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Time-dependent hardness of particulate-filled composites

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Time-dependent hardness of calcium carbonate-polyethylene composites prepared by co-rotating twin screw extrusion has been determined. Hardness of composites were shown to be a power increasing function of the amount of calcium carbonate particles, but decreased as the time under load increased. The degree of time-dependent hardness was observed to be unaffected by filler concentration. All compositions showed similar percentage of hardness decrease with increasing dwell time. A graphical method was devised and able to apply to map the hardness of various filler volume fraction composites at any defined dwell times. © *1998 Kluwer Academic Publishers*

1. Introduction

Owing to their simplicity, hardness measurements are commonly used in industry and laboratory for testing all kinds of materials. In case of polymers, this technique is a relatively new approach with great potential for mechanical characterisation. Initially, hardness measurement has been only used as a quality control tool, but recently has evolved to be employed in fundamental study of the structure-property correlation of both semicrystalline and amorphous glassy polymers [1, 2]. Generally, hardness test is performed at room temperature thus the time-dependent deformation resulting from creep is not observed for most metallic materials since they will creep only at high temperature, except indium and lead. However, this assumption cannot be applied to polymers because they can creep at temperature as low as room temperature. Therefore, it has been observed that hardness of polymers changes with the time over which the load is applied on the indenter and can be used as an indication of the relative creep resistance of polymers [3–5]. The time taken for reading hardness is thus important and, traditionally, should be indicated in the report.

Particulate reinforced polymer composites have been of interest for scientists and engineers as a low-costed alternative for engineering applications. Addition of rigid particles to polymeric matrix can produce a number of desirable effects; for example an increase in stiffness, a reduction in the coefficient of thermal expansion and thermal shrinkage and an improvement in heat resistance, in electrical property and in creep performance [6, 7]. The properties of the composites are the result of a complex interplay between the individual constituent phases namely the matrix, the filler and the interfacial region.

Time-dependent hardness study of particulate-filled polymer composites is rarely found. The inclusion of such rigid fillers in the polymeric matrix has been proved to alter many mechanical properties of the system including time-dependent behaviour. This investigation is thus aimed to study the effect of filler on the hardness of composites and also the effect on time-dependent properties of the composites.

2. Materials and methods

2.1. Composite preparation

$CaCO_3$ powder, grade Omega (average particle size 5.53 μm), supplied by Lime Quality Co., Ltd., and HDPE pellets, grade 7000F (melt flow index 0.04 g/10 min), obtained from Bangkok Polyethylene Co., Ltd., were premixed mechanically at various volume fractions and the mixtures were then fed into a co-rotating twin screw extruder (Betol BTS40L) producing composites with filler volume fractions of 0.00, 0.10, 0.20, 0.30 and 0.40, denoted A0, A10, A20, A30, A40, respectively. The resultant composite pellets were then powderised by a centrifugal mill which was fitted with a 0.5 mm mesh. Liquid nitrogen was employed as a coolant during the powderising process to prevent an excess heat generation that could cause oxidation of the samples. 4 millimeter thick sheets of these composites were prepared by compression moulding at 220 °C and fast cooled under moulding pressure by circulating chilled water.

2.2. Calorimetric measurement

Melting endotherm and crystallinity of the samples were characterised by differential scanning calorimeter (Perkin-Elmer DSC7). The samples were put in aluminium pans and heated from room temperature to 200 °C at the heating rate of 20 °C min^{-1}. Data were collected continuously and then analysed by the DSC analysis programme. Crystallinity of the composites were derived from the ratio of the measured heat of fusion of the polyethylene fraction to the heat of fusion for the finite crystals, 293 J g^{-1}.

2.3. Hardness measurement

The samples of each volume fraction were embedded in an epoxy resin (Epofix, Struers) and then polished on various grades of silicon carbide paper down to 4000 grit. The specimens were then polished with a napped cloth impregnated with 6 and 3 μm diamond paste. The embedded samples were indented at 23 °C/70% RH by using Hardness Tester (Instron-Wolpert Model 930/25) with a Vickers diamond pyramidal indenter having a square base and pyramidal angle of 136°. The hardness was calculated from measuring the diagonal lengths (d) of the indentation on the specimen after the load was removed. This was carried out manually using electronic ruler on the projected screen where an indentation image was displayed through Zeiss objective lenses of magnification 70×. Vickers hardness number (H_v) was then calculated using equation below;

$$H_v = 1.854\frac{F}{d^2} \qquad (1)$$

where F is load (kg) and d is the diagonal length (mm).

A load of 1 kg (9.807 N) was used and fully applied within 5 seconds. The dwell time in the tests were varied from 5 to 360 seconds and three indentations were made at different parts of the specimens for each test. The values were then averaged.

3. Results and discussion

3.1. Thermal properties

In industry, small amounts of fillers such as metallic salt or talc, less than 10% weight fraction, are employed to control the crystallisation process of polymers to enhance the optical and mechanical properties [8]. The addition of such fillers will yield heterogeneous crystallisation where the fillers act as nucleating sites for the growth of the crystals thus fastening the crystallisation process. This process causes the materials to crystallise at higher temperature thus increases the crystallinity and melting temperature. However, in this investigation the addition of calcium carbonate particle did not affect either melting temperature or crystallinity of the composite. From the endotherm curves, all materials exhibited single-peak curves which are belong to polyethylene since at this range of temperature, no change in calcium carbonate occurs. Melting temperature and crystallinity of composites are shown in Fig. 1. All samples exhibited comparable melting temperature, ~ 131 °C, and crystallinity, ~ 63%. This may be due to the amount of filler which is very high and the relatively weak interfacial adhesion, a mechanical interlocking type, of $CaCO_3$/HDPE composites [9]. The interfacial adhesion has shown to influence the heterogeneous crystallisation [10]. It was demonstrated that strong adhesion between a polymer and solid fillers (PE + glass spheres + sodium benzoate) enhanced the overall crystallisation rate when compared to the poor adhesion system (PE + glass spheres). Therefore, no alteration in thermal properties has been made on polyethylene matrix by the incorporation of calcium carbonate.

3.2. Time-dependent hardness

From the hardness test, it is observed that the hardness of composites increases with increasing amount of calcium carbonate, Fig. 2. The relationship is not linear, but a power function. This dependence of hardness on filler amount is consistent with the earlier investigation on compact bone by Evans [3]. However, this

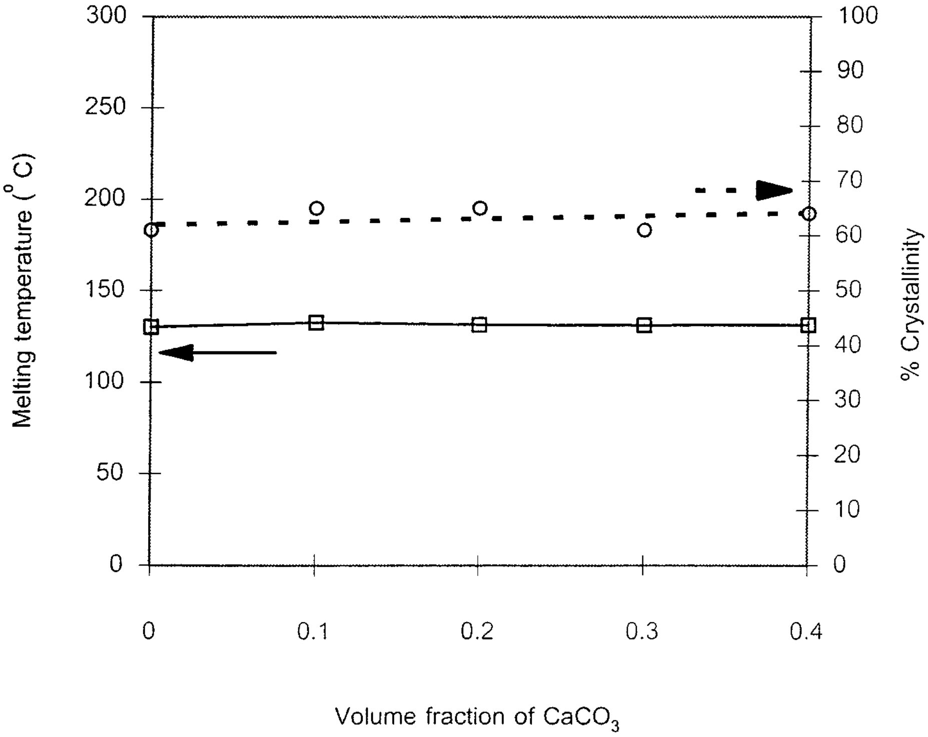

Figure 1 Effect of filler volume fraction on the thermal properties of composites.

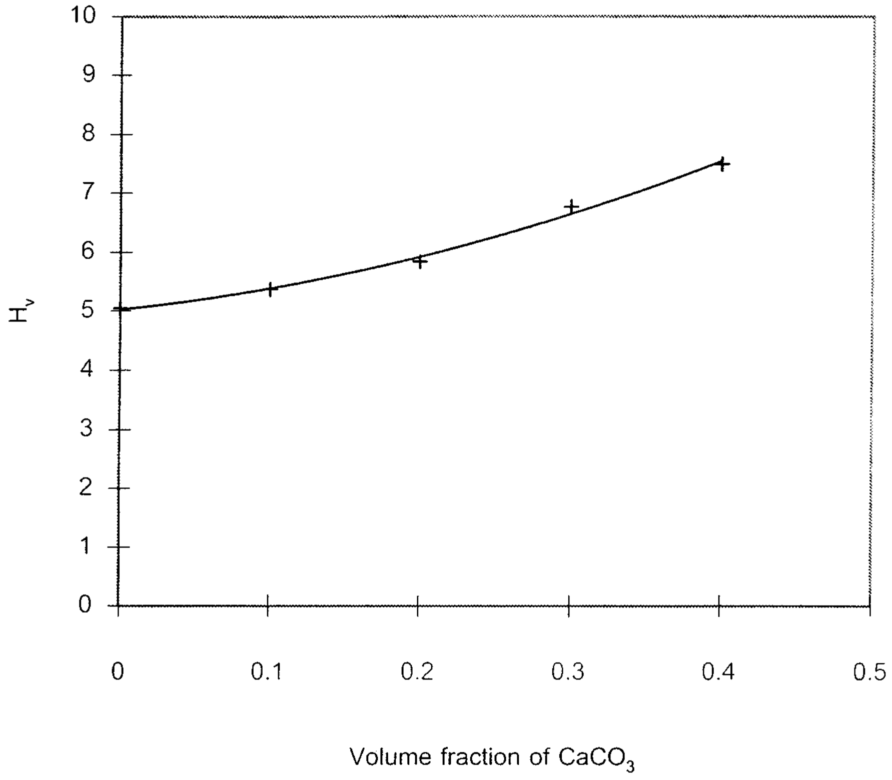

Figure 2 Effect of filler volume fraction on the hardness of composites at dwell time = 20 seconds.

is very different from the recent report of fullerene-polyethylene composites which described hardness as a linear increasing function of fullerene concentration [11]. The explanation is that the weight fraction in the system of fullerene-polyethylene, 0–2.5%, is comparatively much lower than in the present study, 0–65%. Generally, the deformation of composite resulted from the penetration of the indenter occurs in matrix. The presence of rigid fillers will increase the resistance to flow of the materials. In the low filler concentration region, the resistance is resulted from filler-matrix interaction thus the property of the composites is linearly dependent on the amount of filler. When the amount of filler is high, there will also be the filler-filler interaction which enables the resistance to flow of materials to increase significantly thus causing the linear relationship invalid [12]. Therefore, the relationship between hardness and filler volume fraction cannot be generally described by employing a linear function defined previously [11].

$$H = H_{\mathrm{f}}\phi + H_{\mathrm{PE}} \qquad (2)$$

where H is hardness of composites, H_{f} is a constant related to the hardness of filler, ϕ is filler concentration and H_{PE} is hardness of polyethylene.

It is known that for polymers, the time over which the deforming load is applied can cause creep. It was reported previously that this occurred in hardness test as well [4, 5]. This was found to be true in this study. The variation of hardness with dwell time for composites at various filler volume fraction is shown in Fig. 3. Generally, the hardness of all composites is time-dependent. It decreases rapidly with short dwell time and then levels off at longer times. The replot of the relationship in a double-logarithmic axis is shown in Fig. 4. It is observed that the curved graphs are changed into straight lines and hardness linearly decreased with time.

The linear log-log curves of all composites were parallel to one another regardless filler volume fraction. This means that the time-dependent characteristic of composites is not affected by the filler content. Table I shows the percentage of hardness drop of composites with dwell times. It can be seen that the percentage of reduction is slightly decreased with increasing filler content. However, the decrease is not significant for all volume fractions. This is because the properties of the matrix in this study were not significantly changed with the incorporation of the filler, as discussed in Section 3.1. Therefore, the time-dependent hardness of composites is not altered. The deformation mechanism of materials in creating indentation occurs only in a relatively soft matrix, not in the hard fillers. The addition of fillers will only help in resisting the initial deformation when the indenter penetrates the material. After this initial indentation, the size of the indentation increases with time by the creep mechanism of the polyethylene

TABLE I Effect of dwell time on the hardness change of $CaCO_3$/HDPE composites at various filler volume fraction

Materials	% Hardness change due to the increase in dwell time from 5 to 360 seconds
A0	−32
A10	−31
A20	−31
A30	−29
A40	−29

−decrease in hardness.

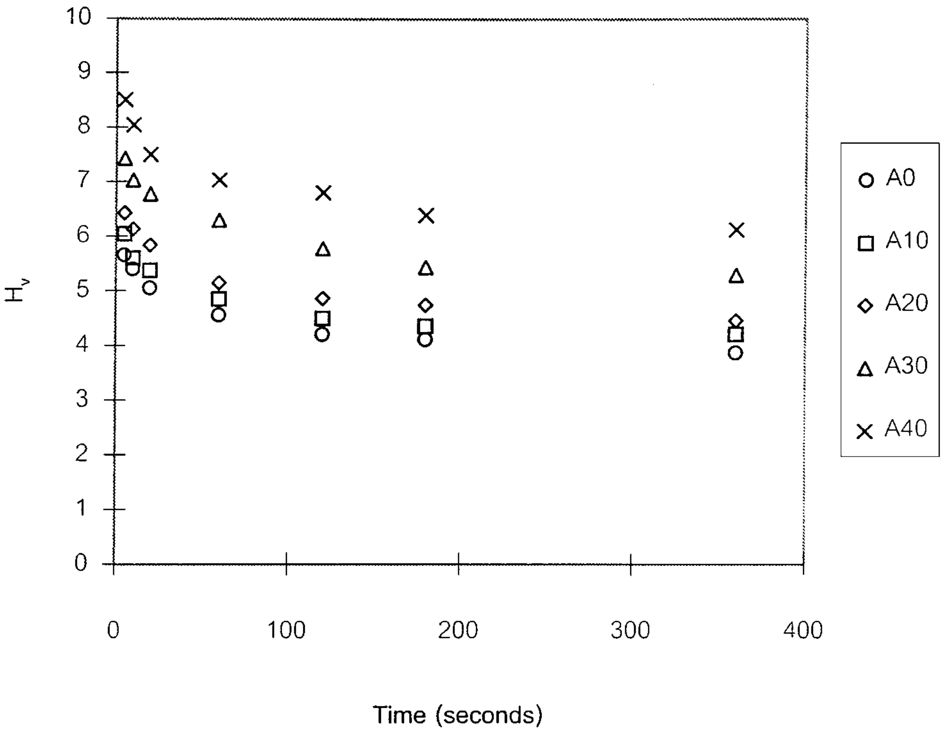

Figure 3 Time-dependent hardness of $CaCO_3$/HDPE at various filler volume fraction.

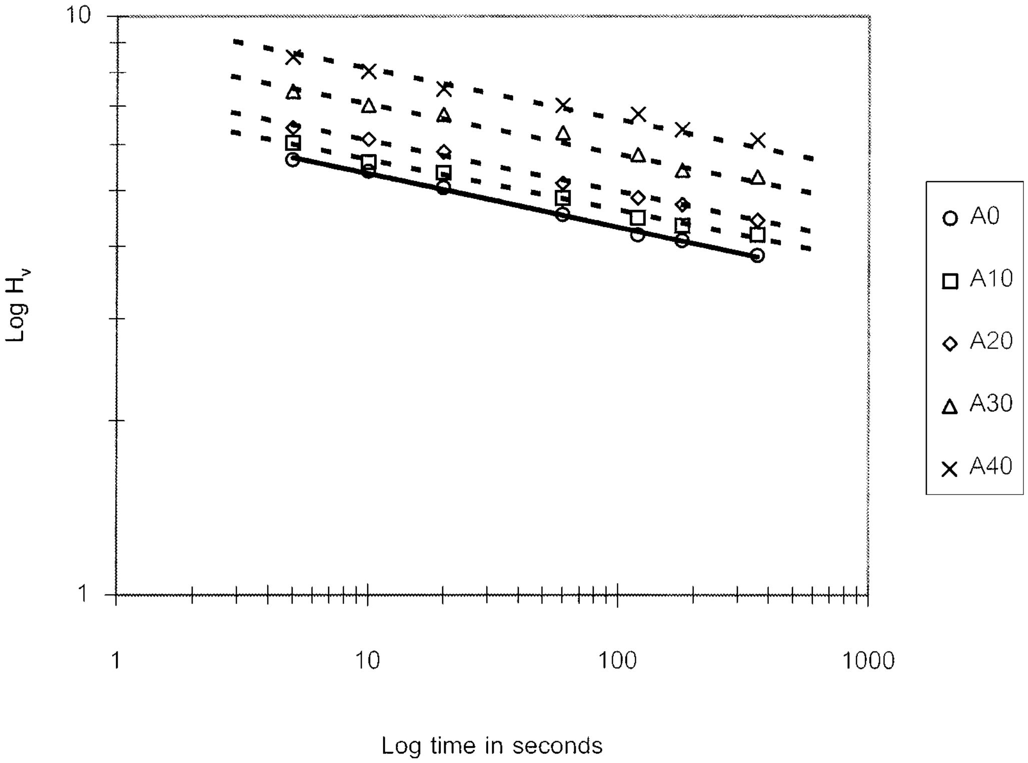

Figure 4 Log-log plot of hardness versus time for $CaCO_3$/HDPE at various filler volume fraction, (—) regression curve, (- - - -) calculated results based on a graphical method.

matrix. Therefore, the time-dependent process will only be affected if the matrix characteristic is modified; for example the formation of crosslinking [4]. These results are consistent with previous investigation that increasing filler volume fraction resulted in the reduction in creep strain [13]. Creep rate was unchanged except at longer time where higher filler content composites crept more significantly than lower filler content composite due to the occurrence of interfacial debonding.

3.3. Prediction of time-dependent hardness

The variation of hardness with time of some materials [14, 15] has been found to follow the relationship:

$$H = At^{-h} \tag{3}$$

where H is hardness, A and h are constants and t is the dwell time.

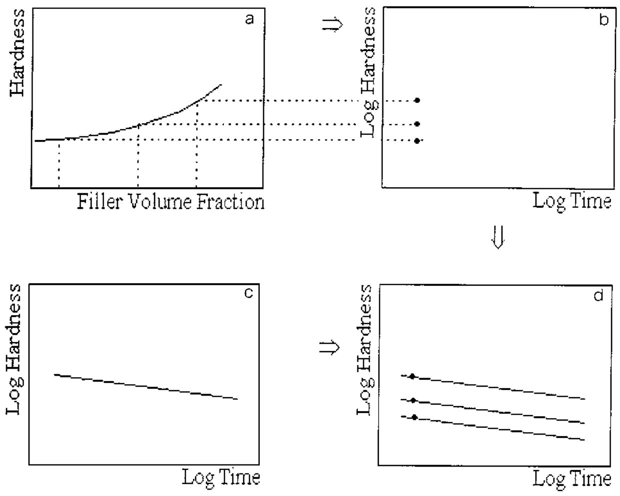

Figure 5 Schematic diagram of a graphical procedure in determining time-dependent hardness.

However, this requires the knowledge of constants in the equation for calculation. From the linear logarithmic relationship, Fig. 4, it is possible to devise an alternative based on a graphical procedure which is simpler to interpolate the time-dependent hardness of particulate-filled composites. The procedure is illustrated in Fig. 5 which is described as following:

1. Measure the hardness of composites at various volume fractions at one fixed dwell time, Fig. 5a. This will give the reference points for spacing in log hardness-log time curves, Fig. 5b.
2. Measure time-dependent hardness of pure polyethylene upto the required dwell time, Fig. 5c.
3. Time-dependent hardness of composites are constructed by drawing linear lines parallel to the experimental curve of pure polyethylene, passing through the reference points for each composites, Fig. 5d.

Although this method is empirical, but it is easy to perform and still yields reasonably accurate results, Fig. 4. Only 2 sets of experiments, hardness test of all composites and time-dependent hardness test of one type of composites, are required to completely map the hardness of various filler volume fraction at any dwell times. Therefore, the testing time and the amount of experiments can be significantly reduced.

4. Conclusions

The incorporation of calcium carbonate into high density polyethylene has not altered its thermal properties. The addition of calcium carbonate increases the hardness of the composite as a power function. However, the time-dependent hardness of materials is not affected by the filler incorporation. Hardness of composites decreased with increasing dwell time with similar degree of decreasing. A graphical procedure has shown to be able to compute the hardness of composites at any filler volume fractions and dwell times.

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