

RHEOLOGY OF CERAMIC-POWDER-FILLED POLYMER MELTS

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ABSTRACT

Ceramic powder (zirconia) was mixed with binder consisting polypropylene, paraffin and stearic acid in elastic extruder. Steady and oscillatory shear flow properties of these materials in the molten state were measured on a cone-plate rheometer; parallel superposed steady and oscillatory shear flow experiments were also carried out. Moreover, flow properties at high shear rates were measured on a capillary rheometer. The studied filled systems showed remarkable non-Newtonian behaviour and apparent yield stress. Viscoelastic properties such as storage modulus and dynamic viscosity were influenced remarkably under the superposed shear flow at low shear rate and angular frequency, and showed significantly different behaviour from unfilled and other fiber-filled systems.

Keywords: ceramic powder, filled system, viscosity, viscoelasticity, superposed flow

1. INTRODUCTION

Thermoplastic composites have been widely used in various fields for decades. In order to improve their dimensional stability and other characteristics, polymeric materials are mixed with carbon and glass fibres and many other fillers. As an interesting example of the fillers, ceramic powders can be mentioned as a component for structural materials used especially in electric and electronic industrial areas requiring heat resistance and high-impact.

One of the powdery fillers used for thermoplastic composites is zirconium oxide (zirconia), which is an attractive ceramic material because of its hardness and low reactivity even at very high temperatures. Unfortunately, the pure form changes its structure at about 1000°C; below this value it has monoclinic structure, above it is tetragonal. The structural change does not require any excitation energy, so the transition in pure zirconia is spontaneous. The change results in a large volume variation, thus commonly sintered ceramic will turn into a powder as it passes the transition, which indeed has no practical use. However, this change can be inhibited by utilization of stabilizer, such as CaO, MgO or Y₂O₃. When sufficient amount of stabilizer is added, the stable phase becomes cubic. If less cations are replaced, then partially stabilized ZrO₂ is produced, which is actually even tougher than cubic or fully stabilized ZrO₂. At crack initiation, the crystallites at the site tend to convert to the stable phase, which absorbs energy and slows down the propagation of the crack.

Through the extrusion of polymer highly-filled with zirconia on a melt spinning apparatus, it is possible to obtain wires or fibers, the same as at solution/gel spinning of superconductive inorganic materials [1-4]. Then, after bending the extrudate into required shape, the green part is burned to remove the organic binder, and sinter remaining ceramic to the final shape.

In order to enhance the mechanical and electrical properties of the materials, loading of polymer has to be maximized by altering the dispersant/polymer system and particle size distribution of the ceramic filler. The dispersant should allow effective mixing of the filler and encourage its wetting by the liquid polymer. For the above described process, the determination of rheological properties of ceramic-powder-filled systems is very important.

2. EXPERIMENTAL

The matrix (binder) for the filler was a mixture of polypropylene (PP, Tokuyama Co. Ltd., Japan), paraffin wax (Nakarai Chemicals Ltd., Japan) and stearic acid (Wako Chemical Industry Ltd., Japan). The ratio of the components was 75:15:10 wt.% (PP:wax:acid). In the preparation the weighted amount of the binder and zirconia powder (ZrO_2 , Tosoh Co. Ltd., Japan) were dry-blended thoroughly mechanically, and then supplied to the especially developed compounding machine called elastic extruder. The mixing process was carried out at 200°C and the content of ZrO_2 powder was up to 50 vol.%. Extruded strands were cooled in a water bath and cut into pellets. After drying in air oven, the pellets were compression molded into 3 mm thick plates, from which circular discs were cut. They served as samples for rheological measurements.

The apparatus employed for the measurements of rheological properties was a cone-plate type rheometer (NRM2000, Nippon Rheology Kiki Co., Japan, diameter of cone 25 mm, cone angle 3°, and the gap between cone and plate was set at 250 μ m), which is suitable for parallel superposed shear flow tests. Steady shear viscosity, η , and the first normal stress difference, N_1 , were determined in the range of shear rates, $\dot{\gamma}$, from 10^{-3} to 10 1/s, dynamic viscoelastic properties (storage modulus, G' , and dynamic viscosity, η'') in the range of angular frequencies, ω , from 10^{-2} to 50 rad/s, under the strain amplitude γ of 10 %. Superposed flow measurements were conducted under steady shear flow at a fixed shear rate, $\dot{\gamma}_0$, during oscillatory sinusoidal flow. After obtaining the steady shear flow condition, the oscillatory shear flow was superposed in a parallel way, and then angular frequency was increased in a stepwise manner. Storage modulus, dynamic viscosity and loss modulus were measured as a function of the superposed shear rate. Shear viscosity at high shear rates (10 to 10^4 1/s) was measured on a capillary rheometer (Koka-shiki rheometer, Shimazu Seisakusyo Co., Japan, diameter of capillary 1 mm, its length 30 mm). All the rheological measurements were carried out at 200°C.

3. RESULTS AND DISCUSSION

The viscosity of pure PP at low shear rates is essentially constant (Newtonian behaviour), however, it shows shear thinning behaviour at higher shear rates. For the filled systems, the viscosity generally increases with rising ZrO_2 content, and in the low shear rate region it increases rapidly with the filler volume fraction. At high shear rates the influence of ZrO_2 becomes diminished.

At moderate to high shear rates, the viscosity of 10%-filled sample is lower than that of PP matrix. This flow behaviour suggests that the rigid structure formed by fine ZrO_2 particles increases viscosity significantly at low deformation rate, however, this structure becomes destroyed under higher shear rates, and then does not increase resistance against flow but acts rather as a lubricating agent.

The yield stress, calculated for the filled systems from the Casson plots, is shown in Fig. 1 as a function of ZrO_2 volume fraction, v_f , in semi-logarithmic coordinates. It can be seen that τ_y versus v_f relation is represented by the straight line, which coincide well with the results obtained for particle/fiber-filled systems in the previous papers [5-7,8-14].

The relationships between the first normal stress difference, N_1 , and shear rate, $\dot{\gamma}$, for PP and Zr/PP systems at 200°C are shown in Fig. 2. In the lower shear rate region (less than 1 1/s), N_1 increases with the content of ZrO_2 powder, and the systems, excluding low-content samples, show higher N_1 than that of PP matrix. However, this trend turns to opposite at shear rates above 1 1/s, and it is probably caused by the disappearance of the three dimensional structure composed by ZrO_2 powder - fractured under high shear. Such properties are remarkably different from other fiber-filled systems [14-16].

In order to avoid non-linear viscoelastic manifestation, dynamic measurements must be carried out under small strain amplitudes. Storage modulus, G' , increases dramatically with the increase of ZrO_2

content. The slope of the curves is constant at low ω , even for low ZrO_2 content, and then increases gradually with ω . The highly-filled sample (Zr40/PP) shows G' almost independent on angular frequency. The matrix dynamic viscosity is Newtonian in the low angular frequency region, and then it decreases with the increase of ω . For the filled systems η' generally increases with the content of ZrO_2 ; it shows high values at low angular frequencies and decreases exponentially with ω , approaching to the value of pure PP. The complex viscosity shows similar behaviour.

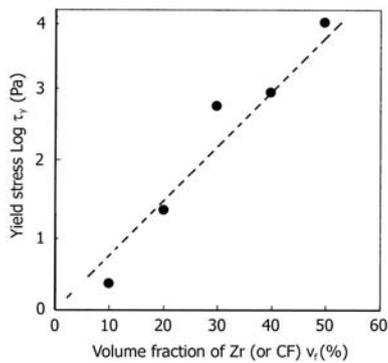


Fig. 1. Relationship between yield stress, τ_y , and volume fraction of ZrO_2 powder, v_f , for Zr/PP melts

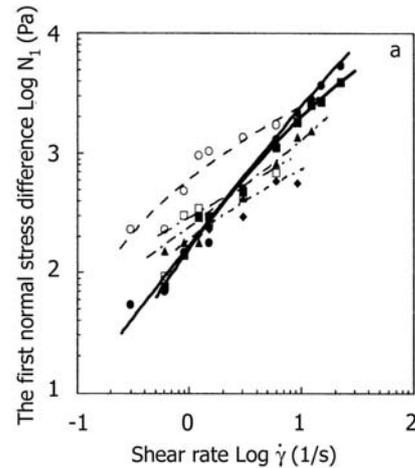


Fig. 2. First normal stress difference, N_1 , as function of shear rate, $\dot{\gamma}$, for PP (■), Zr10/PP (●), Zr20/PP (▲), Zr30/PP (◆), Zr40/PP (□), Zr50/PP (○) melt.

The quantitative comparison between dynamic, complex and steady shear viscosities has already been discussed in a number of papers, e.g. [16,17]. These discussions are based on the Cox-Merz rule for viscous properties, and Roscoe's law for elastic properties. It has been found that the correlation between both types of flow properties is not as conclusive for filled systems as for pure polymers. Especially for loadings close to the maximum packing enormous discrepancies between the two types of measurement might be observed.

Qualitative understanding of the superposed flow properties of filled materials is important for efficient processing, but also for the improvement of the performance of composite products. During the superposed oscillatory flow experiments, the strain amplitude was set to 10%, the same as for simple oscillatory flow measurements. For unfilled PP η' is almost unaffected by the superposed shear rate, but it is influenced by angular frequency; it decreases gradually with the rise of ω in the region measured in this experiment. For pure PP the values, where the curves intercept the vertical axis, are almost the same as η' under simple oscillatory flow.

For Zr/PP systems the behaviour is substantially different. At low angular frequencies (0.0628 and 0.126 rad/s), η' is highly influenced by the superposed shear rate; η' increases with $\dot{\gamma}_0$ and after reaching a maximum, it decreases sharply, while at high angular frequencies the behaviour is similar to that of unfilled PP. In any case, the superposed shear-rate-dependent dynamic viscosity grows over steady shear viscosity. For highly-filled Zr/PP systems (above 40 %) η' decreases simply with $\dot{\gamma}_0$ at low angular frequencies or shows complex behaviour at rather high ω region.

The effect of superposed steady shear rate was further considered from the point of view of $2G'/\omega^2$ corresponding to the coefficient of the first normal stress difference. Experimental data of $N_1/\dot{\gamma}^2$ and estimated values at low shear rate region, which are calculated under the assumption that the coefficient of the first normal difference decreases exponentially with the rise of shear rate, are shown simultaneously (dashed line). For unfilled PP the influence of the superposed shear rate, $\dot{\gamma}_0$, on $2G'/\omega^2$ is quite low, the same as for dynamic viscosity. For the lowest filling, $2G'/\omega^2$ seems to

decrease monotonously with the increase of $\dot{\gamma}_0$, which is again similar to the dependence of η' , although the data in low angular frequency region is scattered. For Zr20/PP and Zr30/PP systems the curves start with an increase, go through a maximum and then decrease again. The maximum shifts to higher frequencies with rising ω .

For all studied materials, dynamic elasticity expressed as $2G'/\omega^2$ under various conditions seems to be smaller than the coefficient of the first normal stress difference, although it was impossible to determine this variable experimentally over the whole range of shear rates.

4. CONCLUSION

ZrO₂-filled systems with high powder content show remarkable non-Newtonian flow behaviour at low strain rates showing yield stresses. This behaviour is attributed to a sweeping change of structure after deformation, and fracture of the structures created by fine ZrO₂ powder. The dynamic viscoelasticity measurements suggest that ZrO₂ powder significantly contributes to elastic properties of the material. Discrepancies between shear and complex viscosities as well as between the coefficient of the first normal stress difference from steady shear flow and $2G'/\omega^2$ from oscillatory flow become larger with the increase of powder content, and the former values are lower than the latter in both cases. This behaviour is different from that reported for short-fiber-filled polymer systems. The effect of steady shear rate, $\dot{\gamma}_0$, on dynamic viscoelastic properties, η' and G' , was investigated by superposed oscillatory flow experiments. The influence of the shear flow on both η' and G' was observed at low angular frequencies; its degree decreases with the rise of ω . Compared to fiber-filled systems, the researched Zr/PP does not show a sharp approach of η' or $2G'/\omega^2$ to the steady shear flow values, η and $N_1/\dot{\gamma}^2$, respectively, with superposed $\dot{\gamma}_0$. The reason may be the variation in the structure composed with different filler size and shape, and also different structural changes under shear deformation.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- [1] Duh J.G., Wan J.U.: *J. Mater. Sci. Lett.* 12, 473, 1993.
- [2] Park J.H., Kim H.W., Song I.T.: *J. Mater. Sci. – Mater. Electron.* 4, 77, 1993.
- [3] Nishio T., Fujiki Y.: *J. Mater. Sci. Lett.* 12, 394, 1993.
- [4] Weyten H., Adriansens W., Cornelis J., Leysen B.: *J. Mater. Sci.* 28, 1252, 1993.
- [5] Lobe V.M., White J.L.: *Polym. Eng. Sci.* 19, 617, 1979.
- [6] Kataoka T., Kitano T., Oyanagi Y., Sasahara M.: *Rheol. Acta* 18, 635, 1979.
- [7] Kataoka T., Kitano T., Oyanagi Y., Sasahara M., Nishijima K.: *Rheol. Acta* 17, 149, 1978.
- [8] Wildemuth C.R., Williams M.C.: *Rheol. Acta* 24, 75, 1985.
- [9] Poslinski A.J., Ryan M.E., Gupta R.K., Seshadri S.G., Frechette F.J.: *J. Rheol.* 32, 703, 1988.
- [10] Carreau P.J., Malik T.M., in: *Xth International Congress on Rheology, Sydney, 1988*, p.220.
- [11] Onogi S., Mikami Y., Matsumoto T.: *Polym. Eng. Sci.* 17, 1, 1977.
- [12] Kitano T., Kataoka T.: *Rheol. Acta* 20, 390, 1981.
- [13] Kitano T., Kataoka T.: *Rheol. Acta* 20, 403, 1981.
- [14] Chan Y., White J.L., Oyanagi Y.: *J. Rheol.* 22, 507, 1978.
- [15] Czaarnecki L., White J.L.: *J. Appl. Polym. Sci.* 25, 1217, 1980.
- [16] Kitano T., Funabashi M., Klason C., Kubat J.: *J., Int. Polym. Proc.* 3, 67, 1988.
- [17] Kitano T., Kataoka T.: *Rheol. Acta* 19, 671, 1980.