ELSEVIER

Optical Materials 17 (2001) 437–442

OPTICAL Materials

www.elsevier.com/locate/optmat

Optical properties of $CaCO_3$-filled poly(ethylene-co-vinyl acetate) films

Alicia Larena, Marcelo A. Villar *,[1]

Departamento de Ingeniería Química Industrial, E.T.S.I. Industriales, Universidad Politécnica de Madrid, José Gutierrez Abascal 2, 28006 Madrid, Spain

Received 6 July 2000; accepted 5 February 2001

Abstract

Optical properties, such as transmittance and diffuse reflectance in the range of 200–800 nm, of hot-pressed films of poly(ethylene-co-vinyl acetate) filled with up to 10 wt% of calcium carbonate were analyzed. A linear relationship between optical properties and film thickness was found for these composites. In the range of compositions analyzed, transmittance of films decreases with an increasing in the filler content following an exponential law. The amount of decreasing can also be related to the average statistics particle diameter for a constant weight fraction of added filler by a square root law. Diffuse reflectance of the films was very low in the visible zone and increases considerably in the UV zone.

PACS: 78.20.–e; 78.90.+t

Keywords: Optical properties; Composites; Diffuse reflectance; Transmittance; EVA

1. Introduction

Considerable quantities of minerals are used as functional fillers in plastics and rubbers. The addition of inorganic fillers constitutes an important way of modification of polymeric materials. The range of minerals used includes calcium carbonate, dolomite, kaolin, talc, silica, alumina trihydrate, feldspar, mica, and wollastonite, among others [1,2].

There have been many studies on melt viscoelasticity and mechanical properties of commodity polymers such as polyethylene, polypropylene, polystyrene, and some copolymers filled with calcium carbonate [3–10], glass fibers [4], mica and talc [11]. However, optical properties of filled polymers have not been analyzed with the same extension.

Optical properties, like total and diffuse transmittance, are of great importance for some applications such as packaging and architectural glasses, among others. In the packaging of materials polymers are being extensively used in the form of films. These films must meet a number of specifications such as total transmittance over a

* Corresponding author. Tel.: +54-291-486-1700; fax: +54-291-486-1600.

E-mail addresses: alarena@iqi.etsii.upm.es (A. Larena), mvillar@plapiqui.edu.ar (M.A. Villar).

[1] Present address: Planta Piloto de Ingenieria Quimica, PLAPIQUI (UNS-CONICET) C.C. 717, (8000) Bahia Blanca, Argentina.

0925-3467/01/$ - see front matter
PII: S0925-3467(01)00063-5

particular spectral range or prespecified values of transparency or opacity. In spite of the importance of optical characteristics in end-use applications, there is little published on polymeric films [12–16].

In this paper, we present results on optical properties, such as transmittance and diffuse reflectance in the range of 200–800 nm (UV–VIS), of hot-pressed films of poly(ethylene-co-vinyl acetate) filled with calcium carbonate.

2. Experimental

Solid state mixtures of poly(ethylene-co-vinyl acetate) (EVA) (Repsol, Spain) and calcium carbonate (Clarianacal, Spain) of 5 and 10 μm of average statistics particle diameter were prepared. An EVA in powder form with an 18 wt% of vinyl acetate was used. The thermal characterization of the polymer was carried out in a Mettler–Toledo Differential Scanning Calorimeter (DSC). The melting temperature (T_m) obtained was 88.2°C with an enthalpy of fusion (ΔH) of 72.9 J/g. The calcium carbonate utilized corresponds to crystallized calcite of high purity. Table 1 shows the nomenclature and composition of the composites studied.

Films of prepared mixtures were hot-pressed for 5 min at 220 bar and 110°C using a pneumatic-press. The material was placed between two films of PET and two aluminum foils. Thickness of molded films ranged from 50 to 150 μm. For each blend four to five films were prepared and at least six rectangles of 2.5 cm × 3 cm were cut from them for optical property measurements. The average thickness of each rectangle was obtained from five measurements (the center and the four corners).

Diffuse transmittance or diffuse reflectance of the films was obtained, in the UV–VIS range (200–800 nm), employing a Cary 1E spectrophotometer with an integrating sphere accessory. White paper was used as a reference and spectra of the samples were taken using the white paper as a background. Fig. 1 shows the UV–VIS spectra in the diffuse reflectance mode of the reference and some of the composites analyzed. Transmittance was measured in four points of the film using the same spectrophotometer with a moving accessory. Fig. 2 shows the UV–VIS spectra in the transmittance mode for

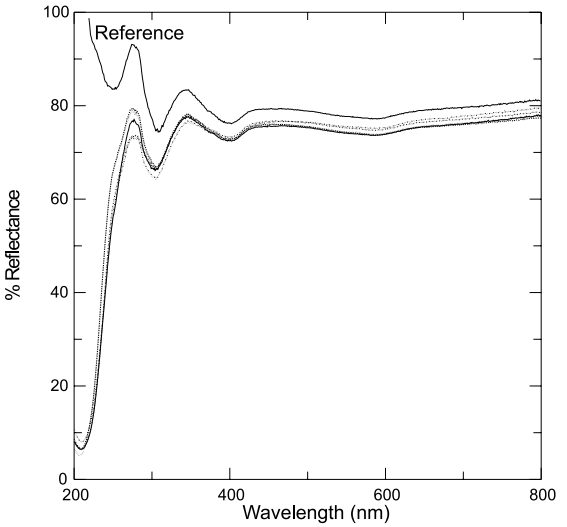

Fig. 1. UV–VIS diffuse reflectance spectra of $CaCO_3$-filled EVA films. Thickness of the films is approximately 70 μm. Symbols: (——) white paper (reference), (—) EVA, (- - - -) C5-01, (···) C5-02, (-.-.-) C5-05, and (-..-..-) C5-10.

Table 1
Nomenclature and composition of films analyzed

Composite	$CaCO_3$ used (μm)	wt% Polymer	wt% $CaCO_3$
C5-01	5	98.98	1.02
C5-02	5	97.99	2.01
C5-05	5	95.00	5.00
C5-10	5	90.01	9.99
C10-01	10	98.99	1.01
C10-02	10	97.99	2.01
C10-05	10	94.99	5.01
C10-10	10	90.00	10.00

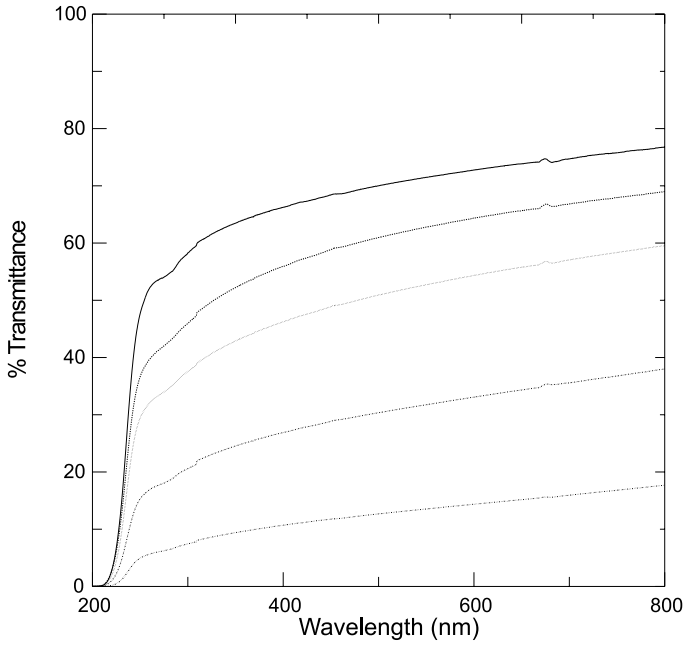

Fig. 2. UV–VIS transmittance spectra of $CaCO_3$-filled EVA films. Thickness of the films is approximately 70 μm and $CaCO_3$ of 5 μm. Symbols: (——) EVA, (- - - -) C5-01, (· · ·) C5-02, (- . - . -) C5-05, and (- . . - . . -) C5-10.

the mixtures prepared with $CaCO_3$ of 5 μm average statistics particle diameter.

3. Results and discussion

Diffuse reflectance spectra were transformed by subtracting the white paper spectrum (reference) and the one corresponding to the samples. Transformed spectra can be interpreted as the attenuation in reflectance due to the polymeric film. A considerable attenuation of the white paper can be observed in the UV and near visible, while little attenuation appears in the VIS and near infrared zone (Fig. 3). In order to analyze the influence of film thickness and amount of filler added to the polymer on diffuse reflectance, wavelengths of 250 nm (UV) and 600–800 nm (VIS) were chosen. Attenuated diffuse reflectance is almost constant in the range of 600–800 nm, then an average of the values in this zone was calculated. A lineal dependency with film thickness was observed for all material as can be seen in Figs. 4–8 for the original polymer and the composites with different amounts of filler. Values of attenuated diffuse reflectance as a function of film thickness were fitted with straight lines

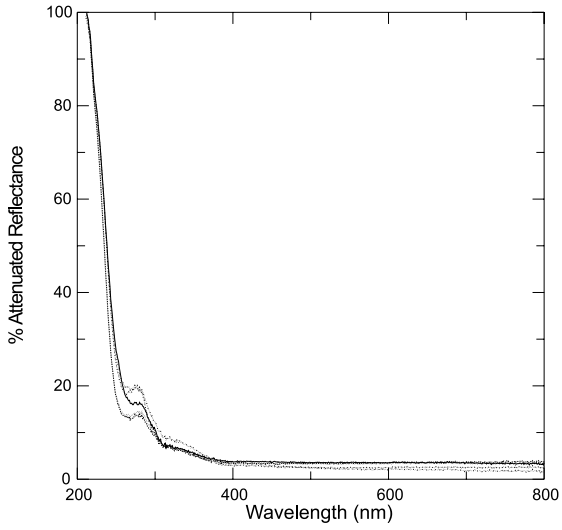

Fig. 3. UV–VIS attenuated diffuse reflectance spectra of $CaCO_3$-filled EVA films. Thickness of the films is approximately 70 μm. Symbols: (——) EVA, (- - - -) C5-01, (· · ·) C5-02, (- . - . -) C5-05, and (- . . - . . -) C5-10.

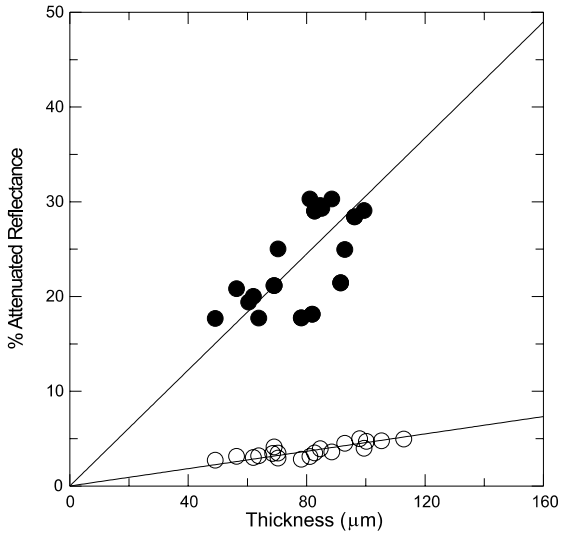

Fig. 4. Attenuated diffuse reflectance as a function of film thickness. Material: poly(ethylene-co-vinyl acetate) (EVA). Symbols: (●) $\lambda = 250$ nm and (○) $\lambda = 600$–800 nm.

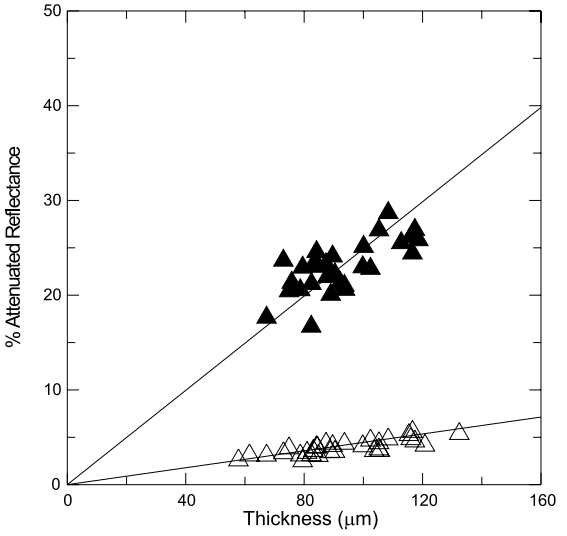

Fig. 6. Attenuated diffuse reflectance as a function of film thickness. Materials: composites of poly(ethylene-co-vinyl acetate) with 2 wt% of $CaCO_3$ (C5-02 and C10-02). Symbols: (▲) $\lambda = 250$ nm and (Δ) $\lambda = 600$–800 nm.

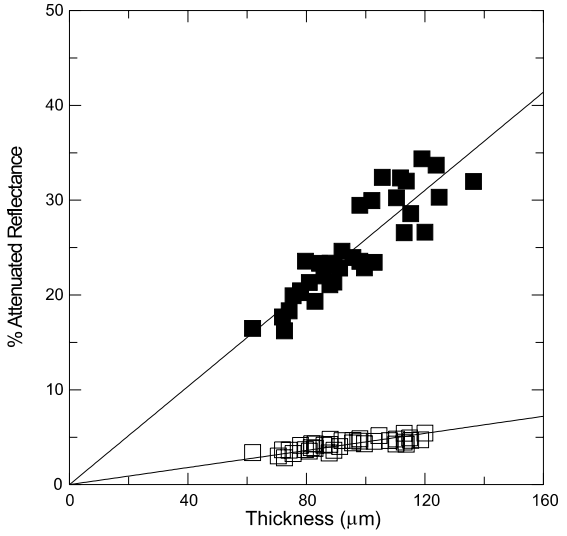

Fig. 5. Attenuated diffuse reflectance as a function of film thickness. Materials: composites of poly(ethylene-co-vinyl acetate) with 1 wt% of $CaCO_3$ (C5-01 and C10-01). Symbols: (■) $\lambda = 250$ nm and (□) $\lambda = 600$–800 nm.

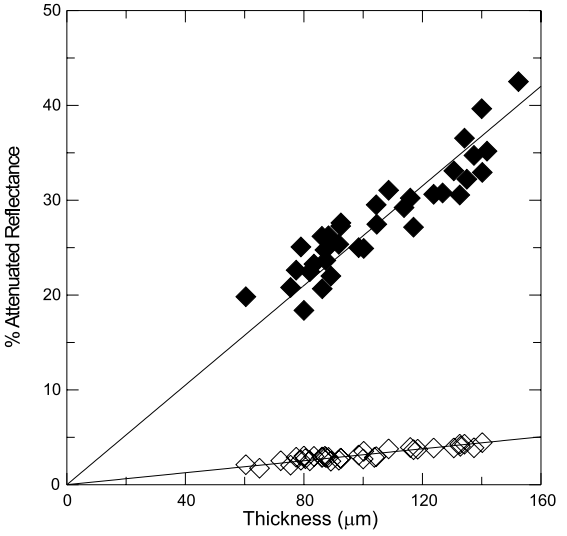

Fig. 7. Attenuated diffuse reflectance as a function of film thickness. Materials: composites of poly(ethylene-co-vinyl acetate) with 5 wt% of $CaCO_3$ (C5-05 and C10-05). Symbols: (◆) $\lambda = 250$ nm and (◇) $\lambda = 600$–800 nm.

through the origin. Table 2 shows the values of the slope of attenuated diffuse reflectance and the square of correlation coefficient (r^2) as a function of the filler content in the film. It was found that $CaCO_3$ particle size has not influence on diffuse reflectance values.

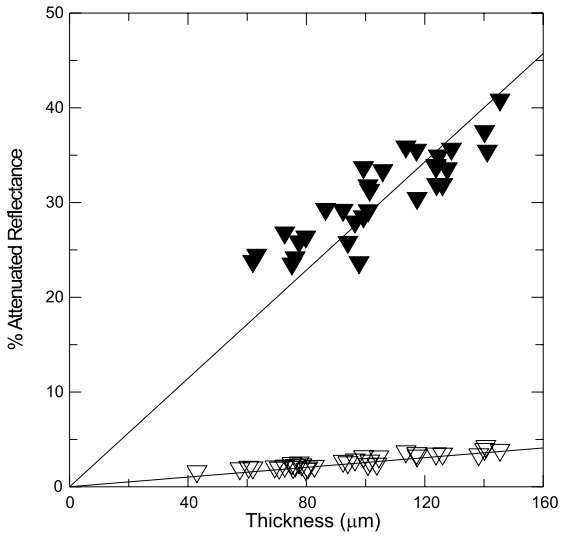

Fig. 8. Attenuated diffuse reflectance as a function of film thickness. Materials: composites of poly(ethylene-co-vinyl acetate) with 10 wt% of $CaCO_3$ (C5-10 and C10-10). Symbols: (▼) $\lambda = 250$ nm and (▽) $\lambda = 600$–800 nm.

An increase in the amount of filler gives an increase in the diffuse reflectance with respect to the unfilled polymer in the range of 600–800 nm. In other words, a decrease in the attenuated diffuse reflectance is observed. At 250 nm a minimum in the attenuation is observed for the blends containing 2 wt% of $CaCO_3$. The functional dependence of attenuated diffuse reflectance with the amount of $CaCO_3$ suggests the action of two competitive process: one with inverse decrease, and other with a lineal increase. This mechanism is more evident in the UV zone.

Transmittance spectra of the films were also studied at two wavelengths: 250 nm (UV) and 600 nm (VIS). For all the materials a lineal dependence of transmittance with film thickness was also observed. In this case, straight lines with negative slope were obtained. The intercepts of these lines, representing the transmittance extrapolated to zero thickness, are shown in Table 3. A considerable decrease in transmittance of the films appears

Table 2
Slope of attenuated diffuse reflectance as a function of filler content

Sample	wt% $CaCO_3$	$\lambda = 250$ nm		$\lambda = 600$–800 nm	
		Slope	r^2	Slope	r^2
EVA	0	0.3062	0.976	0.0458	0.986
C5-01 and C10-01	1	0.2587	0.992	0.0450	0.990
C5-01 and C10-01	2	0.2489	0.989	0.0446	0.987
C5-01 and C10-01	5	0.2616	0.992	0.0316	0.993
C5-01 and C10-01	10	0.2858	0.988	0.0256	0.989

Table 3
Percentage of transmittance extrapolated to zero film thickness as a function of filler content

Sample	wt% $CaCO_3$	$CaCO_3$ particle diameter (μm)	% T	
			$\lambda = 250$ nm	$\lambda = 600$ nm
EVA	0	–	65.2	95.4
C5-01	1	5	51.0	83.9
C5-02	2	5	43.9	76.0
C5-05	5	5	27.4	49.6
C5-10	10	5	11.2	25.8
C10-01	1	10	56.7	91.0
C10-02	2	10	49.0	84.8
C10-05	5	10	31.5	60.4
C10-10	10	10	14.1	35.3

as the amount of $CaCO_3$ increases. In the range of compositions analyzed an exponential dependence of transmittance with filler content was found. On the other hand, at a constant concentration of filler, transmittance of the films is lower for blends containing $CaCO_3$ with average particle diameter of 5 μm. This can be directly attributed to the number of filler particles present in the composite taking into account the geometrical effect introduced by the effective section of the particles. A square root law can express the dependence of transmittance with average particle diameter.

4. Conclusions

A linear relationship between optical properties, such as transmittance and diffuse reflectance, and film thickness was observed for $CaCO_3$-filled EVA films. Transmittance of the films decreases with an increasing in the filler content. The decreasing in transmittance with the amount of filler added to the composites can be expressed, in the range of compositions analyzed, by an exponential function. On the other hand, the dependence of transmittance with average particle diameter follows a square root law. Diffuse reflectance of the films was very low in the visible zone and a slight increase with $CaCO_3$ content can be noticed. A higher diffuse reflectance appears in the UV zone, where the evidence of two competitive processes can be secured.

References

[1] A.J. Gwinn, L.M. Castagno, Plastics Eng., December'85 (1985) 27.
[2] J.B. Griffiths, Plastics Rubber Process. Appl. 13 (1990) 3.
[3] T. Kataoka, T. Kitano, Y. Oyanagi, M. Sasahara, Rheol. Acta 18 (1979) 635.
[4] T. Kitano, T. Kataoka, T. Nishimura, T. Sakai, Rheol. Acta 19 (1980) 764.
[5] J. Jančář, J. Kučera, Polym. Eng. Sci. 30 (1990) 707.
[6] L. Li, T. Masuda, Polym. Eng. Sci. 30 (1990) 841.
[7] Q. Fu, G. Wang, Polym. Eng. Sci. 32 (1992) 94.
[8] J. Jančář, A. Dianselmo, A.T. Dibenedetto, Polym. Eng. Sci. 32 (1992) 1394.
[9] Q. Fu, G. Wang, C. Liu, Polymer 36 (1995) 2397.
[10] S.C. Tjonk, R.K.Y. Li, T. Cheung, Polym. Eng. Sci. 37 (1997) 166.
[11] J.P. Trotignon, L. Demdoum, J. Verdu, Composites 23 (1992) 313.
[12] F.C. Stehling, C.S. Speed, L. Westerman, Macromolecules 14 (1981) 698.
[13] H. Ashizawa, J.E. Spruiell, J.L. White, Polym. Eng. Sci. 24 (1984) 1035.
[14] A. Larena, G. Pinto, Spectros. Lett. 24 (1991) 1287.
[15] E. Bernabeu, J.M. Boix, A. Larena, G. Pinto, J. Mater. Sci. 28 (1993) 5826.
[16] P.F. Smith, I. Chun, G. Liu, D. Dimitrievich, J. Rasburn, G.J. Vancso, Polym. Eng. Sci. 36 (1996) 2129.