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Structure and mechanical properties of polyethylene–fullerene composites

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The microhardness of films of fullerene–polyethylene composites prepared by gelation from semidilute solution, using ultrahigh molecular weight polyethylene (PE) (6×10^6), has been determined. The composite materials were characterized by optical microscopy and X-ray diffraction techniques. The microhardness of the films is shown to increase notably with the concentration of fullerene particles within the films. In addition, a substantial hardening of the composites is obtained after annealing the materials at high temperatures ($T_a = 130\,°C$) and long annealing times ($t_a = 10^5$ s). The hardening of the composites with annealing temperature has been identified with the thickening of the PE crystalline lamellae. Comparison of X-ray scattering data and the microhardness values upon annealing leads to the conclusion of phase separation of C_{60} molecules from the polyethylene crystals within the material. The temperature dependence is discussed in terms of the independent contribution of the PE matrix of the C_{60} aggregates to the hardness value.

1. Introduction

Since the discovery of methods for producing fullerenes in sufficiently large amounts [1], the possibility of developing superconducting and/or ferromagnetic salts has attracted much interest in recent years [2, 3]. Attempts to prepare fullerene containing polymers (polyesters, aminopolymers, etc.) by means of covalent attachment of substituents to the fullerene core using polycondensation reactions have been reported recently [4]. For the development of possible applications (electronic, optical or magnetic) large quantities of fullerenes are necessary. Polymers involving C_{60} are of interest because the fullerene properties can be combined with those of specific polymers. The main drawback of fullerene containing materials is, however, their limited availability. One possibility of overcoming partly this limitation and obtaining macroscopic structures having the properties of fullerene is by preparing C_{60} composites using polymer matrices. The study of the structure–property correlation within this context emerges as an important issue for the characterization of these composites. In particular, the measurement of microhardness (H), has proved to be a powerful method for the investigation of microstructural changes in synthetic polymers [5, 6]. Furthermore, it is well established that the hardness of polymers can be correlated directly with many of the macroscopic mechanical properties [7, 8]. Recent results show that the microhardness of polymer blends depends on composition and can provide information on the degree of interaction of the blend components [9, 10]. Thus, the authors believe that the microhardness measurements can be applied to fullerene–polymer composites to provide some relevant information on the structure–property correlation of these materials. Since the method can be used on small size samples, it represents an advantageous research tool to determine the mechanical properties of samples which are made on a small scale in a laboratory.

The aims of the present investigation are two-fold.

1. To examine the microstructure of C_{60} composites based on a linear polyethylene matrix and correlate it with their mechanical properties (microhardness).
2. To characterize the thermal behaviour of the composites by measuring the microhardness as a function of temperature.

2. Experimental procedure

2.1. Sample preparation

C_{60} fullerene samples were prepared by the arc-discharge method, which produces carbon soots under helium gas [1]. The C_{60} component was extracted from the carbon soots, and, then, purified by a Soxhlet extractor using benzene. Purification was checked by ^{13}C nuclear magnetic resonance (NMR) [11]. Sample films were produced by gelation crystallization from solution [12]. Some 0.5 g of ultrahigh molecular weight polyethylene (PE)

TABLE I C_{60} content in the composites for the original solution and for the dry films

Sample	Gel formation in polyethylene (g)	100 ml Xylene C_{60} (g)	Final content of C_{60} (g)	Final content of C_{60} (wt %)
0	0.5	–	–	–
I	0.5	0.0100	0.0053	1.06
II	0.5	0.0200	0.0092	1.84
III	0.5	0.0285	0.0128	2.56

($M_W = 6 \times 10^6$) were dissolved in 100 ml p-xylene at 135 °C under nitrogen gas. The composites were prepared by addition of C_{60} to the solution, resulting into a red coloured homogeneous mixture. Three different amounts of C_{60} were used to prepare the original mixtures (to be called samples I, II and III). The quantities used are listed in Table I. Sample 0 corresponds to the pure PE sample (without C_{60}). The homogenized solution was quenched at 0 °C in a 200 ml glass beaker surrounded by iced water to form a gel. The gel gradually became thinner by extracting the p-xylene containing C_{60}. Finally, a composite film of 0.5 mm in thickness was obtained after drying the gel for about two weeks. The extracted solution was stored for the estimation of the final content of C_{60} in the samples. The amount of extracted C_{60} was determined accurately by the absorption measurement of the solution. The final content of C_{60} in the composites was nearly half of the original amounts used as listed in Table I. Annealing of the dry composite films was carried out in glass tubes plunged in a silicon oil bath. The temperature of the annealing bath remained constant within ± 0.1 °C. The annealing time was varied from 10 to 10^5 s and the annealing temperature used was 130 °C, the highest possible temperature at which lamellar thickening occurred without partial melting of the crystals [13].

2.2. Techniques

The surface of the composite film was inspected by optical microscopy so that the zones rich in fullerene aggregates could be identified. X-ray diffraction measurements were made by a Rigaku rotating anode generator with 40 kV, 200 mA. Small angle X-ray scattering (SAXS) measurements were carried out using a point collimation camera of 0.15 mm in diameter, with a sample to film distance of 350 mm. The long period was derived applying Bragg's law to the scattering maxima after substraction of background scattering and application of the Lorentz correction.

Microhardness measurements were performed using a Leitz tester adapted with a square based diamond indenter. A loading cycle of 0.1 min to minimize the creep behaviour and loads of 1 and 2 N were used. The microhardness value was derived from the residual projected area of indentation according to the expression, $H = kP/d^2$ (MPa), where d is the length of

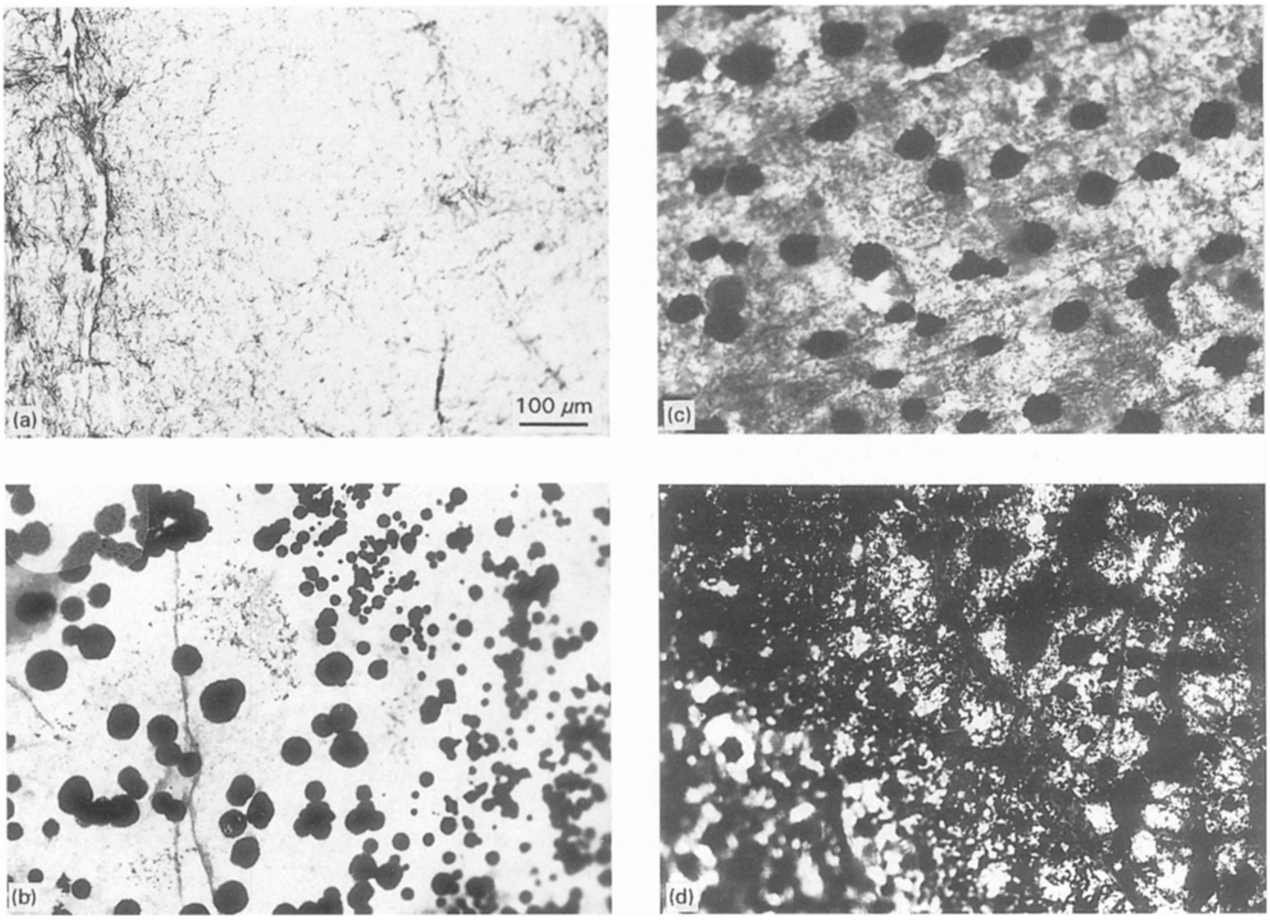

Figure 1 Optical micrographs of dry sedimental gel film (a) ultrahigh molecular weight polyethylene (sample 0) and C_{60}–PE composites with (b) 1.06% (sample I), (c) 1.84% (Sample II), and (d) 2.56% C_{60} content (sample III).

the impression diagonal in millimeters, P the contact load applied in Newtons and k is a geometrical factor equal to 1.854. The microhardness measurements were carried out as a function of temperature in a hot stage with a heat controller in the temperature range 20–95 °C [14]. Inorganic compounds of known melting temperatures were used to calibrate the hot stage to determine the real temperature on the surface of the samples.

3. Results and discussion

3.1. Structure and morphology

Optical micrographs of the original PE samples and of the various C_{60}–PE composites are shown in Fig. 1. The surface of the dry gel films investigated is clearly covered by dark patches of C_{60} aggregates (see Fig. 1). Inspection of the films indicates that the C_{60} aggregates are concentrated on the surface of the composites. The average size of the aggregates is 30 μm in sample I and 50 μm in sample II, while the surface of sample III is thickly covered by C_{60} particles. During the gelation process from solution, the C_{60} molecules are presumably separated from the polyethylene matrix. Hence, on extraction of *p*-xylene from the gel, the C_{60} molecules tend to concentrate and produce large scale C_{60} aggregates. The drying of the gel induces a final accumulation of the C_{60} buckyballs into aggregates that protrude out of the surface of the composite film.

Since the diameter of single C_{60} buckyballs is of about 0.7 nm, inclusion of these molecules in the PE crystal lattice would produce large distortions within the crystals. Wide angle X-ray diffraction patterns of the samples I, II and III indicate, however, that the crystalline structure of polyethylene is not affected by addition of the C_{60} molecules. This result strongly suggests that the polyethylene crystals and the C_{60} aggregates are phase separated during gelation.

The SAXS patterns of the composites show no evidence of scattering from the C_{60} particles. The appearance of meridional maxima in the SAXS pattern of the composite confirms the stacking of the PE lamellae parallel to the film surface. The long spacings of the stacked lamellae, measured for the samples annealed at 130 °C at different annealing times, are shown in Fig. 2. Neither the lamellar orientation nor the molecular orientation changed during the annealing treatment [13]. Results show that the long spacing increases linearly with the logarithm of the annealing time for the samples with various C_{60} concentrations. Most important is the fact that the long spacings are not affected by the C_{60} content, indicating that the thickening of the polyethylene lamellae occurs independently of the presence of the C_{60} aggregates.

From the X-ray diffraction results together with the microscopy observations, one can conclude that neither interaction at a molecular nor at a lamellar level between polyethylene and C_{60} occurs. One may expect that during the gelation process from the homogenized solution, the C_{60} buckyballs are separated from the polyethylene texture, forming aggregates within and at the surface of the composite.

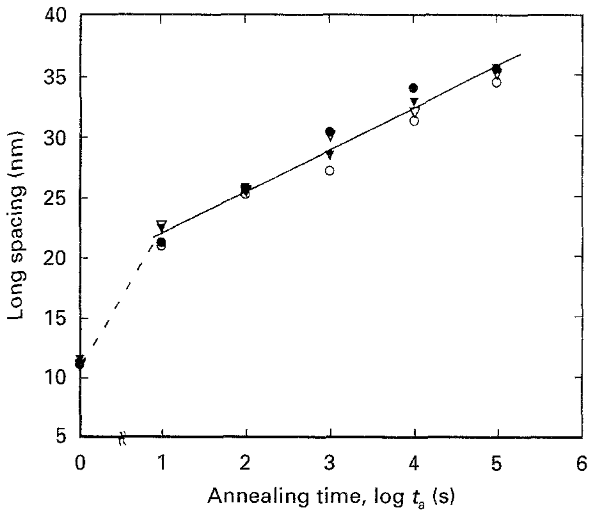

Figure 2 X-ray long period for the different dry gel film C_{60}–PE composites as a function of annealing time t_a, for annealing temperature, T_a = 130 °C. (○) sample 0, (●) sample I, (▽) sample II, (▼) sample III.

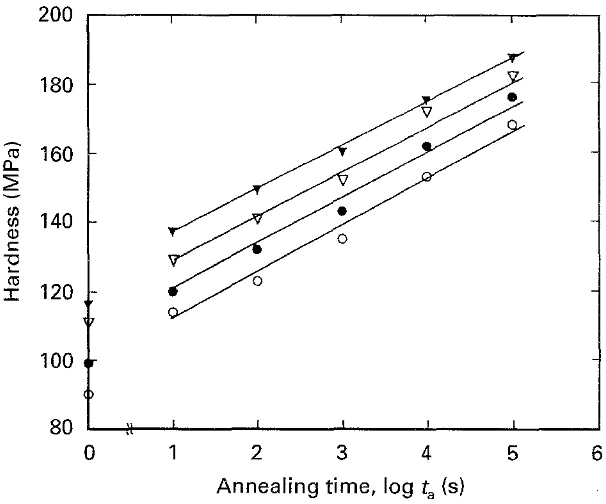

Figure 3 Plot of microhardness, H, for the various C_{60}–PE composites as function of log t_a, with T_a = 130 °C: (○) sample 0, (●) sample I, (▽) sample II, (▼) sample III.

3.2. Mechanical properties

The micrographs of Fig. 1 reveal that the C_{60}–PE composites, namely samples I, II and III, are highly inhomogeneous. Consequently, microhardness measurements were carried out using loads of 1 and 2 N, so that large indentations (~ 100–140 μm in size) covering, both the polyethylene matrix and the C_{60} aggregates could be made. The H-increase with log t_a for the pure polyethylene samples (0 series) is similar to that reported in a preceding study [13]. The increase in hardness, in this case, can be attributed to the thickening of the polyethylene lamellae with increasing annealing time, which is also supported by the increase of the long spacing as shown in Fig. 2.

Fig. 3 shows that the increase of H with t_a for all the investigated composite samples follows a logarithmic variation of the type

$$H = K(\log t_a) \qquad (1)$$

where K is an increasing function of C_{60} concentration. However, in contrast with the SAXS results, from

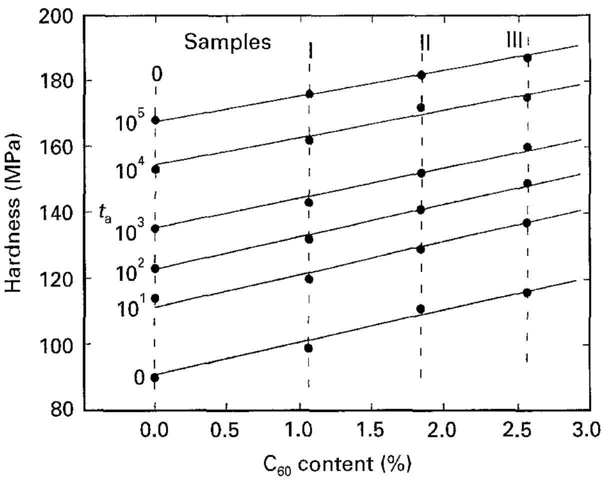

Figure 4 Plot of microhardness of C_{60}–PE composites annealed at $T_a = 130\,°C$ for various times, t_a, as a function of C_{60} content.

Fig. 3 it is evident that with increasing concentration of C_{60}, the hardness of the composite, for a given t_a also increases. This means that the hardness of the composites is a function of the concentration, ϕ, i.e. $H = f(\phi)$. However, the long spacings for samples I, II and III are not affected by the inclusion of C_{60} in the composites, supporting the lack of interaction between polyethylene and the C_{60} buckyballs. The experimental results shown in Fig. 4 emphasize the fact that H is a linear increasing function of the C_{60} concentration, ϕ (Fig. 4). Hence, one can write

$$H = H_f\phi + H_{PE} \tag{2}$$

which represents the equation of a straight line, where H_{PE} is the intercept of the plot and H_f is a constant related to the hardness of the fullerene particles. Since the samples are inhomogeneous, one has an uncertainty concerning the value of ϕ. This value is probably smaller than the local concentration of C_{60} particles where one is indenting the material's surface. Therefore, one cannot give any reliable value of the extrapolated hardness for $\phi = 1$, i.e. for pure C_{60}. Nevertheless, a clear rise of 30% in hardness, when adding about 2.5% C_{60} to the PE matrix is detected. Furthermore, the annealing of the material at $T_a = 130\,°C$ for 10^5 s leads to H values of ~ 190 MPa, which are near to the hardness value for crystalline polyethylene terephthalate [14].

Finally, the authors also wish to discuss the temperature dependence of the hardness in fullerene composites prepared in the following three different ways, namely

1. the original composite II,
2. composite II annealed at 110 °C for 10^3 s, and
3. composite II annealed at 130 °C for 10^4 s.

Results for the three composites show first a decrease in hardness with increasing temperature until 75 °C and, then, for $T > 75\,°C$ a conspicuous increase in hardness (see Table II). Fig. 5 shows that H follows an initial exponential decrease as a function of temperature given by

$$H = H_0 \exp[-\beta(T - T_0)] \tag{3}$$

where H_0 is the hardness measured at a given reference temperature T_0, and β is the coefficient of thermal softening. The latter is related to the thermal

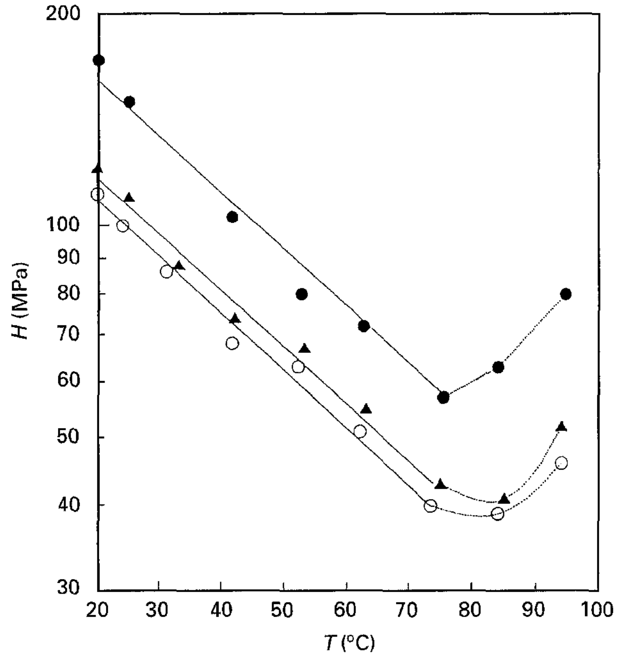

Figure 5 Variation in H as a function of temperature for C_{60}–PE composite II before (○) and after annealing at (▲) 110 and (●) 130 °C, respectively.

TABLE II Temperature dependence of microhardness for various composites

C_{60}–PE composite II		Composite II annealed at $T_a = 110\,°C$ for $t_a = 10^3$ s		Composite II annealed at $T_a = 130\,°C$ for $t_a = 10^4$ s	
T (°C)	H(MPa)	T (°C)	H (MPa)	T (°C)	H(MPa)
20	111	20	121	20	172
24	91	25	110	25	150
31	86	33	88	42	103
42	68	42	74	53	80
52	63	53	67	63	72
62	51	63	55	76	57
74	40	75	43	84	63
84	39	85	41	95	80
94	46	94	52	–	–

expansion coefficient of the material [15]. The present results show β values for the three samples which are equal to $\beta = 0.019$ MPa K^{-1}. This value is slightly higher than that found for pure melt crystallized PE ($\beta = 0.11$ MPa K^{-1}) [13]. The authors have suggested that the β value depends on the crystalline perfection of the polymer [13]. Hence, the slightly higher β values obtained for the composites of the present study may be connected with their lower thermal stability owing to the presence of buckyballs within the material.

Since hardness for polyethylene has been shown to be an exponential decreasing function with temperature [13], the positive hardness dependence with temperature observed in the composite for $T > 75$ °C must be related to the behaviour of the C_{60} particles themselves. One may speculate about a possible rearrangement of C_{60} aggregates within the composite, which could contribute to hardening of the material. The above finding might be connected with the results of Tashibana [16], who found a large hardness increase in the case of C_{60} crystals starting at about 70 °C.

4. Conclusions

1. The above results suggest that there is a sharp phase separation between C_{60} molecules and the PE crystal matrix in dry gel films of fullerene–PE composites.

2. The hardness of C_{60}–PE composites gradually increases with increasing C_{60} concentration. For instance, by adding about 2.5 wt% C_{60} one obtains an increase in hardness of the original composite of about 30%, i.e. a value as high as that of glassy polyethylene terephthalate.

3. Annealing at high temperature (130 °C) for long times (10^5 s) leads to H values of ~ 190 MPa, which correspond to the theoretical limit of fully crystalline polyethylene. The H increase upon annealing is related to the thickness of the PE crystalline lamellae.

4. The temperature dependence of the composite shows an unexpected hardness increase with temperature above 75 °C, which has been ascribed to the hardening of the C_{60} aggregates themselves.

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