JOURNAL OF MATERIALS SCIENCE **29** (1994) 5293–5301

Rheological characterization of polypropylene filled with magnesium hydroxide

P. R. HORNSBY, A. MTHUPHA
Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

Consideration is given to the dynamic viscoelastic and shear flow properties of magnesium hydroxide-filled polypropylene, at a filler concentration of 60 wt%. Five variants of magnesium hydroxide were used, one surface-treated with magnesium stearate. The results reported illustrate the effects of filler particle size, morphology and surface coating on the rheology of the composites. The presence of magnesium hydroxide caused a significant increase in the shear viscosity of polypropylene relative to unfilled polymer, although this was much less pronounced using surface-treated filler, particularly at low shear rates. Complex viscosity and storage modulus data, obtained at very low shear rates (0.002 s^{-1}), demonstrated the presence of a critical shear yield stress for flow to occur, which was greatest for compositions containing uncoated fillers with small particle size. These observations are discussed in terms of structure formation between the particles. Results obtained from capillary and dynamic measurements of melt flow were found to follow the Cox–Merz rule.

1. Introduction

In recent years filler addition to polymers has increasingly assumed a functional role, for example to increase stiffness, creep compliance, toughness, high-temperature performance and flame retardancy [1–3]. Mounting concern over the hazards posed by high levels of smoke and toxic fume emissions, a particular characteristic exhibited by polymers containing halogen-based fire-retardant additives, has stimulated considerable interest in the development of halogen-free fire-retardant alternatives with combined active smoke-suppressing qualities [2].

In this regard magnesium hydroxide is under active consideration, which in common with aluminium hydroxide does not contribute to smoke production, and in many instances reduces the overall level of smoke emitted during combustion [4]. However, unlike aluminium hydroxide, which is limited in application by its relatively low decomposition temperature of around 200 °C, magnesium hydroxide is stable in polymer systems up to 340 °C without breakdown of the filler. Hence, synthetic resins containing high concentrations of magnesium hydroxide are now being incorporated in cable coverings and considered for use in injection-moulded artefacts, where good processability is of prime importance.

The rheological behaviour of particulate-filled polymers generally differs from the corresponding unmodified polymer, since the presence of filler particles normally enhances the viscosity of the melt, which increases with filler volume fraction, especially at low shear rates [5–7]. A critical yield stress generally exists for flow to occur, which has been found to increase with decreasing particle size and increasing volume loading of filler [8, 9]. For example, flow studies with carbon black-filled polystyrene melts suggest that at loadings between 10 and 20 vol %, gel-like characteristics result which can be broken up by shear stresses around 10^5 to 10^6 dyne cm^{-2} (10^4 to 10^5 Pa). Thereafter flow approximates the characteristics of the unfilled viscoelastic fluid [7].

Surface treatment of filler particles normally reduces both the melt viscosity [3, 9] and dynamic modulus [10] of filled polymers through reducing particle interaction effects, resulting in decreased particle agglomeration [9]. Hence, particulate dispersion can significantly influence the viscoelastic response of filled polymers and is related to many factors, including particle characteristics (surface composition, shape and size), particle content, particle–matrix interaction effects and the rheological history of the formulation [11, 12].

According to Hertlein [12] the effect of particle size on viscosity depends on the ability of particles to immobilize molten material and thus restrict the volume of flowable melt. However, this model breaks down in the unlikely event that the average particle diameter is of the same order of size as a chain segment [13]. From this work it was concluded that with decreasing particle size (i.e., higher surface area), a greater amount of melt becomes bound to the particles and is thus immobilized. Furthermore, in the low shear region, high melt viscosity values were observed, an effect attributed to strong interactive forces between particles [14].

Analogous findings have been reported with carbon black aggregates in rubber [15]. These combined to form larger agglomerates, which together with occluded liquid produced so-called domains. The observed decrease in apparent viscosity with increasing shear

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rate was attributed to progressive breakdown of these carbon black structures into smaller domains resulting in less occlusion of liquid.

Boaira and Chaffey [16] have reported a decrease in viscosity with increasing shear rate in mica-filled polypropylene. This behaviour was explained in terms of flake realignment into an orientation more favourable to flow, and a greater predominance of viscous stresses over particle interaction effects as the shear rate was raised. When the mica content was higher, however, the flakes tended to agglomerate into a network structure which was readily destroyed by shear. At high shear rates the viscosity of the composite was then determined largely by the nature of the polymer matrix, being influenced strongly by temperature, but at a lower level of applied shear the composite viscosity showed greater dependency on the integrity of the particle network structure formed, and was found to be relatively unaffected by temperature.

Han [17] has reported results for the melt flow of polypropylene containing glass beads and calcium carbonate fillers with and without silane coupling agents (η-octyltriethoxysilane and γ-aminopropyltriethoxysilane). Both filler treatments decreased the melt viscosity of calcium carbonate-filled polypropylene melts. However, with glass beads the last-mentioned coupling agent decreased the melt viscosity, whereas the former increased it. Hence the rheological properties of filled polymers would appear to depend on both the type of coupling agent and the polymer–filler system under consideration.

Scherbakoff and Ishida [18] measured the dynamic rheological properties of a PS–PMMA–glass bead system. In this study, however, surface treatment of the glass beads was found to enhance the complex viscosity. This was attributed to the filler acting as an interface compatibilizer for the immiscible PS and PMMA phases.

Sothern and Hodd [3] explained differences in the melt viscosity of polypropylene compounds containing calcium carbonate and talc fillers in terms of particle size and surface coating effects. The most pronounced differences were observed at low shear rates. Whilst particle size and surface modification exerted a major influence on polymer melt rheology, the particle morphology also had a significant effect. Plate-like geometries, such as that of talc for example, can significantly increase the viscosity relative to incorporation of calcium carbonate or glass bead fillers [17]. This observation has important implications in the context of the present study, since magnesium hydroxide is available in a variety of particle shapes as well as surface areas.

This communication considers the rheological properties of magnesium hydroxide-filled polypropylene and forms part of an ongoing investigation on the properties of this system. Understanding melt flow characteristics is important, since during processing the composite may be subjected to high shear rates. In addition, low shear rheology may provide information about the extent of structure formation and hence filler dispersion existing in the unstressed state.

Five different types of magnesium hydroxide were used, one surface-coated with magnesium stearate applied to ameliorate the detrimental effect of this filler on the mechanical properties of the composite [2, 4]. Emphasis is given to analysing the effects of particle size, geometry and surface coating on the rheological behaviour of the melt. The filler concentration was maintained at 60 wt %, this loading conferring adequate flame retardancy to polypropylene [2, 19].

2. Experimental procedure

2.1. Sample preparation

2.1.1. Materials

Spherical beads of the polypropylene homopolymer Himont Valtec HS008–MFI 3 (230 °C, 2.16 kg), were used for preparing all the compounds. The magnesium hydroxide fillers used differed in origin, particle morphology, surface area and particle size (Table I and Fig. 1). One sample, E*, was a variant of grade A, surface-treated with 6 wt % of magnesium stearate. It has been shown previously that with high surface-area grades of magnesium hydroxide, treatment levels of this order are required to effect complete surface coverage [2].

2.1.2. Compounding and moulding

Compounds of polypropylene containing nominally 60 wt % (37 vol %) of magnesium hydroxide filler were prepared by feeding a predried premix of the constituents into a Betol BTS40 co-rotating twin extruder (21/1 *L*/*D* ratio) using a screw speed of 100 r.p.m. and an approximate melt temperature of 205 °C. In the case of the surface-treated variant, this required an addition of 63.6% of coated filler, to maintain the hydroxide content at 60 wt %.

The resulting granules were dried in a vacuum oven at 90 °C for 24 h. Material for subsequent dynamic analysis was then compression-moulded for 5 min at 170 °C into discs 25 mm in diameter and 1.8 mm thick, under a pressure of approximately 16 MPa.

The actual filler content in the compounds was determined after ashing in porcelain crucibles for 4 h at 450 °C and found to be within the range 59 to 61 wt %.

2.2. Testing procedures

2.2.1. Capillary rheometry

A Davenport capillary rheometer was used to obtain shear viscosity data at 200 °C for compositions of polypropylene containing magnesium hydroxide, using a 1 mm diameter die with *L*/*D* 40:1 and 180° entrance angle. Die entrance pressures and piston speeds were converted to apparent wall shear rates and stresses without applying Rabinowitsch or end corrections, since in this work the primary interest was to obtain comparative results which would highlight differences in polymer flow behaviour resulting from the presence of the magnesium hydroxide variants.

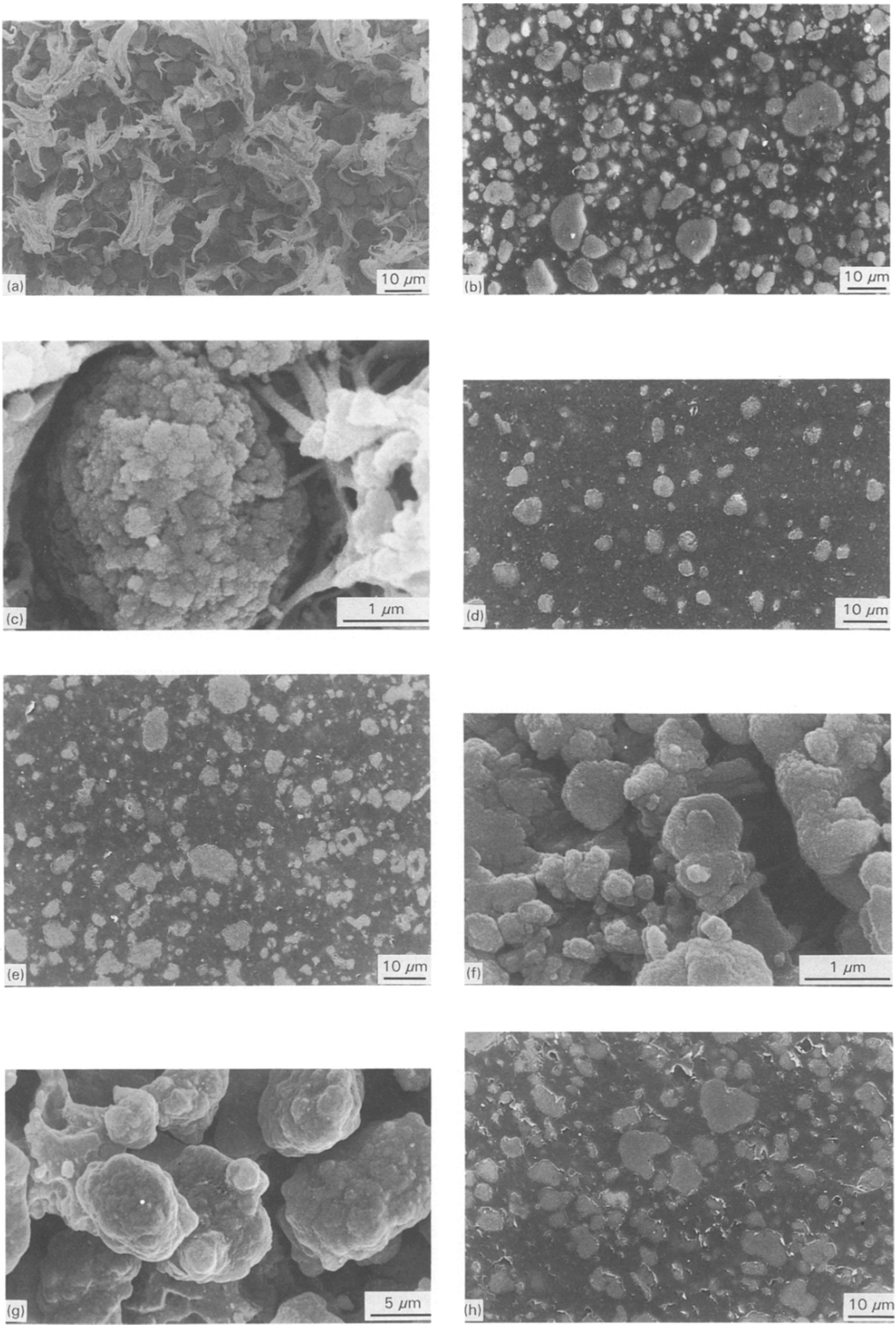

Figure 1 Scanning electron micrographs of polypropylene filled with different magnesium hydroxide variants: (a) type A–tensile fracture surface; (b) type A–polished surface; (c) type B–tensile fracture surface, showing crystallite aggregate formation; (d) type B–polished surface; (e) type C–polished surface; (f) type D–tensile fracture surface, indicating plate-like structure of filler; (g) type E*–tensile fracture surface, showing surface-coated magnesium hydroxide particles comprising aggregated crystallites; (h) type E* –polished surface.

TABLE I Particle characteristics of magnesium hydroxides used in compound preparation

Type	Mean particle size (μm)^a	Surface area (m^2)^b
A	7.7	27.9
B	0.9	12
C	4.0	7.2
D	0.53	11
E*^{c}	3.7	14.3

^{a}Determined by Sedigraph.
^{b}From single-point BET analysis.
^{c}Surface-treated with 6% magnesium stearate.

2.2.2. Dynamic mechanical analysis

Measurements of the complex viscosity (η^*), storage (G') and loss (G'') modulus were carried out on a Rheometrics dynamic analyser RDA II at 200 °C, using 25 mm diameter parallel plates.

Two types of viscoelastic regime were investigated. Firstly, dynamic properties were obtained by adapting a previously reported experiment [10] where the sample was set between parallel plates preheated to 200 °C, and after temperature equilibrium was attained (about 15 min), measurements were recorded between angular frequencies (ω) ranging from 0.01 rad s^{-1} (0.002 s^{-1}) to 398 rad s^{-1} (63.34 s^{-1}), at a strain amplitude of 10%.

In a second procedure, measurements of storage and loss moduli were made after temperature equilibrium was attained (about 15 min) at 200 °C followed by application of a constant low angular frequency, 0.2 rad s^{-1} (0.0318 s^{-1}) again at a strain amplitude of 10%, over a period of 2 h.

These measurements were made in the linear viscoelastic region, where the viscoelastic properties are independent of strain, as determined from a strain sweep and plots of response against strain. The strain amplitude of 10% was selected because this fell below the critical strain above which there was a detectable change in viscoelastic behaviour.

2.2.3. Morphological observations

Direct observation of magnesium hydroxide filler dispersion was undertaken by scanning electron microscopy on both polished and fracture surfaces. Polished samples were prepared from injection-moulded samples of the polypropylene compounds. Representative sections were encapsulated in epoxy resin, then polished with 180 (coarse) to 600 (smooth) grade emery paper before finishing with 1 μm diamond paste. Both polished and fracture samples were mounted on aluminium stubs and sputter-coated with a layer of gold–palladium alloy before examination, in order to reduce the accumulation of electrostatic charge. Analysis was undertaken on a Jeol 840 scanning electron microscope (SEM), with an accelerating voltage of 20 kV.

3. Results and discussion

3.1. Analysis by capillary rheometry

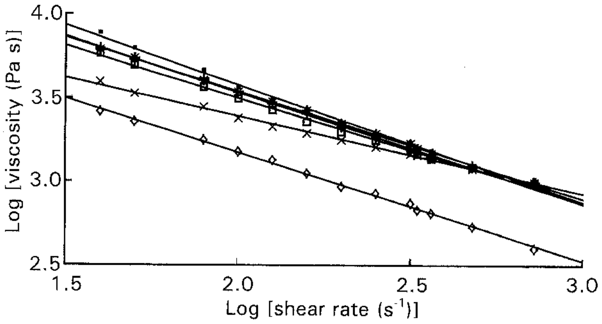

Figure 2 Influence of magnesium hydroxide filler on the shear viscosity of polypropylene at 200 °C. Results obtained by capillary rheometry at a filler level of 60 wt %. (■) type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

Fig. 2 demonstrates that in the region of low applied shear, the addition of magnesium hydroxide to polypropylene results in enhanced melt viscosity compared to unfilled polymer. Amongst the filled compounds studied, polypropylene containing surface-treated magnesium hydroxide (type E*) exhibited the lowest melt viscosity, especially at low shear rates, but as the shear rate increased its melt viscosity tended towards that of other filled compounds. This result is consistent with the assertion of Boaira and Chaffey [16] that the viscosity at high shear rates is dominated by the influence of the polymer matrix, resulting in convergence of the curves. The lower viscosity observed using magnesium hydroxide E* is attributed to enhanced compatibility between polymer and filler leading to a decrease in the degree of particle agglomeration [10].

Analogous results were reported by Chapman and Lee [20], who found that chemically treated talc yielded a lower viscosity in polypropylene than did unmodified filler, which was also explained in terms of reduced particle interaction effects. Sothern and Hodd [3] found the melt viscosity of polypropylene filled with stearic acid-coated calcium carbonate to be substantially lower than when uncoated filler was used. Similarly, Tanaka and White [8] in comparing data for calcium carbonate-filled polystyrene measured a higher composite viscosity with untreated calcium carbonate than with surface-treated filler, at the same level of addition.

At very low shear rates of around 30 s^{-1}, the viscosity of polypropylene filled with untreated magnesium hydroxide appears to increase very slightly with increasing particle size (i.e., D < B < C < A) (Table I and Fig. 2). If significant, these results apparently contradict published data, which suggest that larger particles give rise to reduced viscosities [3, 6, 7, 12, 17]. It is possible, however, that observed differences in viscosity could be influenced by the crystallite size and morphology of the particles. Magnesium hydroxide A, for example, is a high surface-area aggregate of small primary crystallites which forms an approximately spherical structure. In contrast, particles of B and in particular D are essentially hexagonal crystallites of smaller size and lower surface area. Furthermore, the higher surface area of material A may also cause

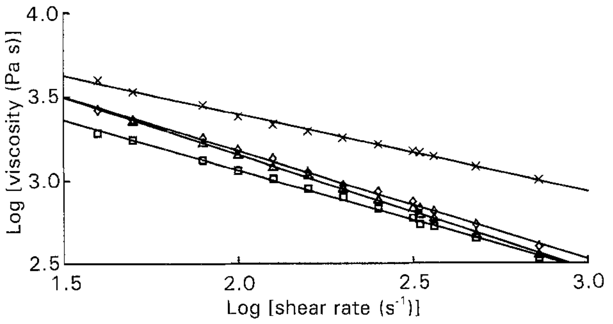

Figure 3 Effect of magnesium stearate on the shear viscosity of polypropylene at 200 °C: (◇) no addition, (△) 5% Mg stearate, (□) 10% Mg stearate, (×) polypropylene filled with 60 wt % of surface-treated magnesium hydroxide (type E*).

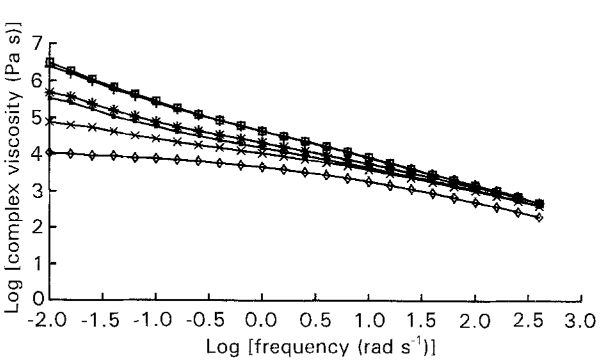

Figure 4 Effect of magnesium hydroxide filler type on the complex dynamic viscosity of polypropylene; temperature 200 °C, strain amplitude 10%. (■) Type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

further polymer "immobilization", thereby raising the viscosity.

Fig. 3 shows how incorporation of magnesium stearate into polypropylene at additions of 5 and 10% causes a reduction in viscosity relative to unmodified polymer, the effect being particularly pronounced at the higher addition level of treatment used. Hence in addition to being a dispersion aid, it is likely that when present in amounts in excess of that needed to fully coat the filler surface, magnesium stearate may also function as a plasticizer or external lubricant for polypropylene.

3.2. Dynamic mechanical analysis

Kataoka *et al.* [21] reported that the parallel-plate rheometer is suitable for studying the flow properties of filled and reinforced polymer compositions, the melts often being highly viscous and sometimes exhibiting a critical yield stress for flow to occur. For example, using glass fibre incorporated into polyethylene and polystyrene, reproducible results were shown to be achievable by this method at filler volume fractions up to 0.5.

Fig. 4 demonstrates that unfilled polypropylene exhibits Newtonian flow in the low frequency region, whereas filled melts containing untreated magnesium hydroxides A to D generally exhibit large increases in viscosity as the test frequency declines. However, it is significant that at very low shear rates polypropylene filled with surface-modified magnesium hydroxide (sample E*) exhibited a much lower melt viscosity than the other compositions containing uncoated filler.

Furthermore, it is apparent that at very low shear rates, the viscosity of polypropylene filled with untreated magnesium hydroxide is raised as the particle size decreases in the following order: $A \simeq C < B \simeq D$. These obervations differ from the shear viscosity results obtained at much high shear rates and discussed earlier, but are in general agreement with literature reports which suggest that as the filler particle size is increased, so the melt viscosity declines [6, 7, 10, 17]. The work reported by Sothern and Hodd [3] attributed differences in the melt viscosity of polypropylene compounds containing calcium carbonate and talc fillers to particle size effects. Han [17] has considered the effect of particle shape on the viscosity of filled polypropylene melts, in which the glass bead fillers used had the same density and particle size as the talc filler. It was found that material with spherical glass beads gave rise to lower viscosities than for the corresponding melt containing talc particles of irregular shape. The explanation put forward was that glass beads have less surface activity than talc and that their spherical shape minimizes the particle surface contact, both factors leading to weaker interaction for the glass beads than for the talc particles. In dilute suspensions with non-interacting spherical particles it has been shown that the viscosity is enhanced by energy dissipation owing to the presence of the solid particles [22]. These principles have been extended to more concentrated systems and to particles with other shapes, with reviews reported by Happel *et al.* [23] and Jeffrey and Acrivos [24].

As mentioned previously, according to Hertlein and Fritz [12] the effect of particle size on viscosity arises from an ability of particles to immobilize molten material and thus reduce the volume of flowable melt, to an extent dependent on their size and surface area. The results obtained for magnesium hydroxide compositions in this investigation are probably, therefore a combination of effects arising from differences in particle size, morphology and degree of aggregation. Firstly, plate-like particles would be expected to effect a greater increase in viscosity than more spherical geometries, as indicated earlier. Also the very high viscosity obtained, particularly from compositions B and D, can be accounted for by increased particle interaction due to the relatively small particle size of these materials (Table I), since it is known that at very low shear rates the rheological properties of polymer melts containing high levels of small particulates may be dominated by structure formation resulting from interacting particles [25]. Beyond a critical shear yield stress, disruption of the structure may take place as flow occurs. However, increasing the effective filler particle size and the presence of surface treatment are likely to diminish these interactive forces, reducing the required yield stress for the onset of flow.

Similar observations were reported by Tanaka and White [8] using polystyrene (PS) containing various fillers at the same addition level. The viscosity at very low shear rates was found to decrease in the following order: carbon black, untreated $CaCO_3 > TiO_2 >$ surface-treated $CaCO_3 >$ PS. The pure polystyrene melt exhibited a Newtonian region at low shear rates with pseudoplastic behaviour occurring at higher conditions of shear. The filled melts possessed higher viscosities which increased with loading level. The highly filled systems exhibited an unbounded increase in viscosity as the shear rate was lowered. Carbon black- and titanium dioxide-filled polymer melts yielded a critical stress of magnitude dependent on many factors, including the nature of the filler and matrix used, filler loading level, particle size and melt temperature [25]. Suetsugu and White [9] also associated the existence of critical yield values with the presence of small particles; however, in compounds containing larger particles such as glass spheres and glass, aramid and cellulose fibres, this effect was absent [12, 22, 26–28].

For pigment–oil suspensions, Casson [29] has developed a theoretical flow equation, giving the shear stress τ as a function of shear rate $\dot{\gamma}$:

$$\tau^{1/2} = S_0 + S_1(\dot{\gamma})^{1/2} \qquad (3)$$

where S_0 and S_1 are constants depending on the pigment concentration. Pigment particles forming long chains by mutual attraction are, for simplification, treated as long rod-like aggregates, which are broken down by the applied shear stress. Casson also proposed a semi-empirical relationship between an equilibrium dimension of aggregates, measured by an axial ratio J which depends on both the shear rate ($\dot{\gamma}$) and cohesive forces between particles in these aggregates [30].

Plots of drive motor torque against frequency for different polypropylene compositions containing magnesium hydroxide are shown in Fig. 5. Critical yield stress values (τ) were subsequently determined from torque values at zero frequency, using

$$\tau = MK_\tau$$

where τ is the stress (Pa), K_τ the stress constant and M the transducer torque (g cm). K_τ is given by $2G_c/\pi(R/10)^3$ where R is the disc radius (mm) and G_c is given as 98.07 Pa g^{-1}.

The results tabulated in Table II show that values for shear yield stress ($\tau^{1/2}$) increase with decreasing magnesium hydroxide particle size: E* < A < C < B < D, consistent with reported particle size effects [8, 9, 12]. It is significant that polypropylene filled with surface-treated magnesium hydroxide (E*) shows a marked reduction in critical yield stress, in accordance with the view that either particle structure formation in this composition is lower, and/or particle interactive effects are reduced by the presence of surface treatment.

Kataoka *et al.* [31] working with polyethylene and polystyrene filled with glass beads and hollow glass microspheres, reported that filler particle size distributions influenced the relative viscosity only at a defined filler concentration. Critical yield stresses were estimated and found to increase exponentially in the volume fraction range from 0.1 to 0.5. The magnesium hydroxide filler volume fraction used in this work was 0.37.

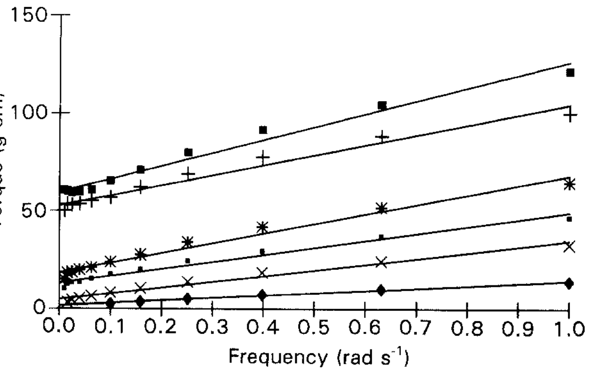

Figure 5 Relationship between rheometer drive torque at 200 °C and frequency for polypropylene containing magnesium hydroxides: (■) type A, (+) type B, (✱) type C, (■) type D, (×) type E*, (◆) unfilled polypropylene.

TABLE II Yield stress values for polypropylene melts containing 60 wt % of magnesium hydroxide filler at 200 °C

Filler type	Particle size (μm)	(Yield stress)$^{1/2}$, $\tau^{1/2}$ ($N^{1/2}$ m^{-1})
A	7.7	20
B	0.9	41
C	4.3	24
D	0.53	44
E*	3.7	12

3.3. The Cox–Merz rule

The Cox–Merz rule [32] is a relationship which states that under some circumstances the complex viscosity is equal to the steady shear viscosity when the frequency (rad s^{-1}) is equal to the shear rate (s^{-1}). This rule is usually applied to polymer melts and can be used to extend the range of measurement of the steady shear viscosity, especially to very low shear rates. Hence at low frequencies and shear rates the complex viscosity and non-Newtonian viscosity reflect similar characteristic relaxation times [33]. However, it has been reported that this rule is not applicable at large values of complex and shear viscosity since steady flow at high shear rates involves different molecular motions from oscillating flow at low amplitudes [33].

The Cox–Merz rule has been confirmed experimentally for a variety of polymer melts [34] (but not previously with filled compositions), and can be predicted by non-linear constitutive equations [35]. More detailed description of these parameters and their inter-relationships can be found in the extensive literature available on the topic [36, 37].

Fig. 6 shows a superposition of complex viscosity data and shear viscosity data for polypropylene and the magnesium hydroxide-filled polypropylene compositions studied in this work. In all cases there is a very close correlation between the complex viscosity–angular frequency curves and the capillary viscosity–

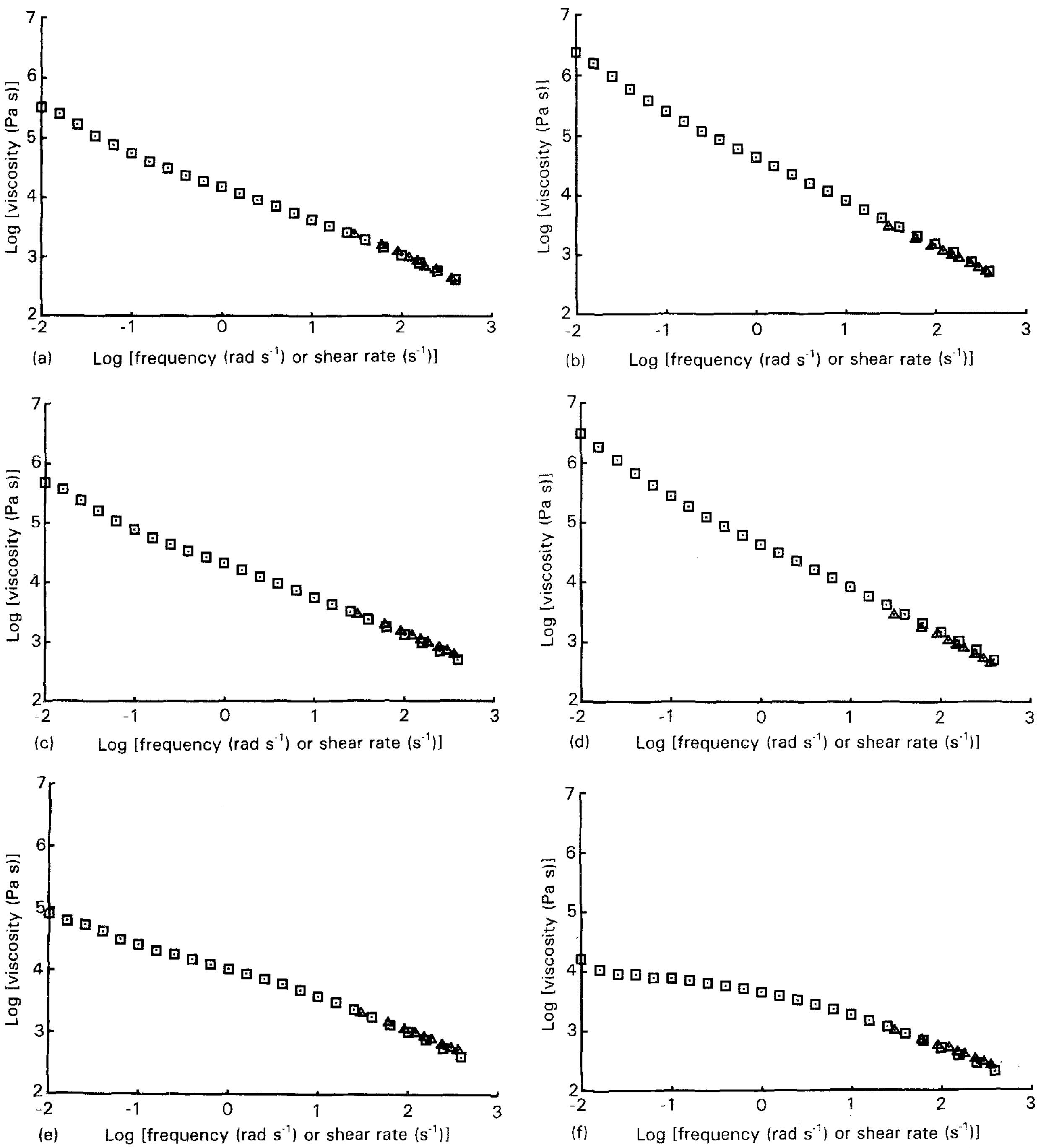

Figure 6 Superposition of (□) dynamic complex viscosity and (△) capillary shear viscosity for magnesium hydroxide-filled polypropylene; 60 wt % of filler, test temperature 200 °C. Magnesium hydroxide variant: (a) type A, (b) type B, (c) type C, (d) type D, (e) type E*, (f) polypropylene.

shear rate data, in accordance with the Cox–Merz rule.

3.4. Dynamic storage and loss moduli

Changes in the dynamic storage (G') and loss (G'') moduli with frequency are shown in Figs 7 and 8, respectively. The dynamic modulus of all the filled polypropylenes decreases more slowly as the frequency is reduced than does the modulus for unfilled polypropylene, in most cases resulting in the formation of a plateau at very low applied frequencies.

In this region, the dynamic modulus of polypropylene filled with uncoated magnesium hydroxide decreases as the particle size increases, i.e. D < B < C < A. As discussed earlier, for complex viscosity results these observations can be attributed to particle interactions between the untreated fillers arising from agglomerate formation. Similar conclusions were drawn by Lin and Masuda [11] in work with calcium carbonate-filled polypropylene to account for the observed enhancement in storage modulus G' for the melt filled with small particles. Surface treatment of the filler (sample E*), however, gave rise to behaviour more like that of unfilled polypropylene, in accordance with the reduced particle interaction effects mentioned previously.

Figs 9 and 10 show changes in dynamic storage and loss moduli with time, measured at 200 °C using a frequency of 0.2 rad s^{-1} (0.0318 s^{-1}) and strain amplitude 10%. Higher values of G' and G'' were recorded for all filled systems at very low times which, most

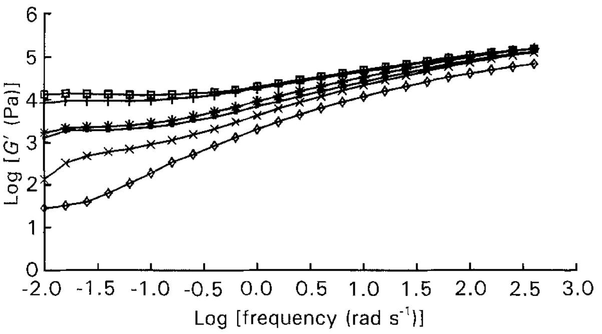

Figure 7 Effect of magnesium hydroxide on the dynamic storage modulus G' of polypropylene; temperature 200 °C, strain amplitude 10%. (■) Type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

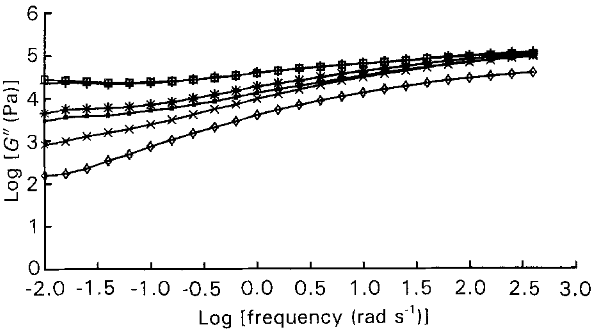

Figure 8 Effect of magnesium hydroxide on the dynamic loss modulus G'' of polypropylene; temperature 200 °C, strain amplitude 10%. (■) Type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

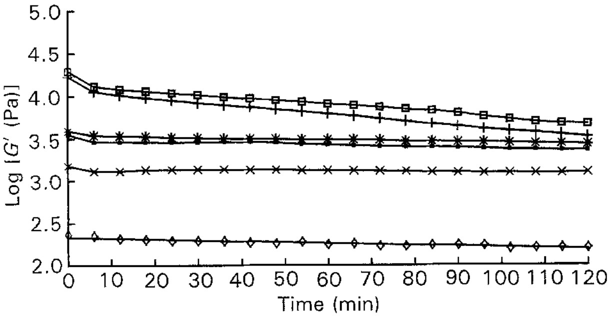

Figure 9 Effect of magnesium hydroxide on the dynamic storage modulus G' of polypropylene as a function of time; temperature 200 °C, strain amplitude 10%, frequency 0.2 rad s^{-1}. (■) Type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

notably with fillers B and D, gradually declined as the experiment proceeded, reflecting a progressive breakdown in particle structure with time.

It is interesting to note, however, that after a small initial decline in G' and G'', samples E*, A and C show stable behaviour indicating that the particles exist in a relatively well-dispersed form. The relatively constant results for polypropylene also indicate that the changes in G' and G'' (particularly for compositions B and D) are not due to degradation of the polymer over the time scale of the experiment.

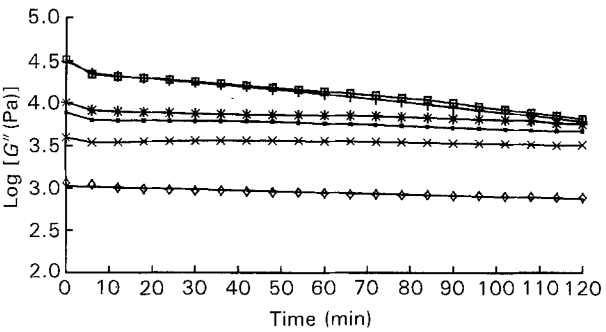

Figure 10 Effect of magnesium hydroxide on the dynamic loss modulus G'' of polypropylene as a function of time; temperature 200 °C, strain amplitude 10%, frequency 0.2 rad s^{-1}. (■) Type A (7.7 μm), (+) type B (0.9 μm), (∗) type C (4.0 μm), (□) type D (0.53 μm), (×) type E* (3.7 μm), (◇) unfilled polypropylene.

3.5. Morphological observations

Representative photomicrographs showing the filler dispersion in fractured and polished samples of polypropylene magnesium hydroxide composites are presented in Fig. 1. Generally all the magnesium hydroxide particles appear to be evenly distributed in the polymer matrix, with no obvious evidence for particle agglomeration although crystallite aggregates were clearly apparent, particularly in samples A, B and E.

Hence, from these micrographs alone it is not possible to draw meaningful conclusions about the relative level of filler dispersion between the magnesium hydroxide variants used in this investigation.

4. Conclusions

It has been shown that magnesium hydroxide particle morphology, size and applied surface coating influence the rheology of filled polypropylene melts. At the level of filler addition under investigation (37 vol %), the shear viscosity increased markedly due to the presence of uncoated magnesium hydroxide, although at low shear rates (between 30 and 363 s^{-1} in particular) this change in viscosity is less pronounced using a filler coated with magnesium stearate. Only small differences in shear viscosity behaviour were observed between the uncoated magnesium hydroxide variants under investigation over this range of shear rates.

However, using dynamic viscoelastic measurement techniques at very low angular frequencies (down to 0.01 rad s^{-1}), clear differences in response were seen between the filler types, with polypropylene containing the smaller particle grades yielding much higher values of complex viscosity and dynamic moduli. These effects are attributed to the formation of networks or agglomerated structures arising from strong interactive forces between the particles.

Additionally, the existence of a critical shear yield stress for flow to occur has been identified which is significantly less pronounced with the larger particle size fillers studied, and in particular when surface treatment is applied.

It has been shown for the conditions used in this work that results for the complex and shear viscosity of polypropylene and magnesium hydroxide-filled polypropylene melts can be superimposed according to the Cox–Merz rule.

Acknowledgements

The authors are grateful to the Polymer Engineering Directorate of the Science and Engineering Research Council and Redland Magnesia Limited (formerly Steetley Magnesia Products Ltd) for their support of the work described in this communication.

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Received 1 March
and accepted 28 April 1994