# The Role of Filler Volume Fraction in the Strain-Rate Dependence of Calcium Carbonate-Reinforced Polyethylene

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ABSTRACT: A study of the influence of filler volume fraction on the strain-rate dependence of  $CaCO_3$ -reinforced polyethylene was carried out. Tensile tests were done at different strain rates ranging from 0.008 to 2.0 min<sup>-1</sup>, whereas the  $CaCO_3$  amount was varied from 0.10 to 0.40. In the range of strain rates in this study, it was found that increasing strain rate generally increased yield stress and Young's modulus, but decreased yield strain for both unfilled and filled polyethylene. The increase in the filler volume fraction resulted in the decrease in the degree of strain-rate dependence of yield stress and strain. The decrease in strain-rate dependence of the composite changed into strain-rate independence when the filler content was beyond 0.20, and more pronounced at a high strain rate than a low strain rate. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1717–1724, 1998

Key words: polyethylene; calcium carbonate; yield; strain rate

## INTRODUCTION

It is well known that the rate of deformation or strain rate strongly affects tensile properties of polymers.<sup>1-4</sup> This is obviously due to the viscoelastic nature of polymers. A high strain rate normally results in the increase in yield or ultimate stress at break and modulus, but the elongation to break decreases. This means that polymers exhibit more brittle behavior when the strain rate is increased because the rapid stress application permits less flow of the polymer chains. The time necessary to adjust and absorb the applied load on increasing the strain rate is

reduced. However, in some cases, the elongation at break can increase as the strain rate increases.<sup>5</sup> The strain-rate dependence of the yield process generally can be described by the Eyring rate theory, which assumes that the deformation of polymer involves the motion of chain molecules or parts of a chain molecule over potential energy barriers or activation energy.<sup>2,4,6,7</sup> Yielding occurs as a segmental flow in which the applied stress biases the activation energy.

Particulate-reinforced polymer composites have been of interest for scientists and engineers as a low-costed alternative for engineering applications. This type of composites is macroscopically isotropic, and the fillers can be either organic or inorganic. Organic fillers are mostly used to increase toughness, while the inclusion of rigid inorganic fillers in polymeric materials enhances physicomechanical properties such as modulus, hardness, and creep

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Sample	Volume Fraction of $CaCO_3$	$\begin{array}{c} \text{Weight Fraction} \\ \text{of } \text{CaCO}_3 \end{array}$
A0	0.00	0.00
A10	0.10	0.24
A20	0.20	0.41
A30	0.30	0.55
A40	0.40	0.65

Table IComposition of Composites

resistance, processability and/or lowers the cost.<sup>8–10</sup> The common inorganic fillers employed for these purposes are calcium carbonate, talc, kaolin, mica, etc. Yield stress or ultimate stress can either increase or decrease with inclusion of filler, depending upon various factors such as the filler volume fraction, the integrity of the interface adhesion, and the type of filler.<sup>8,11</sup>

To date, studies on the effect of strain rate on the mechanical properties of polymers were reported many times, but the study of this effect on particulate-reinforced composites is rather limited and comparatively less on the role of the amount of fillers on the strain-rate dependence of the materials.<sup>5,12,14</sup> The objective of this study was intended to illustrate the relationship between the effect of filler volume fraction and the strain-rate dependence of particulate-filled polymers.

## MATERIALS AND METHODS

#### **Materials**

Matrix material employed in this study was high density polyethylene grade 7000F (melt flow index 0.04 g/10 min), obtained from Bangkok Polyethylene Co., Ltd, in the form of pellets. The filler used was calcium carbonate powder grade Omega (average particle size 5.53 microns), supplied by Lime Quality Co., Ltd.

## **Sample Preparation**

Oven-dry  $CaCO_3$  powder and HDPE pellets were first mechanically mixed at various fractions and the mixtures were then fed into a corotating twinscrew extruder (Betol BTS40L) producing composites with filler volume fractions ranging from 0.10 to 0.40 (Table I). Unfilled polyethylene was also similarly processed as a control. The resultant composite pellets were then powderized by a centrifugal mill that was fitted with a 0.5-mm mesh. Liquid nitrogen was employed as a coolant during the process to prevent an excess heat generation that could cause oxidation. Thick sheets (4 mm) of these composites were prepared by compression molding, and ISO  $527^{13}$  small tensile specimens, type 1BA, were cut from the sheets using a contour cutter. The machined surface was subsequently smoothed by a fine abrasive paper.

#### **Tensile Testing**

Tensile tests were performed on a universal testing machine (Instron 5583) equipped with a 5-kN load cell and a strain extensometer (gauge length 25 mm). All the tests were carried out according to ISO 527 at 23°C and 60% RH. The measurements were carried out at a constant crosshead speed of 0.2, 5, 20, and 50 mm min<sup>-1</sup>, which equal to the strain rate of 0.008, 0.2, 0.8, and 2.0 min<sup>-1</sup>, respectively. Three to five replicates were run for each condition. The reported data are the average values. The load–elongation curves were converted into engineering stress–strain plots by dividing the measured load by the initial crosssectional area and the elongation by the original gauge length.

## RESULTS

Figures 1 and 2 show the representatives of engineering stress-strain plot of composites at different filler volume fraction at the strain rate of 0.2  $min^{-1}$ . The reason in plotting the strain-strain curves separately into two figures is for clarity. Unfilled polyethylene shows typical stress-strain curve with a distinct yield point followed by necking and drawing. The response of the composite is seen to change from ductile to brittle with increasing filler content. The yield stress and yield strain is decreased, whereas the modulus is increased as the volume fraction of CaCO<sub>3</sub> is increased. The ductile/brittle transition is observed at a filler volume fraction of 0.20. The average values of three quantities-yield stress, yield strain, and Young's modulus-are tabulated in Table II for all compositions and strain rates.

Figure 3 shows the plots of yield stresses versus logarithm of the strain rates. It can be seen that the yield stresses for all compositions increase linearly with increasing strain rates, but the increase becomes nonsignificant for the 0.30 and 0.40 filler volume fraction  $CaCO_3/HDPE$ , A30



**Figure 1** Stress-strain curves of  $CaCO_3$ /HDPE composites at volume fractions of 0.00, 0.10, and 0.20. Strain rate: 0.20 min<sup>-1</sup>.

and A40, at the two greatest strain rates, 0.8 and  $2.0 \text{ min}^{-1}$ . The slope of the plots is found to decrease as the filler content is increased.

Conversely, yield strains are decreased with increasing strain rates (Fig. 4). The decrease was significant at all ranges of strain rate for HDPE only. In the case of the composites, the behavior can be divided into two groups. At low filler volume fractions, A10 and A20, the decrease of yield strain was observed for a low strain rate only. Beyond the strain rate of  $0.2 \text{ min}^{-1}$ , no effect of strain rate on the values of yield strain can be observed. At high filler volume fractions, A30 and A40, no change of the yield strain occurs at all strain rates.

Young's modulus of materials increases as the strain rate increases, as shown in Figure 5. However, for the composites containing calcium carbonate greater than a 0.10 volume fraction, the increase of modulus becomes nonsignificant when the strain rate reaches  $0.2 \text{ min}^{-1}$ .

# DISCUSSION

In the case of unfilled polyethylene, yielding can generally be attributed to adiabatic heating of the specimen or to the geometrical reduction in crosssectional area on the formation of a neck.<sup>6</sup> Generally, the strain-rate dependence of polymers can be described by employing a well-known Eyring rate theory in the form of

$$\sigma_{y} = \frac{E}{V} + \frac{RT}{V} \ln \left(\frac{2\varepsilon^{\bullet}}{\varepsilon_{0}^{\bullet}}\right) \tag{1}$$

where  $\sigma_y$  is the yield stress at specified temperature,  $\epsilon^{\bullet}$  is the strain rate, *E* is the activation energy, *V* is the activation volume.

This can be simplified to the relation below:

$$\sigma_{\rm y} = \sigma_{\rm y}^0 + K \ln\left(\frac{2\varepsilon^{\bullet}}{\varepsilon_0^{\bullet}}\right) \tag{2}$$

where  $\sigma_v$  is the yield stress at specified temperature,  $\sigma_y^{0}$  is the yield stress at a specified temperature when the strain rate equals  $1 \text{ min}^{-1}$ , *K* is a material constant at a specified temperature, and  $\epsilon^{\bullet}$  is the strain rate.

This suggests that plots of yield stress against the logarithm of the strain rate should give a parallel straight line. The relationship of the experimental yield stress and the logarithm of the



**Figure 2** Stress-strain curves of  $CaCO_3$ /HDPE composites at volume fractions of 0.30 and 0.40. Strain rate: 0.20 min<sup>-1</sup>.

strain rate of composites was found to be linear as well. Therefore, it is possible to employ eq. (2) to represent the strain-rate dependence behavior of composites. The slope of the curves, equal to degree of strain-rate dependence, decreased with increasing filler volume fraction (Table III). This indicates that the deformation processes of unfilled and filled polymers are not similar.

In the case of composites that have relatively weak interface adhesion, only mechanical interlocking, as in the present investigation, it was pointed out that yielding was assumed to occur in the minimum cross-section of the continuous phase, polymers, which was perpendicular to the applied load.<sup>14</sup> However, another yielding process is thought to occur as well, and is called here a debonded-yielding process. This is caused by debonding at the filler/matrix interface, thus changing the interface from recoverable elastic zone to irrecoverable plastic zone. Therefore, it is hypothesized that the yielding of CaCO<sub>2</sub>/HDPE composites is rather a two-stage process starting with interface yielding and followed by yielding of the matrix. The debonding of the interface usually occurs prior to yielding in particulated composite materials, generally at a very low strain.<sup>15,16</sup> Once the debonded sites were initiated, they will grow further by the applied load and the load will be also transferred to the neighboring matrix. When the degree of separation is great enough and the matrix cannot support it, a sudden increase in the strain occurs, causing the load to drop, thus generating a yielding phenomenon in the load-deformation curve.

In most cases, yielding of composites comprises both processes described earlier, but whether which process predominates depends upon the filler volume fraction. At low filler volume fractions the yielding of the matrix predominates, because although the debonding occurs, the amount of matrix is still great enough to support the load. At a high volume fraction, the debondedyielding process will take over because the debonded sites are great, thus the degree of separation is higher and more severe. The evidence of the effect of volume fraction on the debonding can be seen from the stress-strain curves of composites (Figs. 1 and 2) that the behavior changes from ductile behavior with large elongation to break to brittle behavior with low elongation to break. This can be seen that the yield stress is decreased when the filler content is increased.

The strain-rate dependence of yielding in composites will also be governed by these processes.

$\begin{array}{c} \text{Strain Rate} \\ (\text{min}^{-1}) \end{array}$	Yield Stress (MPa)	Yield Strain (mm/mm)	Young's Modulus (MPa)
		A0	
0.008	14.69	0.140	655
0.2	20.79	0.112	1100
0.8	23.03	0.091	1717
2.0	24.44	0.076	1797
		A10	
0.008	14.18	0.092	904
0.2	17.95	0.070	1237
0.8	18.67	0.069	1796
2.0	20.17	0.070	1851
		A20	
0.008	12.52	0.060	1649
0.2	15.08	0.043	2132
0.8	16.22	0.043	1976
2.0	17.02	0.042	2050
		A30	
0.008	11.39	0.013	2208
0.2	13.32	0.012	2935
0.8	14.34	0.011	2843
2.0	14.49	0.012	2711
		A40	
0.008	12.70	0.005	3252
0.2	14.42	0.007	4014
0.8	15.02	0.005	3560
2.0	14.95	0.005	4125

Table II Tensile Properties Versus Strain Rate



Figure 3 Effect of strain rate on the yield stress of  $CaCO_3$ /HDPE composites at various volume fractions.

**Figure 4** Effect of strain rate on the yield strain of CaCO<sub>3</sub>/HDPE composites at various volume fractions.



**Figure 5** Effect of strain rate on the Young's modulus of  $CaCO_3$ /HDPE composites at various volume fractions.

At a low filler content, the rate dependence is mainly due to the rate dependence of the polymer matrix, and the minority is caused by the rate dependence of the interfacial adhesion, whereas the rate-dependence process is shifted to interfacial adhesion predominance at a higher filler volume fraction. At a high strain rate, especially at a high filler volume fraction where the interfacial response predominates, when the increase in strain rate reaches the maximum rate dependence of the interfacial adhesion response, then a higher strain rate will produce no further effect, displaying as a strain-rate independence. It can be seen that the strain-rate independence of composites was observed for A30 and A40 at high strain rates, 0.8 and 2 min<sup>-1</sup>. This can be supported from the yield strain data (Fig. 4), where the decrease of the yield strain with increasing

Table III Constants for Yield Stress Versus Logarithm of Strain Rate Curves of CaCO<sub>3</sub>/HDPE Composites at Various Volumes

Sample	К	$\sigma_y^0$
A0	1.78	23.39
A10	1.05	19.30
A20	0.81	16.42
A30	$0.63^{\mathrm{a}}$	$14.42^{\rm a}$
A40	$0.51^{\mathrm{a}}$	$15.18^{\mathrm{a}}$

 $^{\rm a}$  Exclusion of data at strain rate of 2.0  $\rm min^{-1}$  in calculation.



**Figure 6** Elastic strain versus The  $CaCO_3$  volume fraction in composites at various strain rates.

strain rate was shown for composites containing  $CaCO_3$  less than or equal to 0.20 at low strain rates only, 0.008 and 0.2 min<sup>-1</sup>. At high strain rates, in the case of A10 and A20, and the above filler volume fraction of 0.20 at all strain rates, the yield strain is independent of the strain rate.

From the experimental yield values, both yield stress and strain, it is suggested that the transitional filler volume fraction is 0.20. Beyond this volume fraction, the yield stress of composites showed the strain-rate independence at a high strain rate, over  $0.2 \text{ min}^{-1}$ , and the yield strain did not change with strain rates either. In addition, the evidence from the elastic strain values also supports this observation. Elastic strain can be approximately obtained by dividing Young's modulus by yield stress.<sup>17, 19</sup> The plots of elastic strain versus the filler volume fraction of composites is shown in Figure 6. It can be seen that elastic strain of materials decreases with increasing the filler volume fraction. Above the volume fraction of 0.20, no effect of strain rate on the elastic strain values can be observed. The yield point is normally defined as the point where the materials change their deformation behaviors from elastic to plastic. If this definition is valid in this investigation, it can be interpreted that yielding is independent of the strain rate for composites containing  $CaCO_3$  greater than 0.20. This is very interesting in that the dependence/independence transition occurs at the similar filler content as the ductile/brittle transition. This is because both transitions of composites are related to the similar parameters, which are the filler con-



**Figure 7** Reduced curves of CaCO<sub>3</sub>/HDPE composites.

tent and filler/matrix interaction. However, The strain-rate dependence phenomena observed in this study cannot be stated to be a general case for the whole range of strain rates because the strain rates employed are relatively low strain rates. Further investigation at higher strain rates or lower temperature is thus needed. Previous investigations<sup>2-4</sup> have shown that yield behavior of many polymers can be controlled by more than one activated process for different magnitude of strain rates; for example, one process at a high temperature and low strain rates and another one at a low temperature and high strain rates.

The method to construct a single master curve by superimposing the data at different strain rate and temperature was suggested previously by Smith.<sup>18</sup> If the master curve can be created, the amount of experiments will be reduced significantly because only one formula of materials can be extrapolated for the others. However, this technique was reported for both success and nonsuccess in constructing a master curve.<sup>3,5</sup> In this experiment, the approach was modified to superimpose the data at a different strain rate only. It was done by plotting the logarithm of  $\lambda \sigma / \epsilon^{\bullet}$  versus the logarithm of  $\epsilon/\epsilon^{\bullet}$  where  $\sigma$  is the yield stress,  $\epsilon$  is the yield strain,  $\lambda$  is the extension ratio equal to  $(1+\epsilon)$ , and  $\epsilon^{\bullet}$  is the strain rate. It can be seen in Figure 7 that this technique was not applicable in this experiment. A single master curve for different strain rates and filler volume fractions cannot be constructed for the whole range of composites. The reduced curve is mainly divided into

two curves, A30 and A40 on one curve and A0, A10 and A20 on another. This is thought to be due to both ductile/brittle and dependence/independence transitions of the composites. At the transition, the yield strain dropped suddenly, brittle behavior; thus, the  $\epsilon/\epsilon^{\bullet}$  values decreased nonproportionally, causing the horizontal shift as seen in Figure 7.

## CONCLUSIONS

The influence of filler volume fraction on the strain-rate dependence of tensile properties of the particulated composite was to alter the degree of dependence. In the scope of strain rates in this study, it was observed that the degree of strain rate dependence decreased with increasing filler content and then became the strain-rate independence at a high filler volume fraction, more pronounced at high strain rates. The critical filler volume fraction and strain rate in changing from strain-rate dependence to independence for the system of CaCO<sub>3</sub>/HDPE in this investigation was found to be 0.20 and 0.8 min<sup>-1</sup>, respectively.

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