

Effects of Stearic Acid Coated Talc, CaCO₃, and Mixed Talc/CaCO₃ Particles on the Rheological Properties of Polypropylene Compounds

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ABSTRACT: The effect of the stearic acid coated fillers and their geometry on the shear/dynamic viscosity and complex viscosity has been investigated using polypropylene (PP) compounds filled with stearic acid uncoated and coated talc, calcite, and mixed talc/calcite particles. The viscosity was measured over a wide range of shear rates (10^{-8} to 10^3) using a capillary, cone-plate and sandwich rheometer. Overall, the rheological properties of the compounds exhibited different behavior upon different filler systems, stearic acid involvement, shear stress or strain, and frequencies due to stearic acid involvement. This implies that the stearic acid lowers the interfacial force between the filler surface and the resin matrix, followed by a favorable processing. In addition, at very low shear stresses, the vis-

cosity of talc(un) compounds was higher than calcite(un) ones; at very high shear stresses, on the other hand, talc compounds became lower than calcite(un) compounds. This is interpreted as due to the different geometry between talc and calcite. The yield value as a function of shear stress was observed for all filler systems and exhibited lower than that obtained from the extrapolation. Furthermore, the Cox–Merz relation between the complex and shear viscosity for both the stearic acid uncoated and coated compounds is found not valid. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2105–2113, 2004

Key words: stearic acid; calcite; talc; polypropylene compounds; rheology; geometry; orientation; Cox–Merz rule

INTRODUCTION

Minerals are compounded with thermoplastics for several purposes such as mechanical reinforcement, enhancement in electrical conductivity and in thermal properties, x-ray shielding, or lowering production cost. Mineral fillers such as calcite, talc, silica, mica, and clay have become important materials in the polymer industry due to their ability to fulfill the above roles. Among these, calcite is one of the most common fillers. Calcite is known as an isotropic particle because of its shape; thus, it affects the compounds equally in all directions. Other particles such as talc, mica, and clay are anisotropic as they consist of two-dimensional layered silicate sheets (disc-like shape) and they are often oriented in thermoplastic parts.

The flow of molten polymers filled with various filler particles has become of importance in the thermoplastic industry. Furthermore, these fillers often contain additives such as stearic acid, which affects the level of agglomeration and which improves the flow behavior of the polymer. Stearic acid is obtained

from tallow, animal fats, or vegetable oils as a glyceride form. Common stearic acid mainly consists of a mixture of octadecanoic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) and palmitic acids and is often used in the rubber industry as a processing aid.^{1–3} Although stearic acid is considered as an important additive, no specific or comparative study on the role of stearic acid on polyolefin compounds has been reported.

There have been many investigations on the rheological properties using filled polymer systems with various filler systems.^{4–12} It is well known that thermoplastic melts with high loading of small particles, such as calcium carbonate, carbon black, titanium dioxide, or talc, may exhibit apparent yield values in shear flow.^{4–13} Measurement on yield values of polymer compounds was made using creep experiment. Modifying sandwich creep rheometer developed by Toki and White,¹¹ Osanaiye et al.,¹⁸ and Li and White¹⁹ resulted yield values in synthetic rubber compounds. Araki and White²⁰ also reported the yield value using the carbon black filled polypropylene. Recently, Kim and White²¹ reported the yield behavior in the talc and calcite filled polystyrene using a third generation modified sandwich rheometer.

In this paper, the shear and complex viscosity of polypropylene (PP) compounds filled with stearic acid

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TABLE I
Characteristics of Materials and Supplier

Materials	Supplier	Avg. particle size aspect ratio
Polypropylene (PP)	Solvay	MI = 8.5 g/min at 230°C
Talc 1 (ABT-2500, Montana talc, uncoated)	Barrets Minerals Inc.	2.5 μm 15 : 1 \approx 20 : 1
Talc 2 (Polytalc 262, Montana talc, coated)	Barrets Minerals Inc.	2.5 μm 15 : 1 \approx 20 : 1
Calcite 1 (Vicron 15-15, uncoated)	Specialty Minerals Inc.	3.5 μm 1 : 1
Calcite 2 (Hi-Pflex 100, coated)	Specialty Minerals Inc.	3.5 μm 1 : 1

uncoated and coated talc, calcite, and mixed talc/calcite particles were measured using various instruments over a wide range of shear rates (10^{-8} to 10^3). The effect of the stearic acid coated fillers on the rheological properties is investigated. The techniques used for the measurement of the shear/complex viscosity are the capillary rheometer, cone-plate, oscillatory, and creep measurements depending on the shear rates. In addition, the relationship between the shear/complex viscosity and the Cox–Merz rule²² is also evaluated.

EXPERIMENTAL

Materials

The homopolypropylene (PP) (MI = 8.5 at 230°C) was a Solvay (Brussels, Belgium) product with a brand name of Eltex P PV 001 P. Uncoated talc (ABT-2500, 2.5 μm) and coated talc (Polytalc 262, 2.5 μm) with stearic acid were supplied by Barret Minerals Inc. (Connecticut, USA). The talc particles characterized using a scanning electron microscope (SEM) were confirmed to be disc shape, having a 0.4 μm thickness and 5.4 μm of diameter.

Uncoated calcite (Vicron 15–15, 3.5 μm) and coated calcite (Hi-Pflex 100, 3.5 μm) with stearic acid were provided by Specialty Minerals Inc. (New York, NY) and have a merely spherical shape. The characteristics of PP, talc, and calcite particles used are summarized in Table I.

Compounding

A Werner and Pfleiderer (W&P, Stuttgart, Germany) ZSK-40 M32.5 modular intermeshing corotating twin-screw extruder was used to disperse minerals in PP matrix. The total weight percentage of the fillers was fixed at 40 wt %, and they are divided into 20 wt % each when using both (talc and calcite). We denote the uncoated talc compound (talc(un)) as 0.6/0.4(un)/0.0, the uncoated calcite compound (calcite(un)) as 0.6/0.0/0.4(un), and mixed uncoated talc/calcite compound as 0.6/0.2/0.2(un). The stearic acid coated compounds are denoted equivalently as (talc(co)) for 0.6/0.4(co)/0.0, (calcite(co)) for 0.6/0/0.4(co), and (talc/calcite(co)) for 0.6/0.2/0.2(co). The detailed com-

positions of the talc and calcite filled system are summarized in Table II.

Shear viscosity

Several different instruments were used depending on shear rates: the capillary rheometer for high shear rates, the cone-plate for intermediate shear rates, and the sandwich creep rheometer for low shear rates. A sandwich rheometer, which was devised by Toki and White,¹¹ and modified by Osanaiye et al.¹⁸ and subsequently by Kim and White,²¹ was used to obtain the yield value. Figure 1(a) schematically represents the sandwich rheometer.

Compound specimens were prepared using a Wabash (Wabash, IN) compression mold machine at 210°C, then cut into 1.9 cm width and 17.8 cm length, and then inserted into between the stationary and moving plate, which has the same dimension as the specimens. The moving plate was pulled down by a weight using gravity force. The displacement of the moving plate was measured using a micrometer dial gauge having sensitivity as low as 0.001 cm. Atmospheric nitrogen gas was introduced into a sandwich chamber to prevent oxidative degradation of the specimen. The experiments using the sandwich rheometer were carried out at 210°C.

The calculation of the shear rate in the sandwich rheometer is as follows^{23,24}:

$$\dot{\gamma} = \frac{V}{H} \quad (1)$$

TABLE II
The Composition of PP Compounds With Talc and/or Calcite Uncoated and Coated With Stearic Acid

Code	PP (wt %)	Talc (wt %)	Calcite (wt %)
talc(un)	60	40(un)	
calcite(un)	60		40(un)
talc/calcite(un)	60	20(un)	20(un)
talc(co)	60	40(co)	
calcite(co)	60		40(co)
talc/calcite(co)	60	20(co)	20(co)

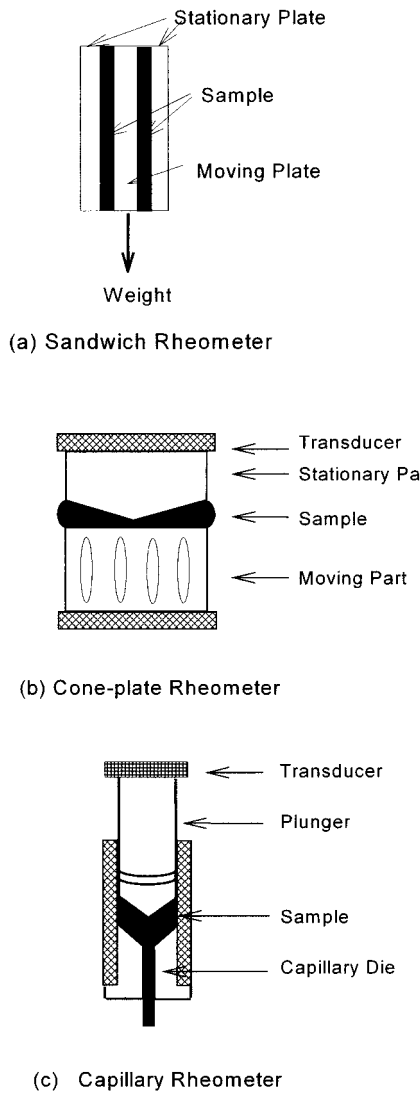


Figure 1 Schematic presentation of (a) sandwich rheometer, (b) cone-plate rheometer, and (c) capillary rheometer.

where V is the constant velocity (mm/s) of the moving plate and H is the specimen thickness (mm) between the moving and stationary plate. The shear stress can be obtained from

$$\sigma_{12} = \frac{F}{2A} \quad (2)$$

where F is the applied shear force and A is the surface area (m²) of the contacting plate.

A cone-plate Rheometrics RMS-800 (Piscataway, NJ) was used to measure the shear viscosity over a range of shear rates from 10^{-2} to 10^0 sec⁻¹. Figure 1(b) schematically represents the cone-plate rheometer. A plate of 25 mm diameter and a cone angle of 0.1 radian were used for the upper part, and the same diameter of the plane plate was used for the bottom part.

The shear rate and shear stress in the cone-plate mode are given by

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad (3)$$

$$\sigma_{12} = \frac{3M}{2\pi R^3} \quad (4)$$

where Ω is the rotation rate and α is the cone angle. The shear stress is determined from the torque, M , and the cone radius, R .^{23,24}

An Instron capillary rheometer (Instron 3211; Boston, MA) was used to measure the steady state shear viscosity at high shear rates from 10^0 to 10^2 sec⁻¹ using a series of dies with diameter of 1.6 mm and length/diameter (L/D) ratios of 9.3, 19.3, and 28.5 at 210°C. Figure 1(c) schematically represents the capillary rheometer. The die wall shear rate at the wall in a capillary rheometer is determined by using the following equation

$$\dot{\gamma}_w = \left[\frac{3n' + 1}{4n'} \right] \frac{32Q}{\pi D^3} \quad (5)$$

where Q is the flow rate and n' is defined by

$$n' = \frac{d \ln(\sigma_{12})_w}{d \ln(32Q/\pi D^3)} \quad (6)$$

The die wall shear stress was determined from the pressure loss in the capillary die. The total pressure, p_T , in the capillary rheometer is expressed as the following form:

$$p_T = \Delta p_{die} + \Delta p_{entrance} + \Delta p_{exit} = \Delta p_{die} + \Delta p_{ends} \quad (7)$$

$$p_T = 4(\sigma_{12})_w \left[\frac{L}{D} \right] + \Delta p_{ends} \quad (8)$$

where D and L are the diameter and length of a capillary, respectively. Equation 8 suggests the Bagley end correction,²⁵ where p_T is plotted as a function of L/D , and $(\sigma_{12})_w$ was determined from the slope and Δp_{ends} from the intercept.

Oscillatory complex viscosity and storage and loss modulus

The complex viscosity was measured using a RMS-800 Rheometer in a parallel plate mode at 210°C over a frequency range of 10^{-2} to 10^2 rad/s. A plate of 25 mm diameter was used for the upper and bottom part. The strain amplitude was constantly maintained at 1% for all measurements. The instruments used for the vis-

TABLE III
The Instruments Used for Viscosity Measurements at Various Frequency Range

Instruments	Frequency/shear rate range	
Sandwich rheometer	$10^{-2} \approx 10^{-8}$ (1/sec)	A sandwich rheometer modified by Kim
Cone-plate rotational rheometer	$10^{-2} \approx 10^0$ (1/sec)	Rheometrics RMS-800 (steady mode)
Capillary rheometer	$10^0 \approx 10^3$ (1/sec)	Instron 3211
Parallel-plate rotational rheometer	$10^{-2} \approx 10^2$ (radian/sec)	Rheometrics RMS-800 (oscillatory mode)

cosity measurements are summarized in Table III with frequency range.

The shear stress for the sinusoidal oscillatory flow experiments has the form:

$$\sigma_{12}(t) = G^*(\omega)\gamma \sin(\omega t + \delta) = G'(\omega)\gamma \sin\omega t + G''(\omega)\gamma \cos\omega t \quad (9)$$

where γ is the shear strain, G' is the storage shear modulus, G'' is the loss shear modulus, G^* is the complex shear modulus, ω is the frequency, and δ is the loss angle. The storage modulus, loss modulus, and complex modulus in the parallel plate mode are related to the torque M through:

$$G'(\omega) = G^* \cos\delta = \frac{2MH}{\pi R^4 \theta} \cos\delta \quad (10)$$

$$G''(\omega) = G^* \sin\delta = \frac{\eta'}{\omega} = \frac{2MH}{\pi R^4 \theta} \sin\delta \quad (11)$$

$$\eta^* = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} = \frac{G^*}{\omega} \quad (12)$$

where R is the plate radius, H is the gap height, and θ is the shear angle.

RESULTS

Effects of stearic acid on the shear viscosity

The representative shear strain creep for the specimen of PP/talc/calcite (un) at various creep levels is expressed as a function of time in Figure 2. In this creep experiment, we observed an increased strain with time at the stress held constant, $\gamma(\sigma, t)$, as shown in Equations 1 and 2.

The shear viscosity is presented in a logarithmic plot as a function of shear rate in Figure 3. The filler systems with uncoated and coated particles are compared in Figures 3(a), 3(b), and 3(c) for the talc, calcite, and the mixed talc/calcite system, respectively. The shear viscosity of all compounds decreased with shear rate. The shear viscosity of pure PP at lower shear rates is much lower than the filled systems and exhibits a plateau in the intermediate

frequency range ($10^{-2.5} \sim 10^0 \text{ sec}^{-1}$) of cone-plate. At very low shear rates near $10^{-5} \sim 10^{-3} \text{ sec}^{-1}$ (sandwich region), the order in viscosity was talc(un) > talc(co) > talc/calcite(un) > calcite(un) > talc/calcite(co) > calcite(co). At high shear rate region, where the shear rate is between 10 and 10^3 sec^{-1} (capillary region), the shear viscosity difference between the uncoated and coated filler system is minimized compared to that observed at low and intermediate shear rates.

In addition, the viscosity of the coated talc compounds exhibits almost the same values as that of the uncoated talc compounds between 10^{-5} and 10^3 sec^{-1} as seen in Figure 3(a). This implies that the stearic acid is more effective in lowering the viscosity of the calcite compounds than the talc compounds.

The shear viscosity is plotted as a function of shear stress of the compounds filled with uncoated and coated fillers in Figure 4. The data obtained using the sandwich rheometer shows good agreement with that obtained using the cone-plate. The viscosity of the uncoated talc system is almost the same as the coated talc system, and the calcite and

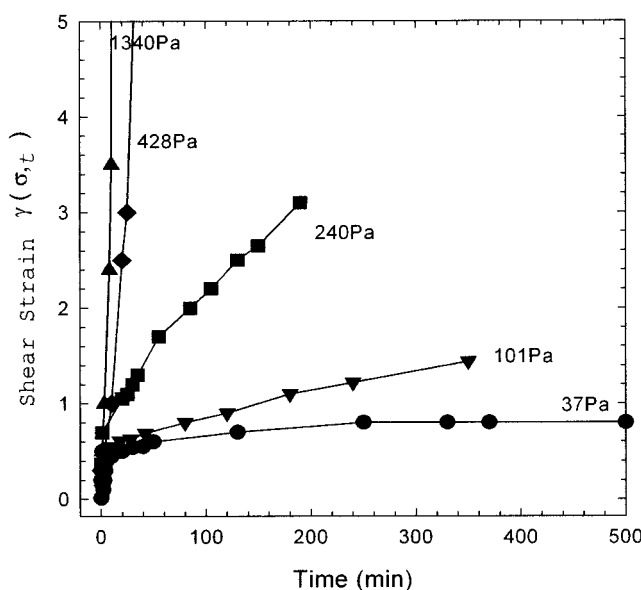


Figure 2 Shear strain creep as a function of time at various creep levels for PP/talc/calcite at 60/20/20(un) wt % at 210°C.

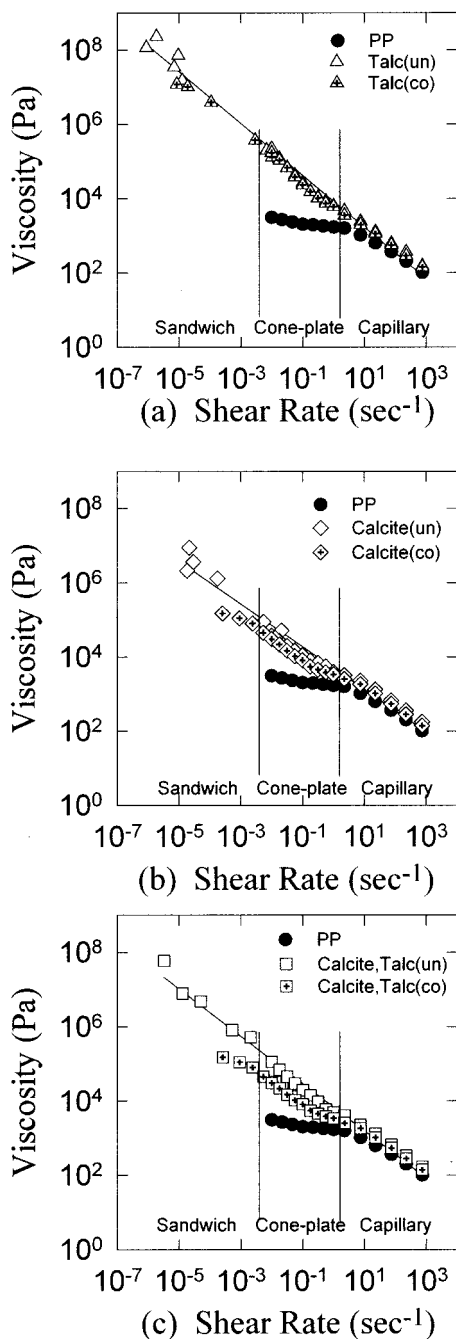


Figure 3 Shear viscosity as a function of shear stress on (a) PP/talc/calcite, (b) PP/talc, and (c) PP/calcite at 210°C.

mixed systems with talc/calcite are as well. In addition, at very low shear stresses, the viscosity of talc(un) compounds was higher than calcite(un) ones; at very high shear stresses, on the other hand, talc compounds became lower than calcite(un) compounds. In particular, for the compounds filled with uncoated fillers with talc, calcite, and talc/calcite mixture, the yield value for talc(un), talc(co), and talc/calcite(un), is approximately 40 Pa as seen in Figure 4.

Storage and loss modulus and complex viscosity

The storage (*G'*) and loss (*G''*) modulus as a function of strain are shown in Figures 5(a) and (b), respectively. Both modulus decreased with strain amplitude.

The effects are much greater with the compounds than the neat polymer melts. The loss modulus of each specimen was slightly higher than the storage modulus. The order of both modulus was consistent with

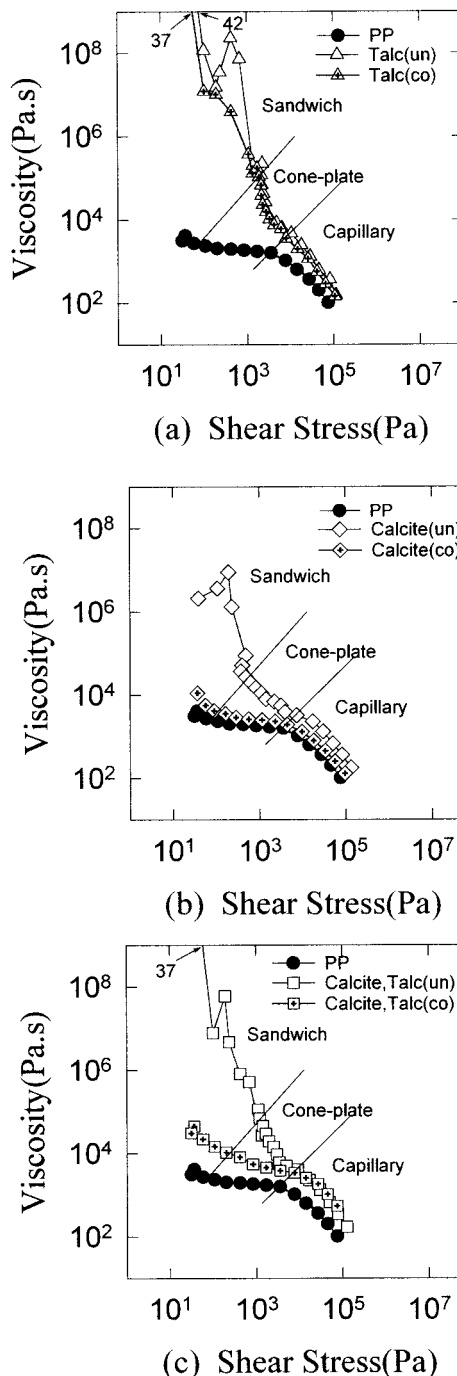


Figure 4 Shear viscosity as a function of shear stress on (a) PP/talc/calcite, (b) PP/talc, and (c) PP/calcite at 210°C.

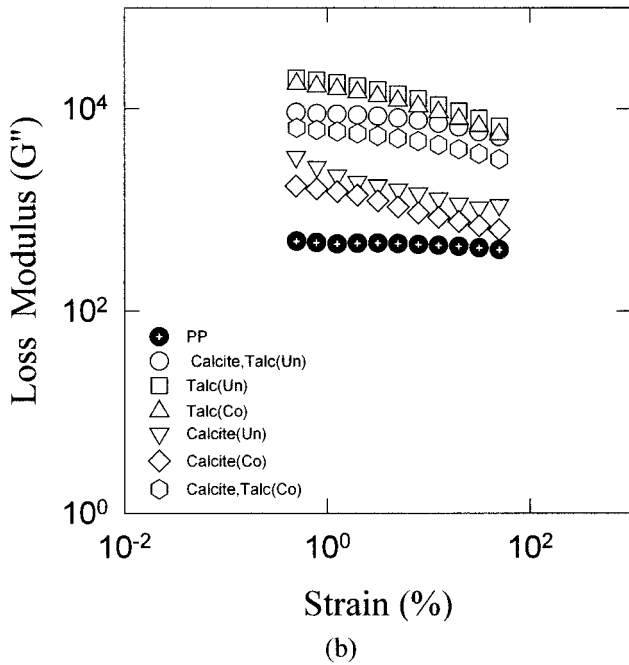
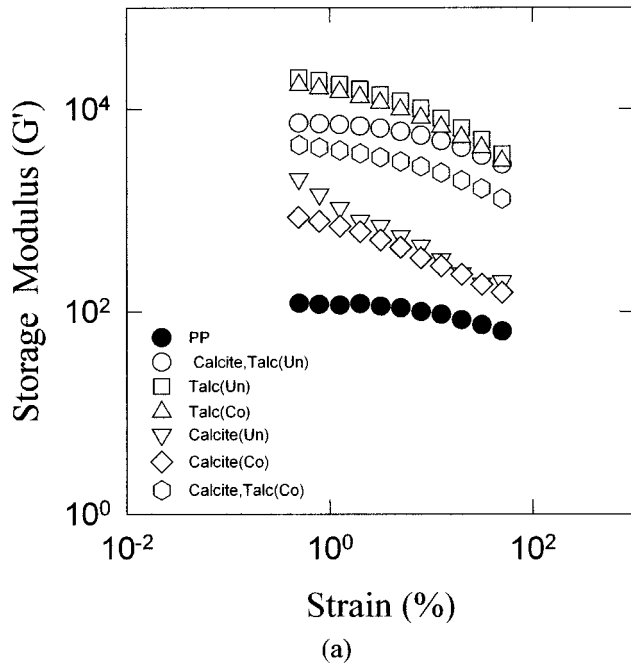


Figure 5 (a) Storage modulus (G'), and (b) Loss modulus (G'') of PP/fillers as a function of strain (%) at frequency of 1 ($\omega = 1$ rad/s) at 210°C.

the order of talc(un) > talc(co) > talc/calcite(un) > talc/calcite(co) > calcite(un) > calcite(co) > PP.

The modulus difference between talc(un) and talc(co) filled PP compounds was smaller than the difference between calcite(un) and calcite(co) filled PP compounds. This result is consistent with the shear viscosity.

The storage and loss modulus as a function of frequency at 1% strain are plotted in Figures 6(a) and (b), respectively. The trend of the storage and loss modulus is the same as seen in Figures 5(a) and (b), and the order of the modulus is PP/talc(un) > PP/talc(co) > PP/talc/calcite(un) > PP/talc/calcite(co) > PP/calcite(un) > PP/calcite(co) > PP. Here again, the modulus difference between talc(un) and talc(co) filled PP compounds is much lower than the modulus difference between calcite(un) and calcite(co) filled PP compounds.

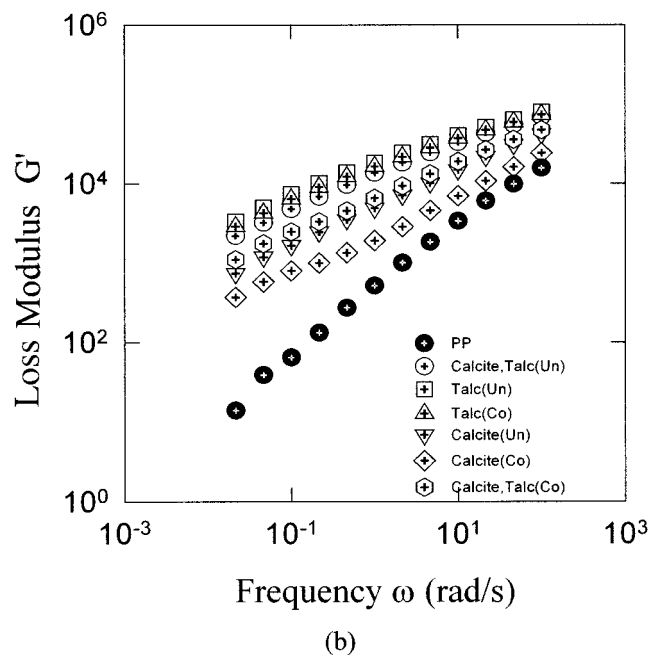
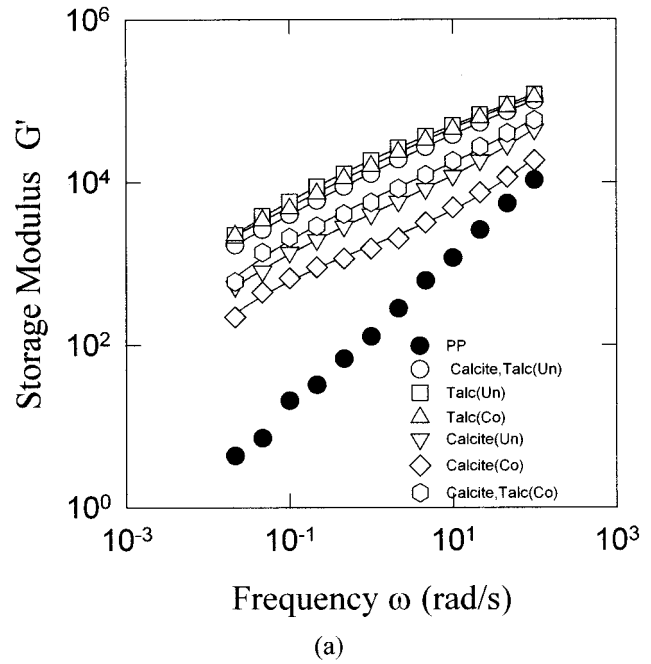


Figure 6 (a) Storage modulus (G'), and (b) Loss modulus (G'') of PP/fillers as a function of frequency at 210°C.

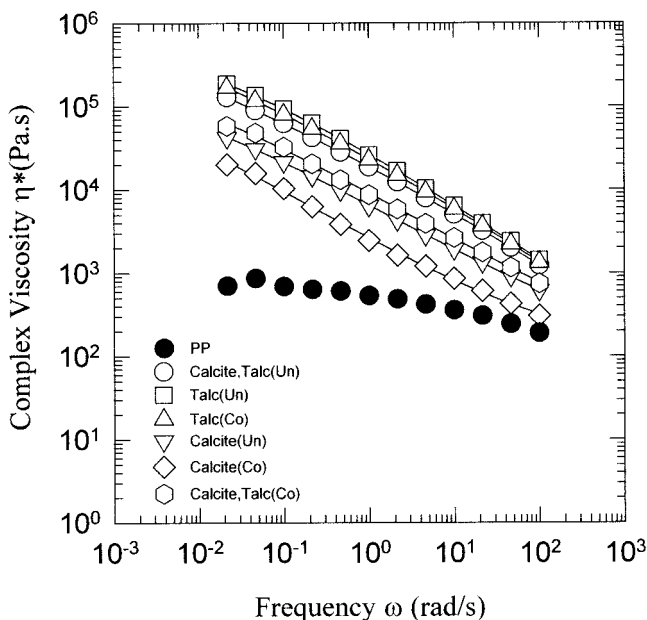


Figure 7 Complex viscosity of PP/fillers as a function of frequency at 210°C.

The complex viscosity (Equation 12) measured using a parallel-plate at the frequency ranges from 10^{-2} to 10^2 (sec^{-1}), is plotted in Figure 7. The order of the complex viscosity is in the same manner as the storage and loss modulus.

The complex viscosity, and the storage and loss shear modulus of the calcite filled PP compounds, are significantly reduced by stearic acid coating, whereas there is minimal reduction in the above properties for the talc compounds.

DISCUSSION

Comparison between the complex viscosity [$\eta^*(\omega)$] and the steady shear viscosity [$\eta(\dot{\gamma})$]

The comparisons between the complex viscosity $\eta^*(\omega)$ and the steady shear viscosity $\eta(\dot{\gamma})$ of the six compounds including pure PP are drawn in Figure 8 as a function of frequency (ω) and shear rate ($\dot{\gamma}$). For pure PP, it is found that $\eta^*(\omega) = \eta(\dot{\gamma})$ when ω equals $\dot{\gamma}$, which is in good agreement with the well-known Cox–Merz rule.²² However, for the filled compounds, the complex viscosity $\eta^*(\omega)$ is greater than the steady shear viscosity $\eta(\dot{\gamma})$ in 40 wt % of PP/talc, PP/talc/calcite, and PP/calcite filled system. Thus, it is found that the Cox–Merz relation failed in PP/talc, PP/calcite, and PP/talc/calcite compounds. Nakajima et al.^{26,27} first reported the failure of the Cox–Merz relation for the small particle filled polymer systems. Suh and White²⁸ also reported the failure of the Cox–Merz rule from 40 v % talc-PP and talc-PPS compound.

Orientation dependent rheological properties upon shear stress

As seen in Figures 3 through 7, the shear viscosity as a function of the shear rate and shear stress, the storage and loss shear modulus as a function of the strain and frequency, and the complex viscosity as a function of frequency, of the PP compounds showed the same trend. The order of the viscosity and modulus is talc(un) > talc(co) > talc/calcite(un) > talc/calcite(co) > calcite(un) > calcite(co) > PP. In addition, there is no significant difference in the rheological properties between the stearic acid uncoated and coated talc particles, whereas the calcite system exhibits difference in the viscosity and modulus. In addition, at very low shear stresses, the viscosity of talc(un) compounds was higher than calcite(un) ones; at very high shear stresses, on the other hand, talc compounds became lower than the calcite(un) compounds. This may be due to an anisotropic character of talc particles at high shear rate region because these two fillers have different geometry. Talc is known as an anisotropic particle consisting of two-dimensional layered silicate sheets (disc-like shape), whereas calcite is an isotropic particle. Anisotropic particles easily align to the flow direction (FD) proportional to the shear force applied. We propose that the orientation of the talc particle depends on the applied shear stress to the talc surface; thus, the tilted talc surface is compared with the calcite particle as seen in Figure 9. At the low shear rate region, the talc particles are oriented randomly to the FD. As the shear rate increases, talc particles oriented further toward the FD to minimize the resistance

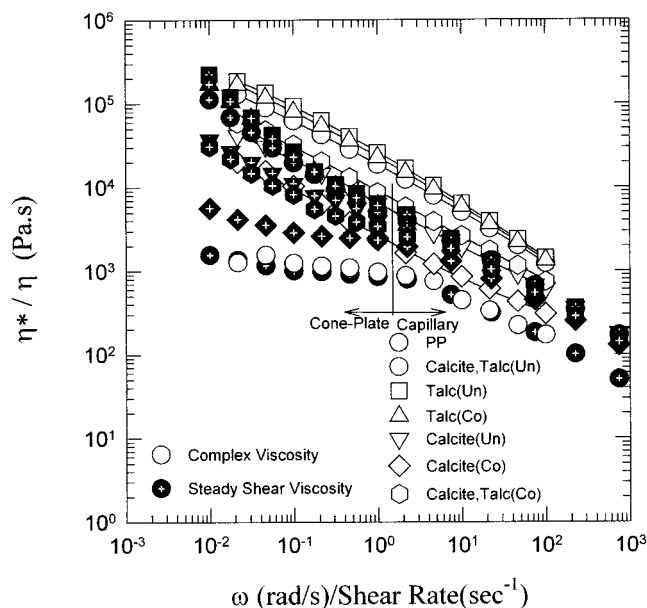


Figure 8 Comparison between complex viscosity (η^*) and shear viscosity (η) of PP/fillers as a function of frequency/shear rate at 210°C.

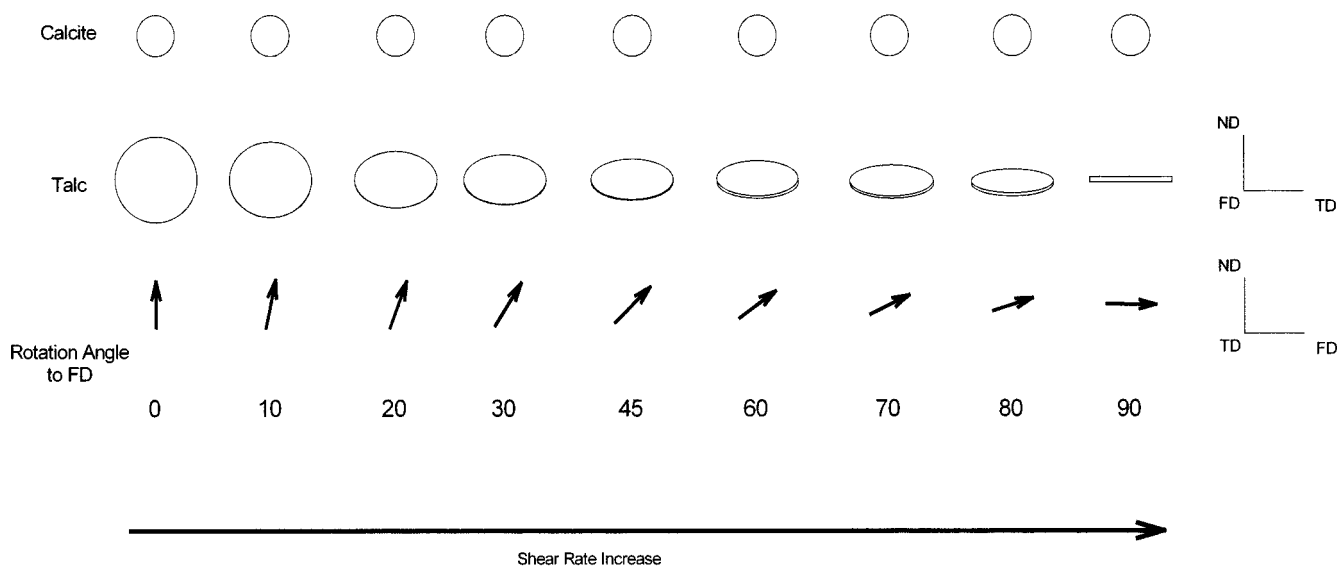


Figure 9 Schematic presentation of the orientation of the talc and calcite particles depending on the applied shear stress.

against flow. At the high shear rate region, while the talc particle orients further to the FD, the surface area of the calcite particle against flow direction remains constant due to its isotropic shape, but the talc surface area facing to the flow direction is smaller than that of calcite. This rationalizes that the compound filled with talc exhibits higher viscosity than the calcite filled compound at the low shear rate/stress region, but reverse behavior was observed at the high shear rate/stress region.

Comparison to other investigations

The existence of the yield value was observed in Figure 4. The yield behavior in particle filled compounds is probably particle–particle interaction, which leads to an agglomeration by forming of three-dimensional network structures. The coated talc system also exhibited a yield value at low shear stress, implying that the particle–particle interaction between the talc particles is dominant.

The rheological properties on the polystyrene compounds with talc and calcite including stearic acid were reported, and similar viscosity reduction occurred with the calcite/stearic acid system, but not with the talc system.²¹ Similar observations on the polystyrene/calcite compounds with stearic acid were reported by Suetsugu and White.¹² The interaction between PP and stearic acid is quite different from that of polystyrene with stearic acid. Ahn and White²⁹ found that octadecanoic acid (essentially stearic acid) induces slip in polyethylene and PP melts along steel walls, but not in the PS system. The reduction in viscosity by the addition of stearic acid to PS/calcite

compounds^{12,21} is reported due to the breakup of calcite agglomerate.

CONCLUSION

The effect of stearic acid on the filler particles and the particle shape on the shear/dynamic viscosity have been investigated using uncoated and coated talc, calcite, and mixed talc/calcite filled PP compounds. Stearic acid treated calcite particles significantly reduced the shear/dynamic viscosity; however, the talc compound did not exhibit considerable reduction, implying that the stearic acid is more effective on calcite filled compound than the talc compound. In addition, no significant shear viscosity difference between the stearic acid uncoated and coated talc was observed, whereas the viscosity difference between the uncoated and coated calcite system was observed. The order of the viscosity in the mixed talc/calcite systems was talc > talc/calcite > calcite. Thus, the isotropic calcite is suggested to give less interfacial force and hydrodynamic resistance between the filler and the PP matrix than an anisotropic talc material.

The existence of the yield value in uncoated compound systems was observed. The coated talc system also exhibited a yield value at low shear stress, implying that the particle–particle interaction between the talc particles is dominant. The failure of the Cox–Merz relationship between $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ was noted on 40 wt % particle filled compounds with both the stearic acid coated and uncoated talc, calcite, and talc/calcite particles.

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