USE OF FILLERS TO ENABLE THE MICROWAVE PROCESSING OF POLYETHYLENE

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Microwave heating has a number of advantages over conventional heating due to the ability to heat specimens directly through specific interaction of electromagnetic radiation with the material. Thus it is possible to consider highly localised, rapid melting of thermoplastics using microwave radiation as a means of forming and welding. However, most polymers exhibit very low dielectric losses in the GHz region, which means that it is difficult to heat them efficiently by this means. We have therefore studied the use of fillers such as talc, zinc oxide and carbon black as a way of increasing the susceptibility of common polymers to microwave processing. Carbon black was found to be the most effective susceptor for high density polyethylene and its efficiency was directly proportional to its surface area and loading.

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INTRODUCTION

Microwave radiation is a rapid and highly specific means of heating materials. Microwave heating has been used in many applications successfully, such as cooking of foodstuffs, chemical synthesis, ceramics sintering and medical therapy. In the area of polymer technology, microwave heating has been used for vulcanizing rubber [Krieger, 1992], joining and welding plastic parts [Potente *et al.*, 2002], polymerisation [Bogdal *et al.*, 2003], and the preparation of polymer foams [Clarke *et al.*, 2004]. Our particular interest is the area of

localised melting and welding of thermoplastics as a means of rapid processing and shaping.

Most thermoplastics are relatively transparent to microwaves; i.e. they do not absorb microwaves to a sufficient extent to be heated. This limits applications to thermosets and the removal of moisture from materials [Wei *et al.*, 1996]. Previous work has concentrated on the dielectric properties of thermoplastics [Bur, 1985; Chen *et al.*, 1993b], and although a few studies involved the heatability of some thermoplastics [Chen *et al.*, 1993a; Chen *et al.*, 1993c; Ku *et al.*, 2000] there has been little emphasis on improving the microwave response of thermoplastics with low dielectric properties. Brosseau *et al.* [2001] have reported microwave dielectric spectroscopic measurements on

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carbon and silica filled polyethylene as well as an epoxy resin [Brosseau *et al.*, 2001]. The aim of our research is to investigate the effect of the use of commonly used fillers such as talc, zinc oxide and carbon black on the improvement of microwave response of high-density polyethylene (HDPE) so as to be able to thermoform such materials without significantly compromising the mechanical properties of the virgin polymer.

MATERIALS AND METHODS

High density polyethylene (HDPE) molecular weight 2.2×10^5 g/mol, melt flow index 0.3 g/min (190°C, 2.16 kg), Borealis BS2581 was used as the matrix. Talc (Luzenac A3 C) from Luzenac Europe SAS and zinc oxide from US Zinc and range of carbon blacks were supplied by the Columbian Chemicals Company (Table 1).

A Haake PolyLab Rheomix (Thermo Electron Corporation Waltham, MA) was used to mix the HDPE with different amounts of filler. The mixing temperature was 180°C, mixing time was 10 minutes and rotational speed was 40 rpm. The materials were then made into sheets 1.5 mm thick by compression moulding at 180°C.

Microwave absorptivity of the materials was measured according to the method described by Lorenz [1999]. An 800 W domestic microwave oven was employed, which was modified so that the magnetron could be operated continuously on reduced power. Test specimens of a filled polymer sheet (1 cm × 5 cm × 0.15 cm) were oriented vertically in the centre of the oven, turntable using a block of ceramic foam as support. The change in temperature of the sample was recorded using a thermal imaging camera (Thermovision® A40, FLIR Systems Inc., Wilsonville, OR).

A Lloyd Tensometer, Model L10000, was used for tensile testing at room temperature. The crosshead speed was 50 mm/min. Dumbell

Table 1. Carbon black used in this study.

code	surface area (m ² /g)	oil absorption (cc/100 g)
MT	7.5	41
N550	39	121
C7055	67	166
N330	77	102
N326	78	72
N339	92	120
N115	137	113

specimens were prepared according to BS903, except their thickness was 1.5 mm. A Leica Cambridge Stereoscan (Model S360) was used to visualize the surface morphology of the composites. Surfaces included cut surfaces and failure surfaces. A cut surface was obtained by cutting a specimen when it was heated at 120°C; a failure surface was obtained from a failed tensile testing specimen. The surfaces were sputter coated with gold before SEM measurement.

RESULTS AND DISCUSSION

Table 2 shows the relative temperature rise for carbon black, zinc oxide and talc at the same volume % loading for exposure to 200 W of microwave power for 60s. Tests on unfilled HDPE under the same conditions gave no

detectable temperature rise.

It is clear from this preliminary screening that carbon black is the most effective filler for imparting microwave heatability to HDPE, therefore more extensive measurements were carried out on this (and other grades) of carbon black. For comparative measurements between specimens containing different types of carbon black, a higher power setting of microwave energy (800 W) was employed for a duration of 15 seconds.

Figure 1 shows the effect of the addition of carbon black on the temperature rise of samples after one minute exposure to different microwave powers. It can be seen that there is a critical content of carbon black for every microwave power, below which negligible rise in temperature is recorded. The threshold carbon black content for heating to occur is related to microwave power, being 8.5, 6.4 and 2.2% for 100 W, 200 W and 400 W respectively. When the carbon black content is above this level, the temperature rise recorded for the same time exposure to the microwave field increases linearly with increasing the content of carbon black, all specimens showing the same ($7.2 \pm 0.2^\circ\text{C}/\%$) increase in temperature with increasing carbon black content.

Plots of the temperature rise on microwave heating against filler loading for different carbon blacks are shown in Figure 2. Again, there is a threshold above which the temperature rise is directly proportional to carbon black content. The slope and onset of these linear trends were calculated and used to define the heating efficiency (in $^\circ\text{C}/\%$) and threshold (%) for each carbon black type (Table 2). The second set of experiments resulted in different values for N550 compared to those obtained in the initial screening experiments. This is probably due to the shorter time of the measurement, which would result in different heat losses to the oven from the sample.

Figure 3 shows a plot of the heating efficiency versus the surface area of the carbon

Table 2. Relative temperature rise for HDPE at 16% v/v loading of different fillers.

filler	temperature rise ($^\circ\text{C}$)
Carbon Black N550	177 ± 10
Zinc Oxide	30 ± 5
Talc	3 ± 1

black. There is a good correlation between surface area of the carbon black and the extent to which it promotes microwave heating, whereas the oil absorption (or “structure”) of the carbon black did not correlate with its effectiveness under microwave irradiation. It is apparent from the shape of the heating curves in Figure 1 and Figure 2 that the microwave response does not correlate with the usual sigmoidal response which is observed for electrical conductivity [Yi and Choi, 1999]. This implies that the heating is not caused by ohmic effects resulting from currents induced in the specimen by microwaves. Furthermore, the threshold for heating shows no clear relationship between the surface area and/or structure, although it is apparent that the onset of heating is below the percolation threshold for conductivity in this class of material, which is usually reported as lying between 10 and 20% w/w [Wang *et al.*, 2005]. Instead, according to Figure 1, the threshold for heating is related to the power applied, and thus we conclude that it is a consequence of the apparatus and sample geometry. The percolation threshold varies with the shape and degree of agglomeration of the carbon black; it occurs at higher loadings for carbon particles with low surface-to-volume ratio and low structure [Modine *et al.*, 1996]. There is no evidence of a clear relationship between the nature of the carbon black and the onset of heating although there is limited data to

FIGURE 1. Temperature rise vs. carbon black N550 content for different microwave powers.

FIGURE 2. Temperature rise vs. carbon black content for different carbon blacks.

FIGURE 3. Relationship between microwave heating efficiency and the surface area for different carbon blacks.

FIGURE 4. Effect of carbon black N550 content on elongation at yield and elongation at break (the dashed line shows predicted behaviour according to Nielsen [Nielsen, 1974].)

Table 3. Heating efficiency and threshold level from data in Figure 2.

carbon black	heating efficiency (°C/%)	threshold (%)
MT	0.8	7.8
N550	3.8	5.8
C7055	5.8	5.8
N330	6.0	4.6
N326	7.4	6.0
N339	8.6	6.0
N115	10.5	3.6

suggest that this should be the case for a semi-crystalline matrix [Krupa and Chodak, 2001].

Mechanical testing on all of the filled HDPE compositions that were prepared showed that at low filler content the tensile strength and elongation at yield were unaffected by the incorporation of an additive. However, beyond 10-15% of filler the material rapidly became very brittle. Figure 4 shows the elongation at yield and the elongation at break for HDPE/N550 blends. The elongation at break (ϵ_B) can be modelled according to the equation given by Nielsen [1974]:

$$\epsilon_B = \epsilon_B^0 (1 - X_f^{1/3}) \quad (1)$$

Where ϵ_B^0 is the elongation at break of the unfilled material and X_f is the volume fraction of filler. The predicted behaviour of the system is

also shown in Figure 4. The difference between the observed response and the predicted one can be attributed to the change in failure mode shown by the SEM images of the fracture surfaces of pure HDPE and blends containing 3 and 30% N550 in Figures 5-7. Both the pure polymer and blend containing 3% underwent ductile failure, whereas the blend containing 30% carbon black underwent brittle failure. Nielsen's model assumes good adhesion between the filler and the matrix, and that the particles behave as perfect spheres. The elongation at yield and the elongation at break for 10% w/w carbon loading is plotted against the surface area of the carbon used in Figure 8. Only in the case of the highest surface area (*i.e.* smallest particle size) grade of carbon black does the elongation at break behaviour show a behaviour approaching theoretical. Furthermore, Nielsen's model is correct only if a deformation is uniform. For

FIGURE 5. SEM micrograph of the failure surface of pure HDPE.

FIGURE 6. SEM micrograph of the failure surface of 3% carbon composite.

FIGURE 7. SEM micrograph of the failure surface of 30% carbon composite.

FIGURE 8. Plot of elongation at yield and at break vs. carbon black surface area (10% w/w carbon black content).

polyethylene, necking occurs and the presence of defects in this region has a critical influence on the drawability [Krupa and Chodák, 1999]. Chodák *et al.* [1999, 2001] have found a coincidental relationship between the electrical conductivity and elongation at break. This may also explain why there is a decrease in ductility for the material as the surface area of the carbon increases if we relate the mechanical properties back to the microwave heating observations. No relationship was found concerning the oil absorption of the carbon and its mechanical properties. This finding indicates that a balance must be sought between the improved microwave heatability afforded by high surface area carbon blacks and the consequential embrittlement that they cause [Yi *et al.*, 1998].

CONCLUSIONS

Tests on carbon black, zinc oxide and talc indicated that carbon black was the most

efficient susceptor for high density polyethylene. The effectiveness of carbon black to improve the heatability by microwave irradiation was directly proportional to the amount of filler (above a certain threshold) and the surface area of the carbon black. Above 10-15% carbon black had a detrimental effect on the mechanical properties of the HDPE, this effect was worse for higher surface area carbon blacks. Selecting a carbon black with a high surface area which can be used at low loading without significant deterioration in the mechanical performance of the product would appear to be a good compromise.

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