. The curve approaches that of the virgin film and the sample becomes fragile only after about 2500 h.

The half time of the elongation at break is the time at which the value of the elongation at break is one half of the initial one and can be considered as the maximum time at which the agricultural film can be used for coverage applications. It is, then, an important parameter for the use of these films. In Table II, the half time of the elongation at break is reported. The half time of the elongation at break of the rF film is only about 600 h, about one half of the vF/rF blend film, while the multilayer vF/rF/vF and the vF films show significantly higher values of the half time. It is interesting to highlight that the different disposition of the postconsumer material in vF/rF blend and in multilayer vF/rF/vF films ensures different service life-time, i.e., the half time

TABLE II
Half Time of the Elongation at Break of All the Investigated Films

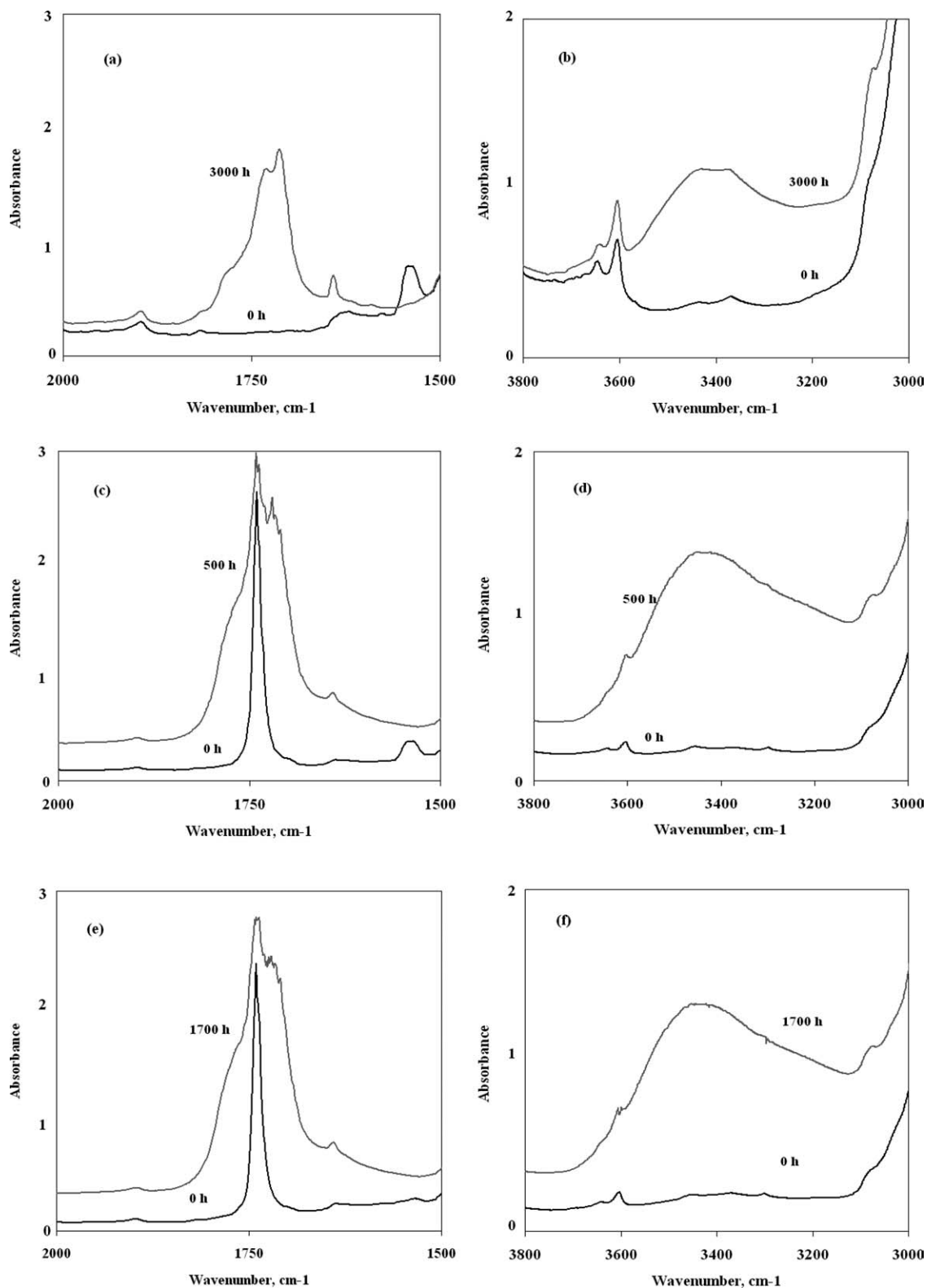| Films	Half time of the elongation at break (h)
vF	2250
rF	600
vF/rF blend	1300
Multilayer vF/rF/vF	2050

Figure 4 FTIR spectra of all the investigated sample: unexposed and at the maximum photo-oxidation time: (a,b) vF; (c,d) rF; (e,f) vF/rF blend; and (g–j) multilayer vF/rF/vF.

of the elongation at break increases from about 1300 to 2050 h, respectively.

The trend of the dimensionless tensile strength follows the trend of the dimensionless elongation at break for all the films, see Figure 3. The vF/rF blend and multilayer vF/rF/vF films show significantly higher values of the tensile strength that the rF film but they are lower than the values of the vF film.
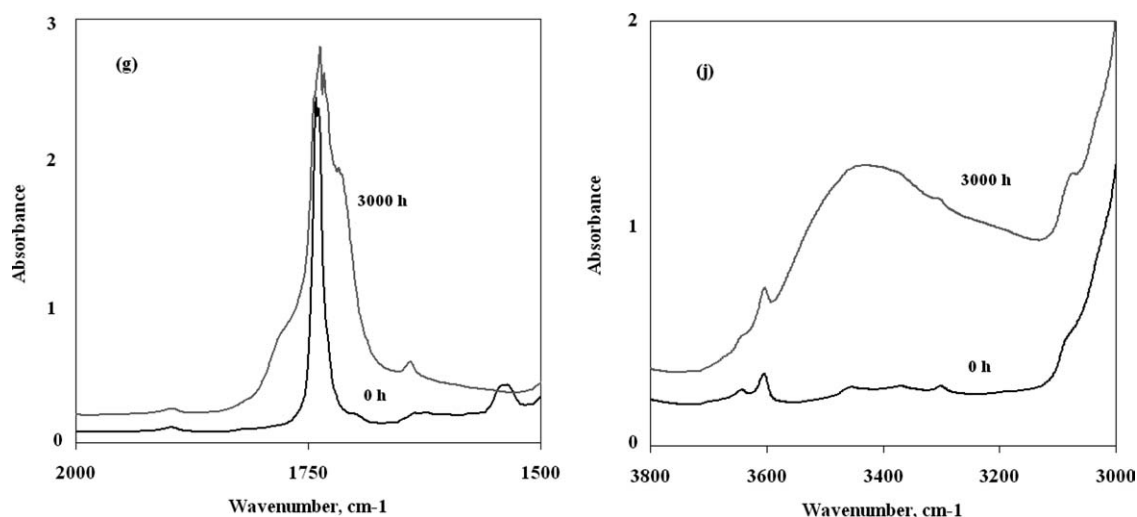
Figure 4   (*Continued.*)

The trend of the tensile strength as a function of the exposure time is influenced by the disposition of the same quantity of postconsumer materials, as in the elongation at break.

The FTIR analysis of all the films as a function of the exposure time were carried out and in Figure 4(a–j), the carbonyl and hydroxyl regions of FTIR spectra of all the investigated films: unexposed and at the maximum exposure time for each samples, are reported. The carbonyl and hydroxyl indices as a function of the exposure time for all the investigated samples has been calculated and reported in the Figures 5 and 6, respectively. The trends of the carbonyl and hydroxyl values are similar and are in complete agreement with the mechanical properties. It is interesting to highlight that the carbonyl and hydroxyl formation rate in multilayer vF/rF/vF film are slower than the formation rate in the rF and blend vF/rF and faster than the formation rate in the pristine vF. In fact, the presence of the virgin thin films

in the multilayer film formulation ensures that the oxygenated groups, coming from the postconsumer materials, are not directly involved in the photo-oxidation artificial aging. This causes a significant slow-down of the photo-oxidation process of the multilayer film that, however, remains faster than the photo-oxidation process of the pristine vF film.

The photo-oxidation rate of the films depends significantly on the intrinsic properties of the polymer (chemical nature and structure), on the oxygen permeability and on the possible presence of the oxygenated groups, that act as chromophore sites. This case study demonstrates that the photo-oxidation rate significantly depends on the initial oxygenated group concentration,[10] i.e., on the concentration and disposition of the initial chromophore sites. The total initial concentration of the oxygenated groups in both vF/rF blend and multilayer vF/rF/vF films is the same, while their disposition is different. The vF/rF blend film degrades faster than the vF film
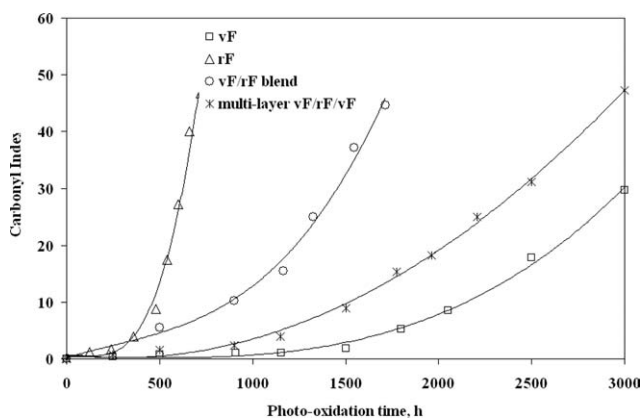

Figure 5   Carbonyl index of all the investigated films as a function of the photo-oxidation time.
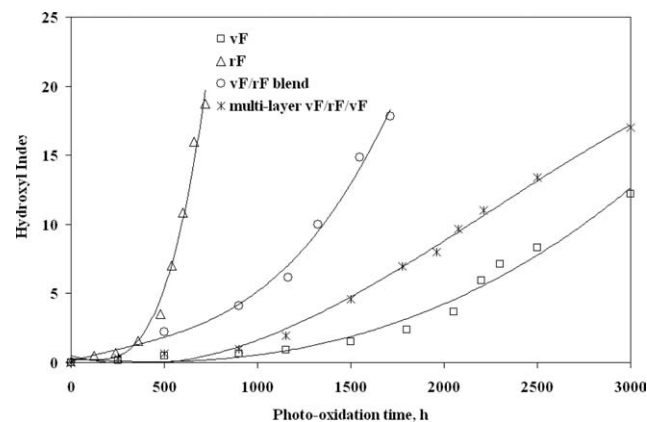

Figure 6   Hydroxyl index of all the investigated films as a function of the photo-oxidation time.

because the chromophore sites are contained into the whole bulk and cause a significant prodegradant effect. On the contrary, the presence of the two thin virgin polyethylene layers in the multilayer film reduces the photo-oxidation rate with respect to the blend but remains faster than that of the virgin film. These results highlight the relevance of the disposition of the cromophore sites in the film formulation and give useful information about the photo-oxidation resistance of the film containing postconsumer materials.

The interpretation of this result can be connected with both the low thickness of the external layer and with the oxygen permeability of the PE. Indeed, the UV radiation can reach, because of the low thickness, the internal recycled layer and the presence of oxygen gives rise to the photo-oxidation whose rate is strongly enhanced by the presence of oxygenated groups in the recycled layer at the interface between the virgin and postconsumer materials.

CONCLUSIONS

All the obtained results suggest that the multilayer-structure of films made by using the postconsumer polymer in the central layer leads to greenhouse coverage films with suitable properties for several agricultural applications. The multilayer vF/rF/vF films show several good performances, among them, improved photo-oxidation resistance and good mechanical properties. The photo-oxidation resistance of the multilayer film is similar to the resistance of the polyethylene film and it is significantly superior than the resistance of film formulated by blending of the virgin and postconsumer materials. The presence of the oxygenated group only in the central layer of the multilayer vF/rF/vF film, and not directly involved in the photo-oxidation reaction during the accelerate artificial aging, suggests a beneficial use of the postconsumer polymer.

References

1. La Mantia, F. P. In Recycling of PVC and Mixed Plastics; La Mantia, F. P., Ed.; ChemTec Publishing: Toronto, 1996.
2. Scott, G. Polym Degrad Stab 1995, 48, 315–324.
3. Scheirs, J., Ed. Polymer Recycling; Wiley: England, 1998.
4. Ranby, B., Rabek, J. F. Photdegradation, Photo-oxidation and Photostabilization of Polymers, Wiley: England, 1975.
5. Davis, A.; Sims, D.; Eds. Weathering of Polymers; Applied Science Publisher Ltd: England, 1983.
6. La Mantia, F. P. Polym Degrad Stab 1994, 42, 213–218.
7. Ma, W. G.; La Mantia, F.P. Polym Recycling 1995, 1, 69–75.
8. Tzankova Dintcheva, N.; La Mantia, F. P.; Acierno, D.; Di Maio, L.; Camino, G.; Trotta, F.; Luda, M. P.; Paci, M. Polym Degrad Stab 2001, 72, 141–146.
9. La Mantia, F. P.; Tzankova Dintcheva, N. J Appl Polym Sci 2004, 91, 2244–2255.
10. La Mantia, F. P.; Tzankova Dintcheva, N. Plastic, Rubber and Composites: Macromol Eng 2004, 33, 184–186.
11. Drake, W. O.; Franz, T.; Hoffmann, P.; Sitek, F. Recycle '91, Davos (Swiss), 1991.
12. Sitek, F. A.; Todesco, R.; Hoffmann, K. Recycle '92, Davos (Swiss), 1992.
13. Kartalis, C. N.; Papaspyrides, C. D.; Pfaendner, R. Polym Degrad Stab 2000, 70, 189–197.
14. Khan, J. H.; Halim Hamid, J. Polym Degrad Stab 1995, 48, 137–142.
15. Marrone, M.; La Mantia, F. P. Polym Recycling 1996, 2, 9–15.
16. Tzankova Dintcheva, N.; La Mantia, F. P.; Scaffaro, R.; Paci, M.; Acierno, D.; Camino, G. Polym Degrad Stab 2002, 75, 459–464.
17. La Mantia, F. P.; Curto, D.; Scaffaro, R. J Appl Polym Sci 2002, 86, 1899–1903.
18. Basfar, A. A.; Idriss Ali, K. M.; Mofti, S. M. Polym Degrad Stab 2003, 82, 229–234.
19. La Mantia, F. P.; Tzankova Dintcheva, N. Macromol Rapid Commun 2005, 26, 361–364.
20. La Mantia, F. P.; Tzankova Dintcheva, N. Macromol Mater Eng 2005, 290, 970–975.
21. Scaffaro, R.; Tzankova Dintcheva, N.; La Mantia, F. P. Polym Degrad Stab 2006, 91, 3110–3116.
22. Adam, A.; Kouider, S. A.; Youssef, B.; Hamou, A.; Saiter, J. M. Polym Testing 2005, 24, 834–838.
23. Dintcheva, N. Tz.; La Mantia, F. P. In Special Topics on Materials Science and Technology: An Italian Panorama; Acierno, D., D'Amore, A., Caputo, D., Cioffi, R., Eds.; Brill: The Netherlands, 2009.