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Crystallinity of filled compositions of low-density polyethylene and poly(ethylene-co-vinyl acetate)

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Abstract

Low-density polyethylenes and poly(ethylene-co-vinyl acetate)s containing talc, Al_2O_3 and $Al_2O_3 \cdot n\ H_2O$ were studied by differential scanning calorimetry and density measurements to study the relationships between crystallinity, filler type and filler content. The fillers were characterised by n-hexane adsorption measurements, optical microscopy and densitometric measurements. Mass crystallinity decreased in an almost linear manner with increasing filler content. The decrease in mass crystallinity was proportional to the total surface area of the fillers for both types of polymers with a significantly stronger decrease for poly(ethylene-co-vinyl acetate) than for low-density polyethylene. It is suggested that this behaviour reflects adsorption of the polymer molecules at the filler particle surface leading to reduced interfacial crystallinity.

1. INTRODUCTION

Polyethylene and poly(ethylene-co-vinyl acetate) containing mineral powder fillers are extensively used in multilayer anticorrosive coatings [1,2]. It was shown in an earlier study that the density of the polymer component decreased in the filled compositions [3]. The magnitude of the density decrease was found to depend on filler type and on the specific surface area of the filler particles [3]. Later work using infrared spectroscopy indicated that the decrease in polymer density in the filled systems was due to a decrease in polymer crystallinity [4]

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The decrease in crystallinity obtained from the infrared spectroscopy was in agreement with the corresponding values obtained by density measurements [4]. Both these measurement suffered however from the risk of being influenced by artefacts: the density measurements from remaining micro-voids and the infrared spectroscopy measurements from interfering absorption bands originating from the filler material. This paper presents data from differential scanning calorimetry (DSC), a technique which provide accurate crystallinity data, and the measured crystallinity values are compared with the corresponding data obtained by density measurements.

2. EXPERIMENTAL

Commercial grades of low-density polyethylene,11503-070 (USSR), and a commercial grade of poly(ethylene-co-vinyl acetate) with a vinyl acetate content of 6.6% (w/w), D-13-EA Mirawitten (Germany), were used with talc, Al_2O_3 (A1) and $Al_2O_3 \cdot nH_2O$ (A2,A3) The aluminium oxide fillers were prepared by thermo-dehydration of $Al(OH)_3$. All fillers used were characterised by light microscopy, n-hexane adsorption measurements, and densitometric measurements and these data are presented in Table 1.

Table 1.
Characteristics of the fillers

Filler	ρ (kg m^{-3})	$\langle r \rangle$ (μm)	r_{min}/r_{max}	$S_0 x 10^{-3}$ (m^2 kg^{-1})
talc	2750	3.6	0.070	6
A1	3970	6.0	0.085	37
A2	3110	1.2	0.070	75
A3	2770	1.4	0.032	120

ρ is the density; $\langle r \rangle$ is the average radius of filler particles (light microscopy); r_{min}/r_{max} is the polydispersity of particle size (light microscopy); S_o is the specific surface area (n-hexane adsorption measurements applying the BET theory)

Filled polymer samples ranging from 0.01 to 0.50 in filler mass content were obtained by melt mixing for 15 min of the polymer and dry filler mixture in a two-roll equipment. Sheet samples were made by compression moulding, the melt being cooled at a rate of 10 K min^{-1}.

Density at 293 K was measured in a density gradient column as described in ref.[5]. Water, ethanol and a zinc chloride solution were used as column liquids. The accuracy of the method was 1 kg m^{-3}. The apparent density of polymer ρ_p was calculated using the equation:

$$\rho_p = \frac{1-w_f}{\left(\frac{1}{\rho_s} - \frac{w_f}{\rho_f}\right)} \qquad (1)$$

where w_f is the mass fraction of filler, ρ_s is the density of the sample and ρ_f is the density of the filler material. The mass crystallinity (w_c) values of the polymer component were then calculated according to:

$$w_c = \frac{\left(\frac{1}{\rho_p} - \frac{1}{\rho_c}\right)}{\left(\frac{1}{\rho_a} - \frac{1}{\rho_c}\right)} \qquad (2)$$

where ρ_a and ρ_c are the densities of the amorphous and crystalline components. The following values for the room temperature densities taken from ref. [6] were used: ρ_a= 855 kg m^{-3} and ρ_c = 999 kg m^{-3}.

The melting endotherms were obtained in a Perkin-Elmer DSC-4 at a heating rate of 10 K min^{-1} and the recorded values of heat of fusion ΔH_f were transformed into mass crystallinity w_c using the total enthalpy method [7], considering 293 kJ kg^{-1} as the heat of fusion (Δh_f^o) for 100% crystalline polymer at the equilibrium melting point (418.1 K) [8]:

$$w_c = \frac{\Delta h_f}{(1-w_f)\left(\Delta h_f^o - \int_{T_1}^{418.1}\left(c_{pa} - c_{pc}\right) dT\right)} \qquad (3)$$

where T_1 is an arbitrary temperature below the melting range, and c_{pa} and c_{pc} are the specific heats of the amorphous and 100% crystalline phases, respectively. Data for c_{pa} and c_{pc} of Wunderlich and Baur [9] have been used.

3. RESULTS AND DISCUSSION

The decrease in mass crystallinity as determined by DSC with increasing filler content is virtually linear as shown in Figure 1. The slopes for the different combinations of polymer and fillers are different with a greater crystallinity decrease for fillers of larger specific surface areas (A3>A2>A1). The crystallinity decrease is also greater for poly(ethylene-co-vinyl acetate) (EVA) than for low-density polyethylene (LDPE), in both cases combined with filler A1. The decrease in crystallinity in the talc-containing polymer is very small. A few of the data points originating from systems with the highest filler content deviate significantly from the overall linear trend in the crystallinity -

filler content data. It is not clear whether this is a "true" physical effect or whether it is attributed to experimental error.

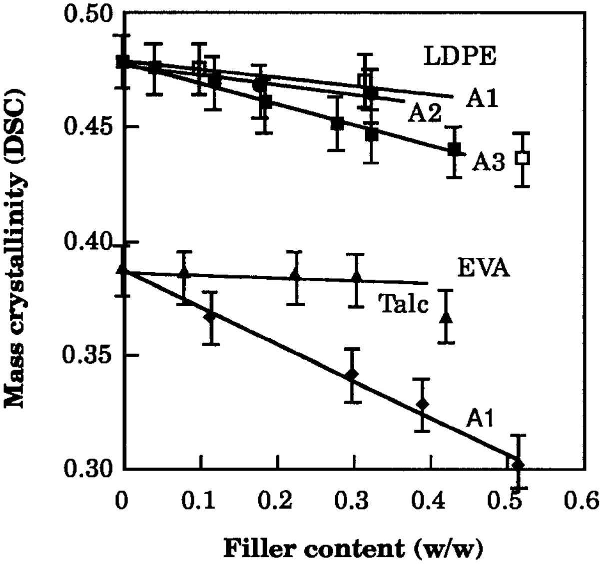

Figure 1. Mass crystallinity by DSC as a function of filler content: ❑ LDPE/A1; ● LDPE/A2; ■ LDPE/A3; ◆ EVA/A1; ▲ EVA/talc

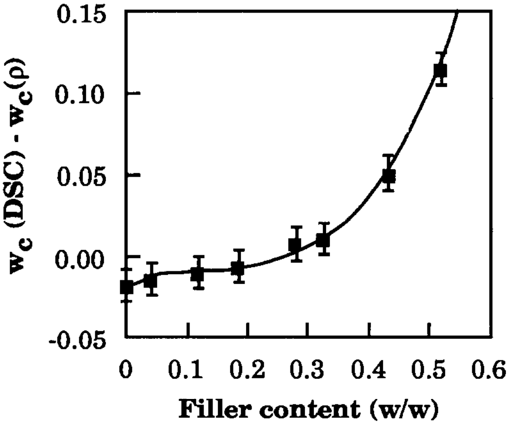

Figure 2. Difference in measured mass crystallinity by DSC (eq. (3)) and by density measurement (eqs. (1) and (2)) for LDPE/A3 as a function of filler content.

Figure 2 shows for one of the series of systems (LDPE in combination with filler A3) that there is good agreement between crystallinity data obtained by DSC and by density measurements for systems with filler contents less than 0.3 (w/w). The apparent "density-crystallinity" is however much lower than the "DSC-crystallinity" for samples of greater filler content (Figure 2). The same trend was found in all the systems of polymers/fillers studied. This deviation is most probably due to the presence of micro-voids in the systems with higher filler content.

Figures 3 and 4 show that the crystallinity decrease is approximately proportional to the filler surface area of the samples. The data for the LDPE systems filled with aluminium oxide (A1-A3) fall essentially on the same line in Figure 3. The reason for the only minor decrease in crystallinity recorded for EVA filled with talc is the small contact area between polymer and filler (Figure 4).

The decrease in mass crystallinity for a given increase in filler area is clearly different for the two polymers (Figs. 3 and 4). The slopes are 8.45 x 10^{-5} kg m^{-2} (LDPE) and 4.277 x 10^{-4} kg m^{-2} (EVA).

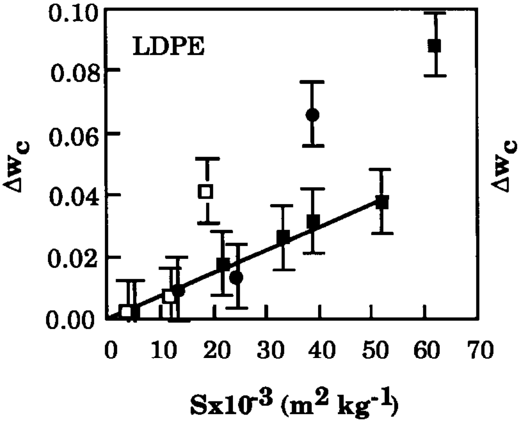

Figure 3. Decrease in w_c (with reference to unfilled polymer) as a function of the total filler surface area for low-density polyethylene (LDPE): □ A1; ● A2; ■ A3

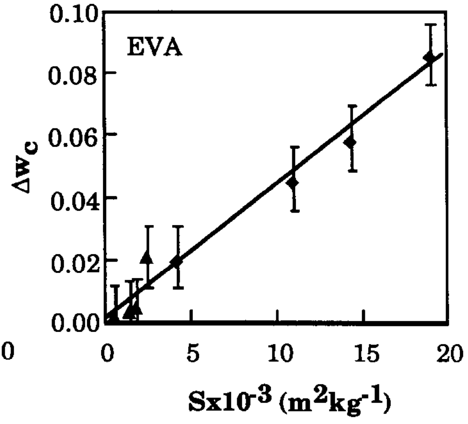

Figure 4. Decrease in w_c (with reference to unfilled polymer) as a function of the total filler surface area for poly(ethylene-co-vinyl acetate) (EVA): ◆ A1; ▲ talc

The reason for the crystallinity decrease in the filled polymer samples can at this stage only be speculated on. It can be explained by the formation of an adsorbed layer of polymer at the filler particle interfaces, the crystallisation being fully or partially inhibited in the adsorbed layers. It is likely that the greater polarity of the poly(ethylene-vinyl acetate) compared with polyethylene leads to more interaction between polymer and filler surface and hence a greater effect on the crystallinity.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

1. A.Varkalis, I. Brants, I. Jaunromans and A. Metra, Plastics (USSR), 2 (1985) 37.
2. L. Malers, A.Varkalis, A. Jansons and S. Lemberga, Modification of Polymer Materials, Riga (1989) 4.
3. A. Varkalis, A. Metra and A. Kreituss, Modification of Polymer Materials, Riga (1984) 73.
4. A. Kreituss, V. Kronberga and A. Varkalis, Proc. Latvian Acad. Sci., Chem. Ser., 6 (1982) 695.
5. J. F. Rabek, Experimental Methods in Polymer Chemistry, Interscience, New York, 1980.
6. B. Wunderlich, Macromolecular Physics: Crystal Structure, Morphology, Defects, vol.1, Academic Press, New York, 1973.
7. A. P. Gray, Thermochim. Acta, 1 (1970) 563.
8. B. Wunderlich, Macromolecular Physics: Crystal Melting, vol. 3, Academic Press, New York, 1980.
9. B. Wunderlich and H. Baur, Adv. Polym. Sci., 7 (1970) 151.