

THE EFFECT OF FILLERS ON RHEOLOGICAL PROPERTIES OF FILLED MATERIALS

9.1 VISCOSITY

Viscosity determinations are the simplest means of the rheological characterization of materials.¹⁻¹⁸ Viscosity measurements lack sufficient precision for the generalization purposes because filled materials are most frequently non-Newtonian liquids and a singular numerical parameter cannot adequately describe complex properties. In spite of this deficiency, many important conclusions can be drawn from viscosity data.

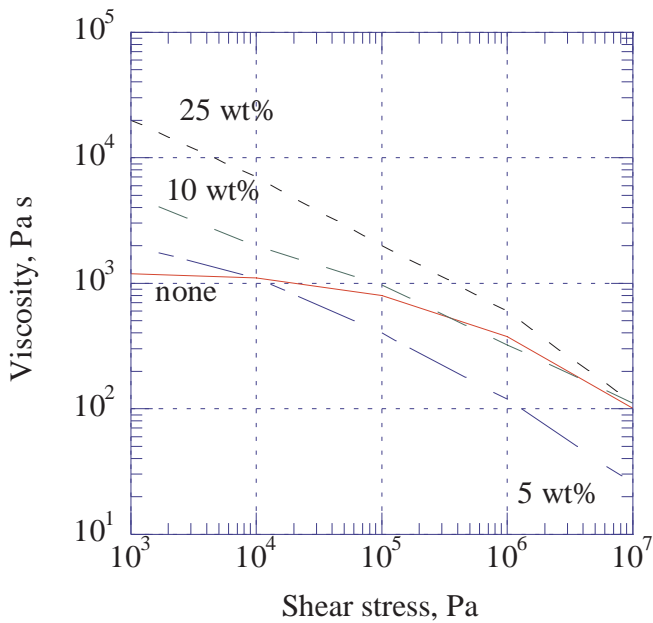


Figure 9.1. The effect of carbon black on the viscosity of polycarbonate. [Adapted, by permission, from Joo Y L, Lee Y D, Kwack T H, Min T I, Antec '96. Vol. I. Conference Proceedings, Indianapolis, 5th-10th May 1996, 64-8.]

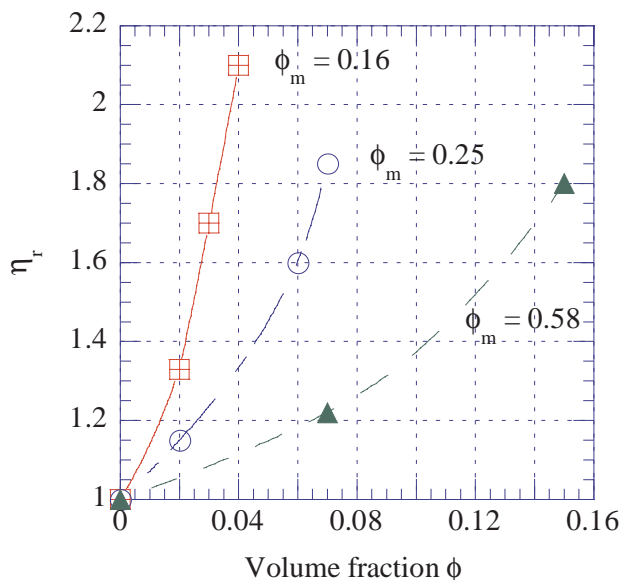


Figure 9.2. Reduced viscosity of polypropylene filled with different grades of calcium carbonate as a function of volume fraction. [Adapted, by permission from Gendron R, Daigneault L E, Tatibouet J, Dumoulin M M, *Adv. Polym. Technol.*, **15**, No.2, 1996, 111-25.]

Increasing the amount of filler in a filled material increases shear stress and viscosity (Figure 9.1).⁶ In addition to an increase in viscosity with increasing additions of carbon black, zero-shear viscosity and shear-thinning increase more rapidly when the amount of carbon black is increased. This data shows that there is always a certain region in which viscosity does not increase as rapidly (in this case, in the range of shear stress of 10^5 - 10^6). It is this region which is best suited for processing.

Note that the viscosity increase with filler addition depends on the properties of filler such as its maximum packing fraction (Figure 9.2).⁹ With an increased volume fraction, viscosity increases but this increase would not be the same for example, for three different grades of calcium carbonate. What causes this is difference in their maximum packing fraction. The rate of viscosity increase depends on the ratio ϕ/ϕ_m where ϕ is volume fraction of filler added and ϕ_m is the maximum packing fraction.

Viscosity measurements helped to understand the reaction rate in the formation of polyurethane in the presence of lead powder (Figure 9.3).¹¹ A smaller addition of lead powder (10%), does not accelerate the reaction rate but larger amounts of lead powder increase the reaction rate rapidly. At 30% lead powder, the reaction rate is increased by a factor of 3.

As investigation of the process of mixing based on viscosity data shows (Figure 9.4) that viscosity increases at the beginning of mixing but continues falling shortly afterwards.¹⁶ This rapid decrease of viscosity occurs only at the beginning

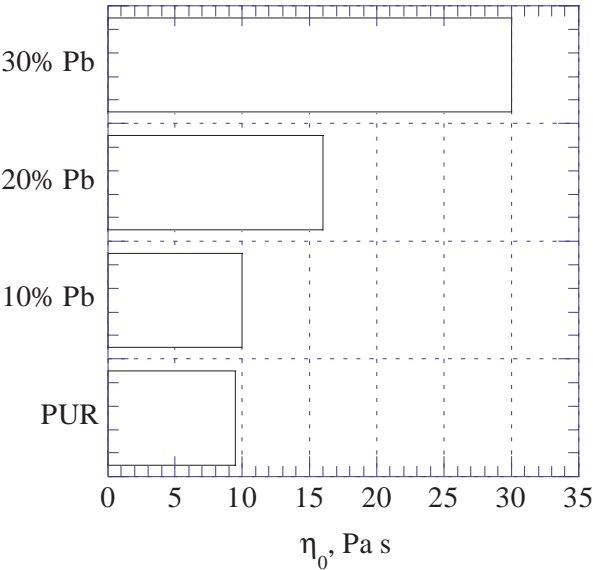


Figure 9.3. Viscosity of formation of polyurethane in the presence of lead powder. [Data from Caillaud J L, Deguillaume S, Vincent M, Giannotta J C, Widmaier J M, *Polym. Int.*, **40**, No.1, 1996, 1-7.]

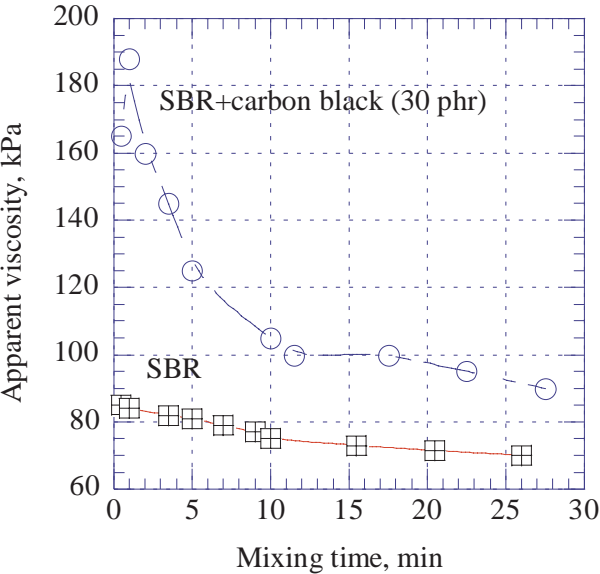


Figure 9.4. Viscosity of SBR filled with carbon black vs. mixing time. [Adapted, by permission, from Clarke J, Freakley P K, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 700-15.]

of the mixing process. Further decreases in viscosity are more difficult to obtain. Figure 9.5 gives information on the effect of amount of added filler and quality of mixing.¹⁶ A poorly mixed compound increases in relative viscosity less rapidly be-

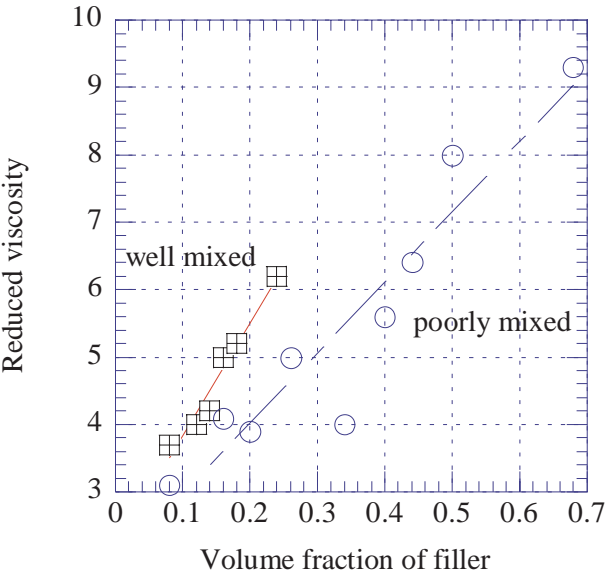


Figure 9.5. Reduced viscosity of SBR vs. fraction of carbon black in relationship to quality of mixing. [Adapted, by permission, from Clarke J, Freakley P K, *Rubb. Chem. Technol.*, **67**, No.4, 1994, 700-15.]

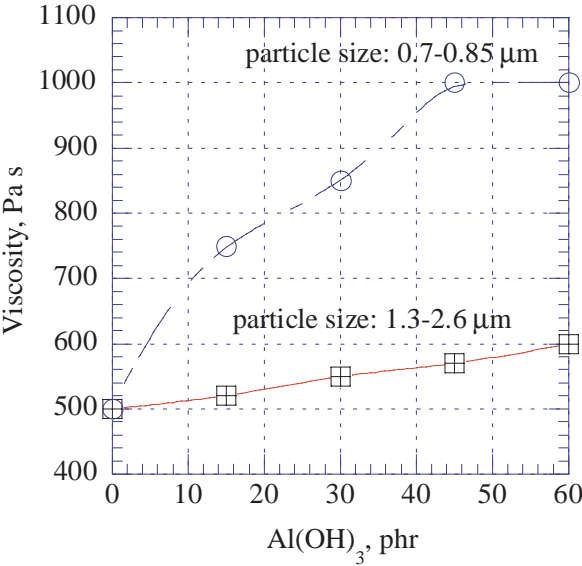


Figure 9.6. Viscosity of plasticized PVC vs. fraction of $\text{Al}(\text{OH})_3$. [Data from Liptak P, Zelenak P, *Int. Polym. Sci. Technol.*, **20**, No.9, 1993, T/57-9.]

cause undispersed aggregates behave in a manner similar to spherical particles which create less resistance to mixing.

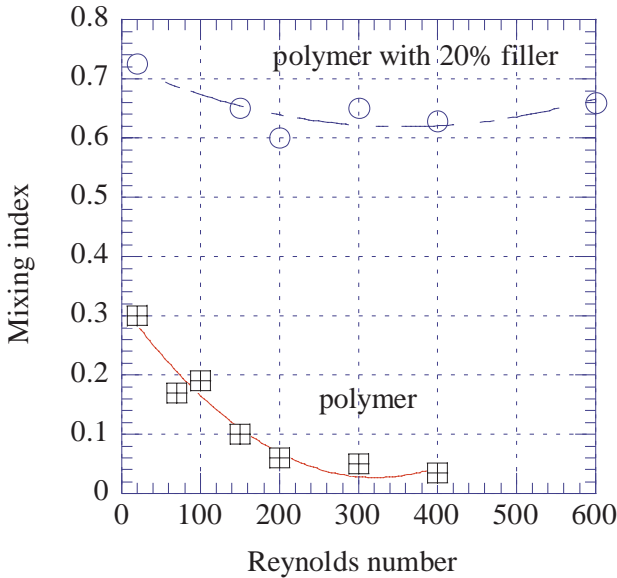


Figure 9.7. Mixing index as a function of volume fraction of filler and Reynolds number. [Data from Agarwal S, Campbell G A, Antec 95. Volume I. Conference proceedings, Boston, Ma., 7th-11th May 1995, 839-42.]

The quality of mixing depends both on filler properties and on the dispersing medium or its rate of flow during the mixing process. If a filler has a low oil absorption, it does not affect viscosity over a certain range of loading (Figure 9.6). But a filler having a high oil absorption increases viscosity as the load of filler increases.¹⁴ Selectivity is a measure of filler particle segregation. The closer to zero the selectivity is the better the dispersion of the filler. Increase Reynolds number on mixing increases the effectiveness of mixing (Figure 9.7).⁵ So the same filler will give better results if the mixing medium and the mixing process are matched.

9.2 FLOW

Many industrial processes are affected by the influence of particulate materials on the flow properties of material. Flow properties of materials can be adjusted by fillers to meet the requirements. Flow properties can also be adversely affected by numerous phenomena related to the presence of filler in formulations.^{13,19-24} One common example is related to the flow of industrial slurries which contain concentrated suspensions of small particles.¹⁹ Such suspensions are usually non-Newtonian fluids with a yield stress which is formed through strong interactions between particles. During flow, these interactions are continuously broken and rebuilt. A solid deposit formed on the slopes and walls is an adverse effect of this property.

Materials with a yield value have a specific stress value below which the material is deformed as an elastic solid and above which it flows. Concrete mixes are

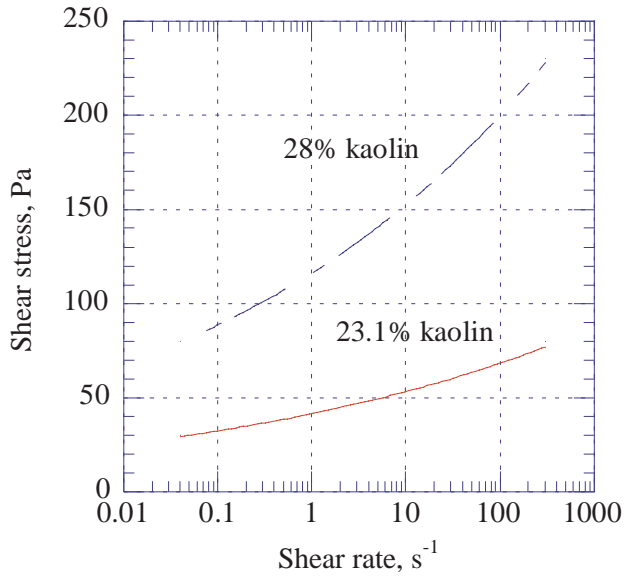


Figure 9.8. Water clay mixtures. [Adapted, by permission, from Coussot Ph., Proust S, Ancey Ch, *J. Non-Newtonian Fluid Mech.*, **66**, 1996, 55-70.]

tested by the “slump test” in which a truncated cone is filled with a concrete mix and slump and flow is measured. Slump stoppage depends on the rheological properties of mix which cause flow to stop when shear stress falls below yield value. Another demonstration of this effect is observed in sealants during the “sag test”. This test determines the thickness of a layer formed on the wall of testing device at which thickness flow stops (the stress formed by gravity falls below yield stress). These properties can be more precisely measured by rheometry as Figure 9.8 shows. A small difference in the concentration of a clay filler substantially increases the yield value. In spite of the much higher precision of rheometric measurements, rheological measurements cannot replace practical tests because they do not capture the complex relationships of interplaying factors in practical applications.

One difficulty in flow measurement in suspended systems is caused by particle distribution close to walls. A slip layer forms on the surface of the walls which consists of particle-free binder. The thickness of this layer is given by equation:²¹

$$\delta = u_s \eta_s / \tau_R \tag{9.1}$$

where:

- δ layer thickness
- u_s slip velocity at the wall
- η_s Newtonian shear viscosity
- τ_R corrected shear stress

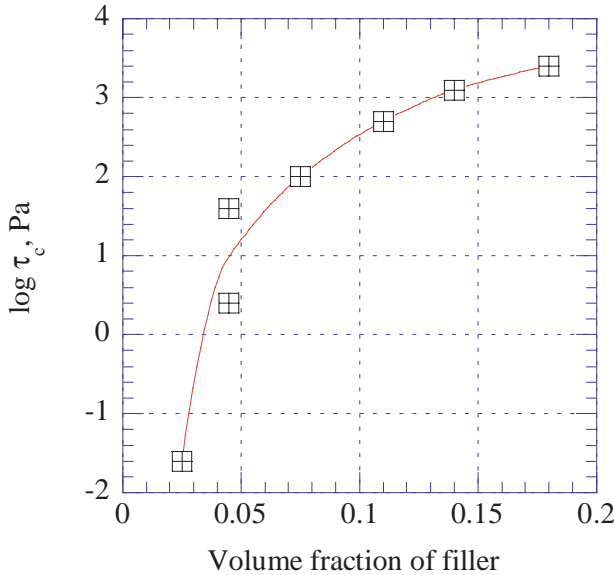


Figure 9.9. Flow limits vs. filler content. [Adapted, by permission, from Mamunya E P, Shumskii V F, Lebedev E V, *Polym. Sci.*, **36**, 1994, 835-8.]

Wall slip affects flow properties in tubes.²⁰ Concentration of particles in the cross-sectional areas of a tube changes due to the radial migration of particles. Such process affects also filtration.

Flow restrictions are also observed in flow of melts.²³ Figure 9.9 shows flow limits of carbon black filled polyolefins. Data show that yield stress appears at low concentrations of carbon black and that the type of the matrix does not affect flow characteristics which are caused by the presence and properties of fillers. The viscosity of these systems are well described by Fedor's equation:

$$\frac{G}{G_p} = \left(\frac{125\phi}{F - \phi} \right)^2 \quad [9.2]$$

where:

- G viscosity of filled system
- G_p viscosity of matrix
- φ filler fraction
- F packing factor

Viscosity increase and, therefore, flow decrease depend on filler concentration and the packing factor which is related to filler volume. Polyethylene filled with metal particulates behaves in a similar way.²² Flow was decreasing linearly with the concentration of metal particles.

9.3 FLOW INDUCED FILLER ORIENTATION

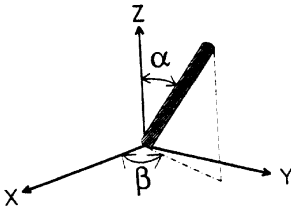


Figure 9.10. Coordinate system used to determine fiber orientation. Z is a direction of elongational flow. [Adapted, by permission, from Kobayashi M, Takahashi T, Takimoto J, Koyama K, *Polymer*, **36**, No.20, 1995, 3927-33.]

To make practical use of fillers, a knowledge of filler orientation during the flow is needed.²⁵⁻³¹ The best description of orientation principles can be obtained from modelling.²⁵ Figure 9.10 gives the coordinate system used to describe orientation of fibers.

The elongational flow field is determined from equation:

$$\tan \alpha = \exp\left(-\frac{3}{2}\varepsilon\right) \tan \alpha_0 \quad \beta = \beta_0 \quad [9.3]$$

where:

α, β angles given in Figure 9.10
 ε elongational strain rate

The rotary motion is given by the following equation:

$$\frac{d\alpha}{dt} = -\frac{3}{4}\varepsilon R \sin(2\alpha) \quad \frac{d\beta}{dt} = 0 \quad [9.4]$$

$$R = \frac{r_p^2 - 1}{r_p^2 + 1} \quad \tan \alpha = \exp\left(-\frac{3}{2}\varepsilon R t\right) \tan \alpha_0$$

where:

R shape factor
 t time
 r_p aspect ratio
 α_0 initial orientation angle

From the above equations it can be seen that orientation increases with aspect ratio and elongational strain rate.

Figure 9.11 shows that the average angle α of whiskers decreases with the elongational strain rate, ε .²⁵ Figure 9.12 shows the effect of the aspect ratio of ferrite on the apparent permeability of a composite.³⁰ Both sets of experimental data are consistent with the model. The orientation of fiber increases with the elongational strain rate and fiber aspect ratio.

It should be noted from Figure 9.12 that the magnetic permeability increases as the effective aspect ratio increases. Conductive thermoplastics, which contain carbon fiber, have a maximum injection rate above which electric conductivity will not increase. These composites also depend on fiber orientation which increases the

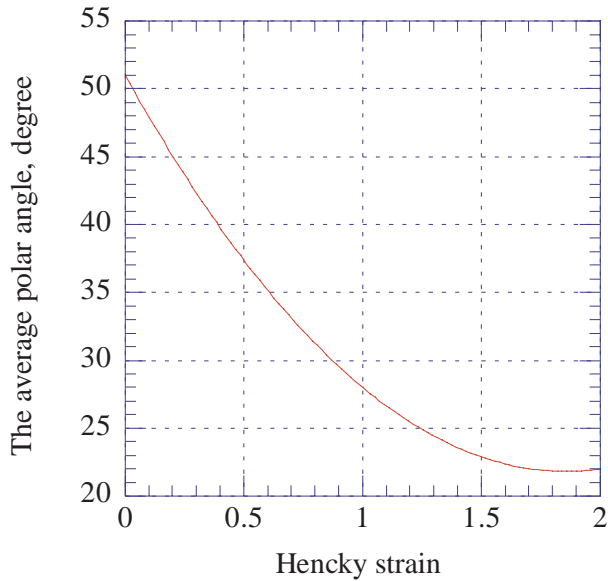


Figure 9.11. The average polar angle, α vs. elongational strain rate, ϵ . [Data from Kobayashi M, Takahashi T, Takimoto J, Koyama K, *Polymer*, **36**, No.20, 1995, 3927-33.]

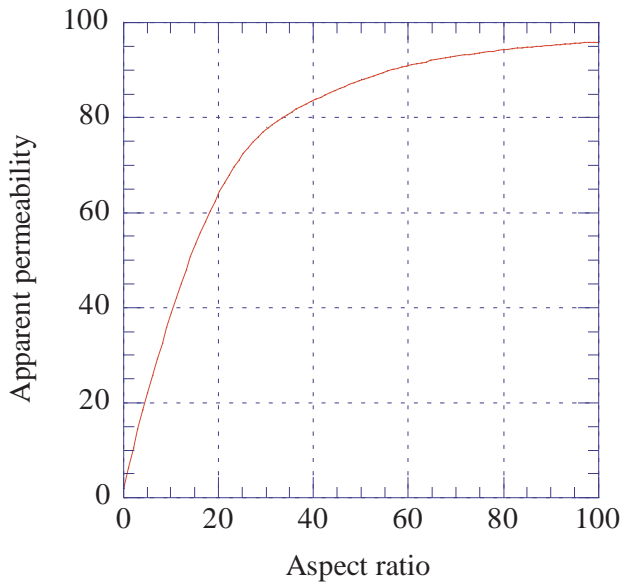


Figure 9.12. Apparent magnetic permeability vs. effective aspect ratio. [Adapted, by permission, from Fiske T, Gokturk H S, Yazici R, Kalyon D M, *Polym. Eng. Sci.*, **37**, No.5, 1997, 826-37.]

number of contacts and thus the conductivity. Higher injection rates increase the number of fiber breakage which reduces conductivity.²⁹

Talc filled thermoplastic materials were studied in rheometers of different geometries (elongational, capillary, parallel plate). Geometry of the testing method and the flow paths had an important influence on the orientation of talc particles.²⁷ In addition to flow decrease, an increased concentration of filler had a pronounced effect on both flow and orientation. The cross-sectional distribution of particles depends also on the size of particulate material.²⁸ The concentration of particles on the free surface of advancing material increases as particle size increases.

9.4 TORQUE

Torque increases as viscosity increases which is typically a result of an increase in filler loading.³²⁻⁴ The viscosity of mixtures containing fillers depends on the nature and concentration of filler, its shape, size and interaction with matrix. Figure 9.13 shows how various fillers cause torque increase.³² A magnesium carbonate addition causes a relatively small increase in torque. Glass fiber creates an extreme effect, increasing torque very rapidly. Silicon dioxide causes a torque increase between these two extremes. The high aspect ratio of glass fiber is responsible for its extreme effect and the low interaction of magnesium carbonate with the matrix causes the torque increase to be slight.

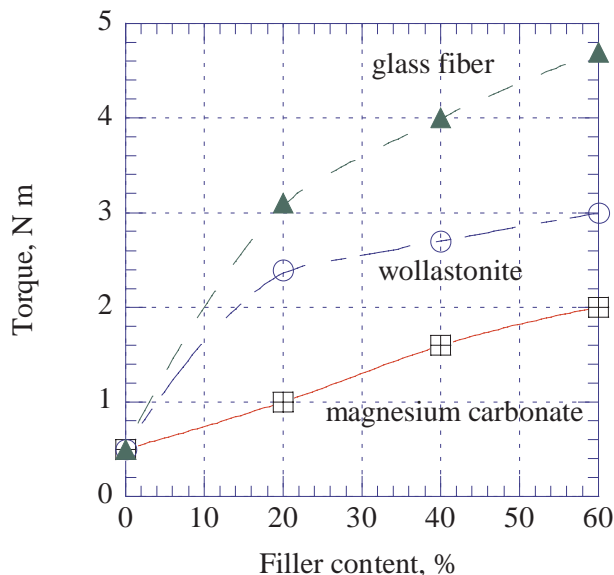


Figure 9.13. Torque vs. filler content. [Adapted, by permission, from Scaffaro R, Pedretti U, La Mantia F P, *Eur. Polym. J.*, **32**, No.7, 1996, 869-75.]

Measurement of torque also provides data on the effect of fillers on the curing rates of reactive systems.³³⁻⁴

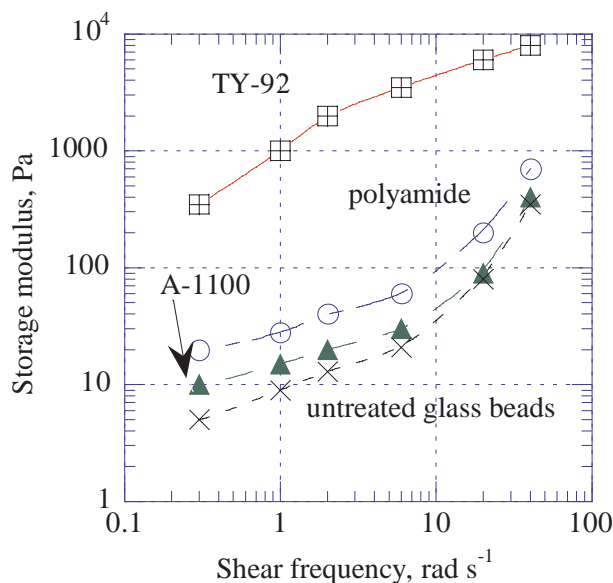


Figure 9.14. Storage modulus of glass bead filled polyamide-6 vs. shear frequency. [Adapted, by permission, from Ou Y-C, Yu Z-Z, *Polym. Int.*, **37**, No.2, 1995, 113-7.]

9.5 VISCOELASTICITY

Rheological properties of filled systems are complex and formulation specific, largely dependent on fillers and other materials, especially materials which form a matrix.^{5,27,35-40} Flow through tubes demonstrates the unusual properties of filled system. Plug flow is typical of filled systems much different from the characteristics of unfilled system.⁵ This phenomenon is frequently observed with highly filled systems which behave in a manner similar to both solids and liquids.

Figure 9.14 compares untreated glass beads with glass beads treated with γ -aminopropyltriethoxysilane. The untreated beads decrease storage modulus in all probability because the surface treatment decreases hydrogen bonding between polymer chains. Introduction of surface treatment (TY-92), which improves surface adhesion, contributes to a considerable increase in storage modulus. The loss modulus of a system containing TY-92 decreases as Figure 9.15 shows.³⁵

The storage modulus of a polymer filled with polymeric particles is less dependent on frequency when these particles do not interact with the matrix polymer. They form clusters during storage which contribute to the non-Newtonian behavior of the filled polymer.⁴⁰

Carbon black interacts strongly with polymer (HDPE) to produce a large increase in storage modulus in a manner similar to the surface treated glass beads.³⁶ The storage modulus is less sensitive to frequency. The storage modulus increase is explained by the effect of modifier on crosslinking.

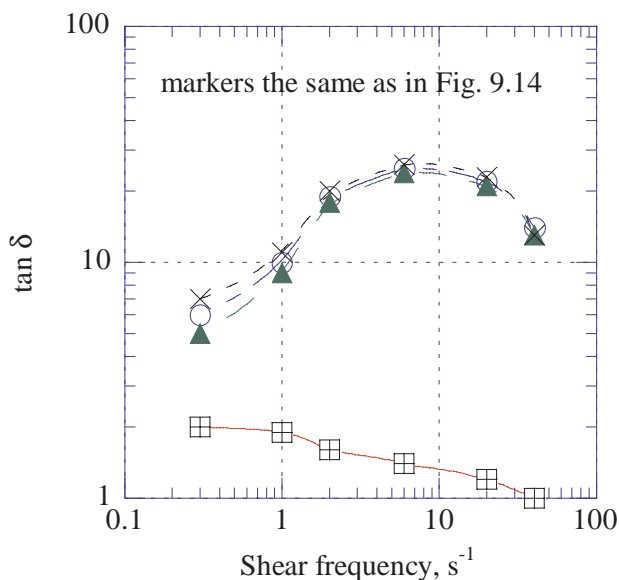


Figure 9.15. Loss modulus of glass beads filled polyamide-6 vs. shear frequency. [Adapted, by permission, from Ou Y-C, Yu Z-Z, *Polym. Int.*, **37**, No.2, 1995, 113-7.]

Both the storage and the loss moduli have linear relationship with filler concentration (iron particles) when the measurements of compounded gels are done in a magnetic field.³⁹

9.6 DYNAMIC MECHANICAL BEHAVIOR

The addition of a filler which interacts with the matrix restricts molecular mobility which can be measured using the dynamic mechanical analysis.^{12,41-49} Figure 9.16 shows the effect of particle size of glass beads on $\tan \delta$. Smaller beads with higher surface area available for interaction restrict molecular mobility.⁴² Increasing the concentration of filler causes a decrease in the magnitude of main relaxation (related to T_g). In some cases the concentration of filler does not influence T_g . Changes in dynamic mechanical properties are related to matrix-filler interaction and chemical coupling.

In Chapter 7, the Figure 7.10 models tightly and loosely bound polymer and shows gradual changes which occur when filler concentration increases. Figure 9.17 complements this model with experimental data which show changes in $\tan \delta$ peak positions associated with tightly and loosely bound polymer. The second $\tan \delta$ peak changes when a loosely bound polymer transits to a tightly bound polymer.⁴³

Figure 9.18 gives one more example of how interaction affects dynamic mechanical properties. Two polymers were tested with various concentrations of alumina. Polystyrene was almost unaffected by various concentrations of filler. Sulfonated polystyrene interacts more strongly with its filler than polystyrene which contributes to increase in T_g .⁴⁹

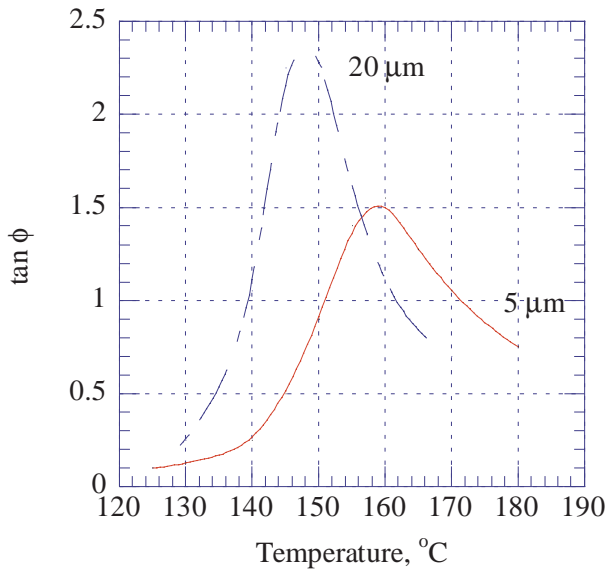


Figure 9.16. Tan δ vs. temperature for styrene-methacrylic acid copolymer filled with glass beads of different diameter. [Data from Bergeret A, Alberola N, *Polymer*, **37**, No.13, 1996, 2759-65.]

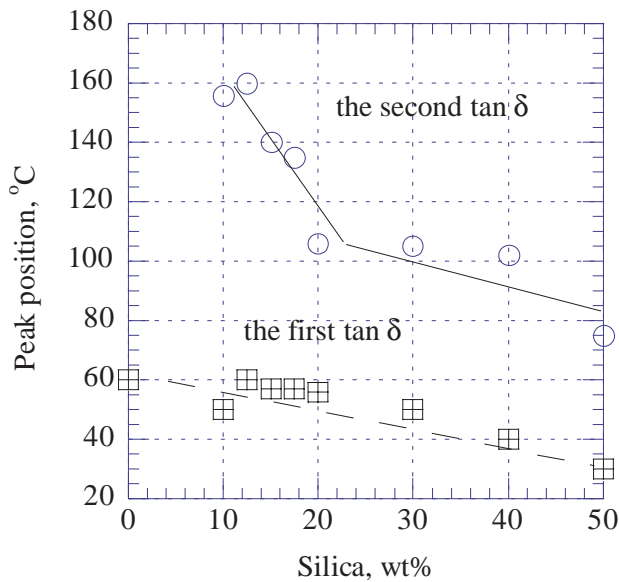


Figure 9.17. Peak positions of the first and second tan δ peaks vs. silica contents in PVAc composites. [Adapted, by permission, from Tsagaropoulos G, Eisenberg A, *Macromolecules*, **28**, No.18, 1995, 6067-77.]

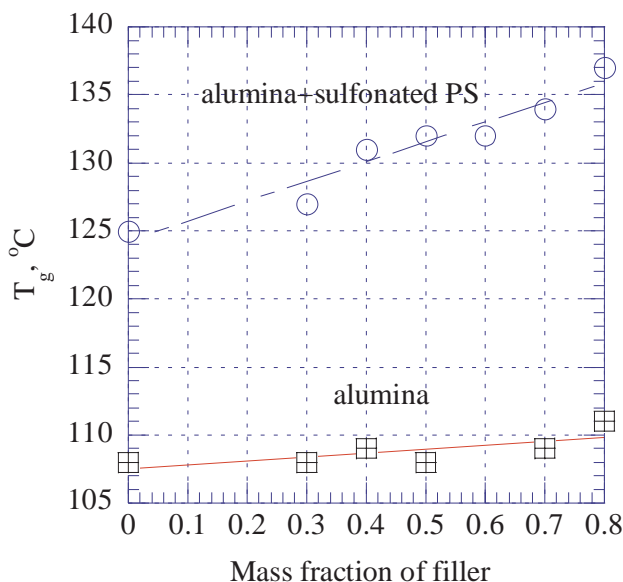


Figure 9.18. T_g versus concentration of alumina. [Data from Cousin P, Smith P, *J. Polym. Sci., Polym. Phys.*, **32**, No.3, 1994, 459-68.]

9.7 COMPLEX VISCOSITY

Complex viscosity data also shows how fillers interact with the matrix.^{27,50-58} Figures 9.19 and 9.20 show the effect of filler loading on the complex viscosity of two polymers (PP and PPS).²⁷ Two conclusions can be drawn from these figures: polymer type affects the rate of viscosity increase and the increase of viscosity is not proportional to the concentration of filler. Figure 9.21 shows that viscosities of polypropylene loaded with 10 and 20% calcium carbonate are almost identical whereas a large increase in viscosity is observed on addition of 40% calcium carbonate.⁵⁴

The process of mixing has an interesting influence on complex viscosity (Figure 9.22).⁵⁸ The first mixing was performed in a Brabender, the second by a hand held spatula for a prolonged time (5 hr). The viscosity of the mixture was considerably decreased and, in addition, the shear-thinning properties of the material were reduced. It should be noted that, for a proper evaluation of fillers, the mixing regime is a very important consideration since viscosity may change by as much as 1000 times depending upon how the compound was mixed. By proper mixing, it is possible to change material properties so as to be able to process it rather than by adding complex combinations of additives.

Figures 9.23 and 9.24 show that complex viscosity decays with time of mixing. The magnitude of this decay depends on the surface treatment of the filler as well as on its concentration.⁵⁷ Again the conditions of the experiment influence the

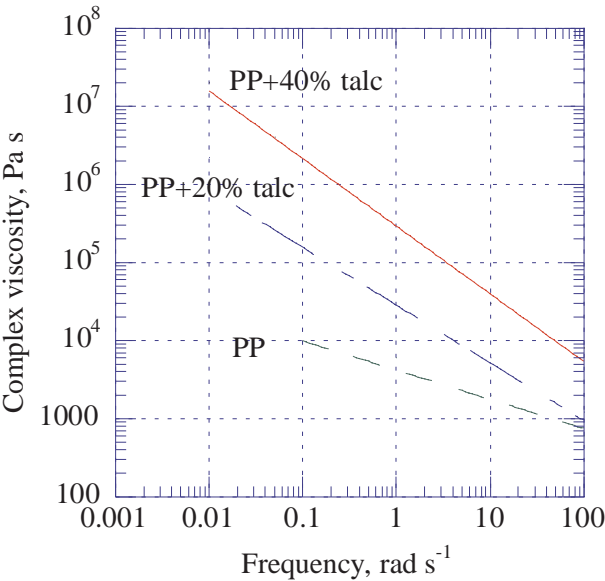


Figure 9.19. Complex viscosity of talc filled PP vs. frequency. [Data from Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.]

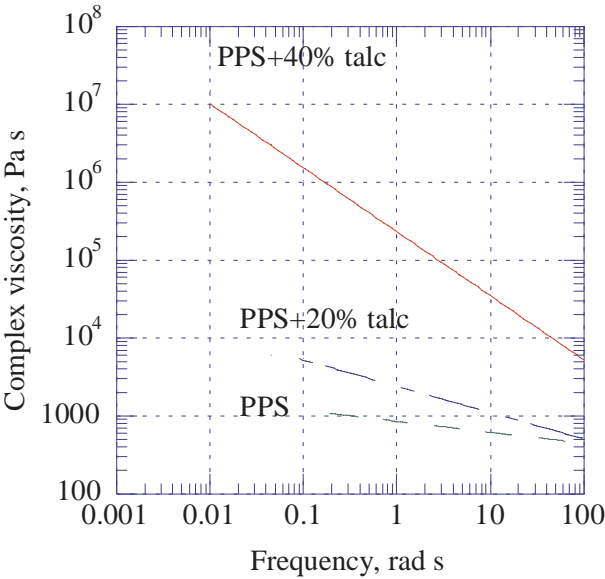


Figure 9.20. Complex viscosity of talc filled PPS vs. frequency. [Adapted, by permission, from Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.]

result. The slower decay in the complex viscosity of a mixture of particles of glass beads treated with fluorosilane is explained by a reduction in the interfacial adhesion followed by a reduction in dynamic slip.

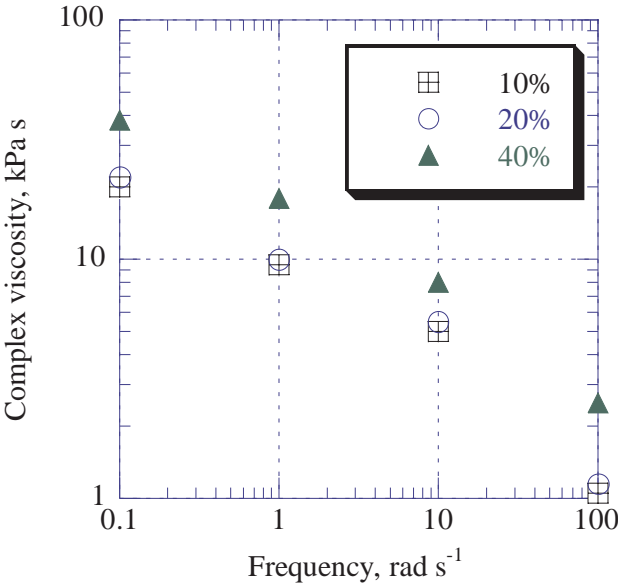


Figure 9.21. Complex viscosity of calcium carbonate filled PP vs. frequency. [Adapted, by permission, from Johnson K C, Antec '96. Volume III. Conference proceedings, Indianapolis, 5th-10th May 1996, 3545-9.]

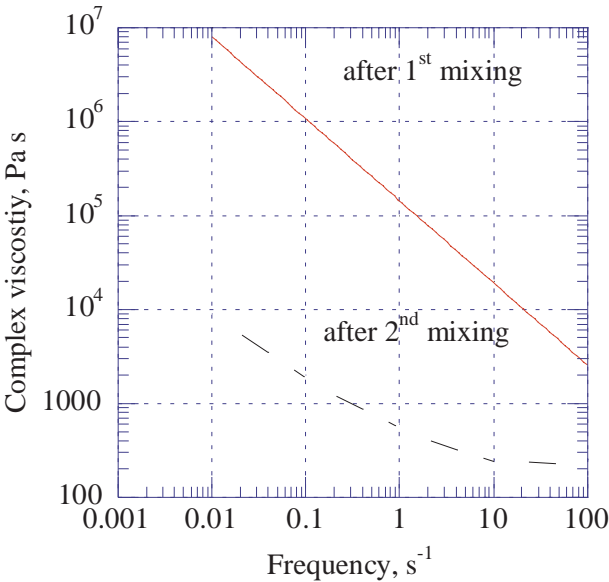


Figure 9.22. Complex viscosity of 31% TiO₂ in polybutene vs. frequency. [Data from Carreau P J, Lavoie P A, Bagassi M, *Macromol. Symp.*, **108**, 1996, 111-26.]

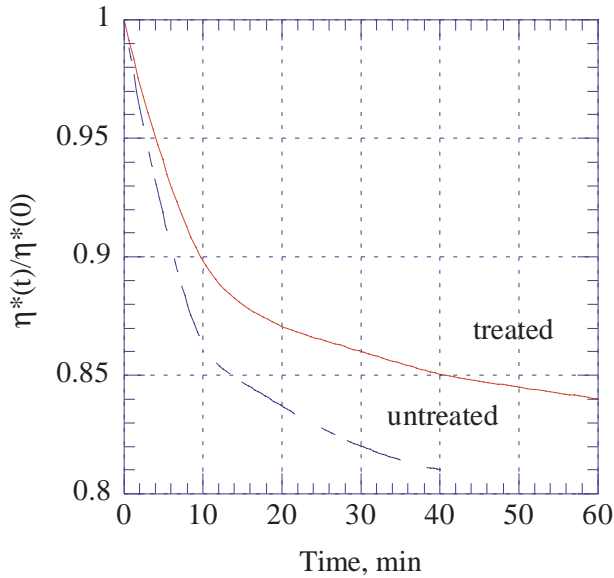


Figure 9.23. Decay of reduced complex viscosity of PDMS filled with glass beads vs. determination time. [Adapted, by permission, from Wang S Q, Inn Y W, *Rheol. Acta*, **33**, No.2, 1994, 108-16.]

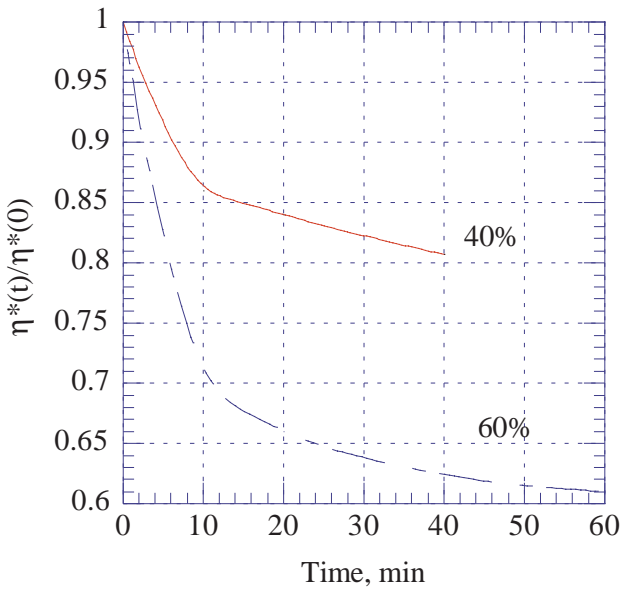


Figure 9.24. Effect of glass beads concentration on the decrease of reduced complex viscosity of PDMS vs. determination time. [Adapted, by permission, from Wang S Q, Inn Y W, *Rheol. Acta*, **33**, No.2, 1994, 108-16.]

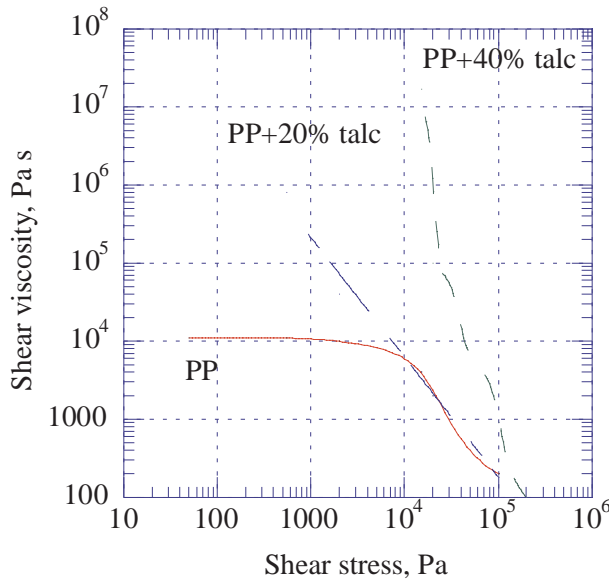


Figure 9.25. Viscosity of talc filled PP vs. shear stress. [Data from Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.]

9.8 SHEAR VISCOSITY

A filled system's rheology depends on conditions of shearing.^{6,11,19,21,27,40,59-61} Figures 9.25 and 9.26 show the effect of shear stress on two polymers filled with talc.²⁷ The reaction of both systems differs in the rates of viscosity change and in the character of non-Newtonian properties but the responses of both systems are similar in their reactions to high shear rates where viscosities of the filled and the neat polymer are almost the same.

Figure 9.27 shows dependence of viscosity on filler concentration. Note that, as with previous data, viscosity increases more rapidly at lower shear rates.⁶¹

9.9 ELONGATIONAL VISCOSITY

The mode of deformation induced in elongational viscosity studies differs from other methods of measurement.^{27,62-3} Figure 9.28 shows that elongation to break decreases when a filler content increases but, at the same time, the relationship with rate is linear and only slightly affected by changes in elongation rate.²⁷

In fiber filled systems, the elongation of a material correlates with the orientation of fibers (Figure 9.29). This phenomenon is frequently exploited in industrial processes to increase reinforcement and other properties which depend on fiber orientation. Hencky strain shown in Figure 9.29 is a parameter entering in the equation of elongational viscosity.⁶²

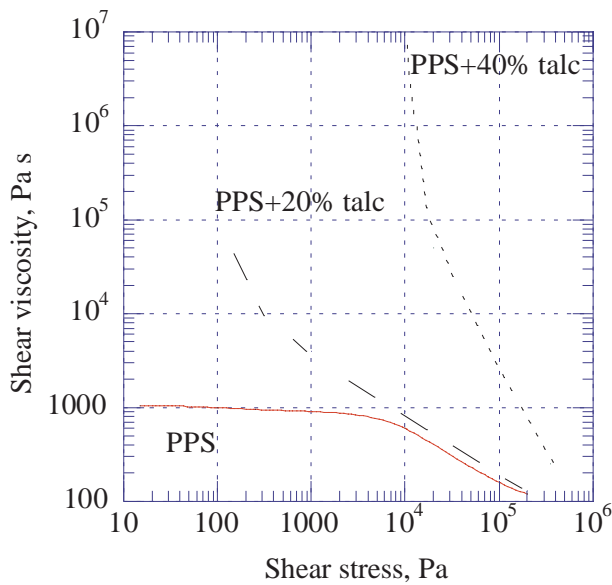


Figure 9.26. Viscosity of talc filled PPS vs. shear rate. [Data from Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.]

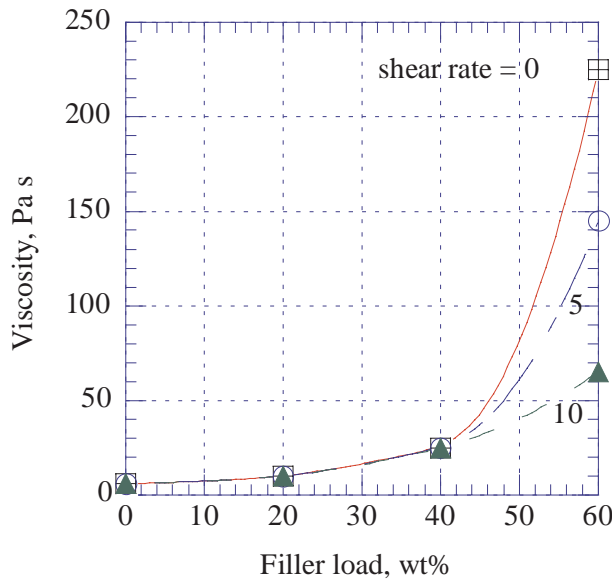


Figure 9.27. Shear viscosity vs. filler concentration. [Adapted, by permission, from, Cheng J, Bigio D I, Briber R M, Antec '97. Conference proceedings, Toronto, April 1997, 162-7.]

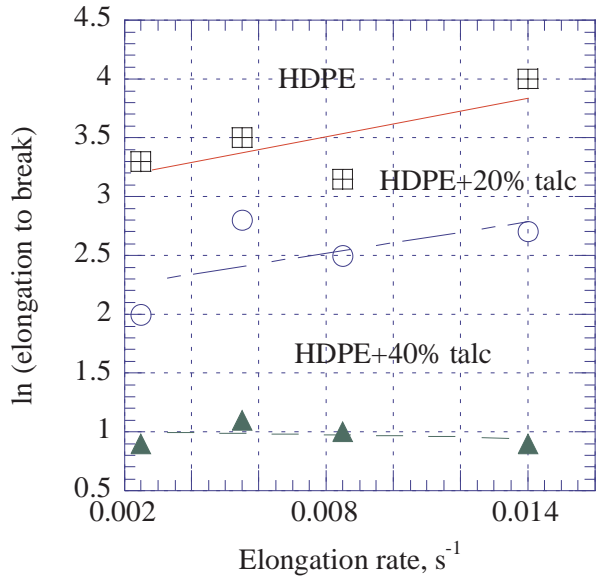


Figure 9.28. Elongation to break of HDPE filled with talc vs. elongation rate. [Adapted, by permission, from Chang Ho Suh, White J L, *J. Non-Newtonian Fluid Mechanics*, **62**, Nos.2/3, 1996, 175-206.]

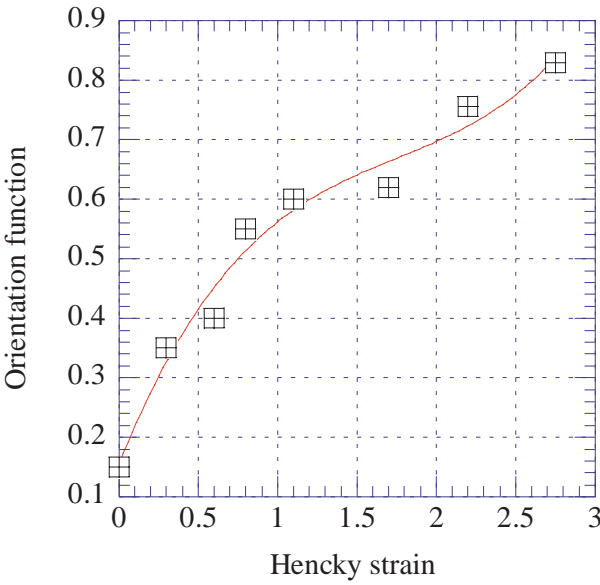


Figure 9.29. Fiber orientation function vs. Hencky strain for PA-6 filled with glass fiber. [Adapted, by permission, from Wagner A H, Kalyon D M, Yazici R, Fiske T J, Antec '97. Conference proceedings, Toronto, April 1997, 996-1000.]

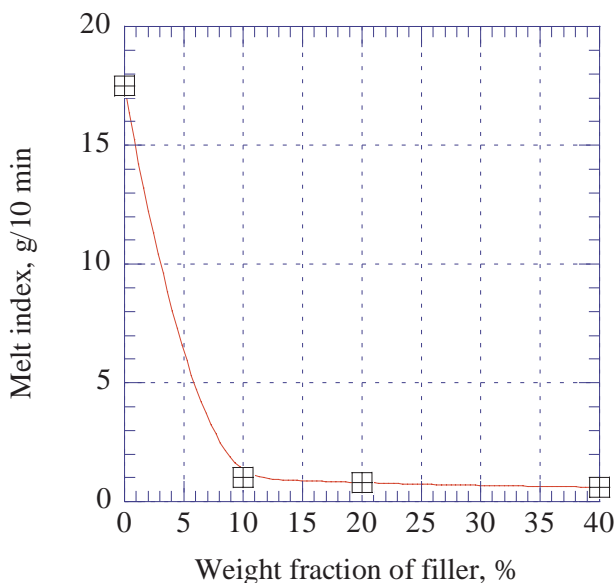


Figure 9.30. Melt flow index vs. weight fraction of calcium carbonate in PP. [Adapted, by permission, from Johnson K C, Antec '96. Volume III. Conference proceedings, Indianapolis, 5th-10th May 1996, 3545-9.]

9.10. MELT RHEOLOGY

The effect of filler on polymer melts is discussed in several papers.^{10,12,52,64-72} Figure 9.30 shows that the melt flow index decreases rapidly on calcium carbonate addition. The changes as concentration increases are much less pronounced.⁵² This study was conducted for a large particle sized (50-400 μm) grade of calcium carbonate.

Figure 9.31 shows the effect of coating of calcium carbonate with stearic acid on the relative melt viscosity.⁷⁰ The surface coating reduces the melt viscosity by a factor of 3 at higher concentrations of filler. The maximum packing depends on filler type and particle size. For 10 μm calcium carbonate, the maximum packing was 0.52, for precipitated calcium carbonate (2 μm) it was 0.44 and for glass beads 0.68. The surface treated calcium carbonate had maximum packing of 0.77.

The melt flow index of filled PP changes during reprocessing (Figure 9.32).⁷² The magnitude of the change depends on the amount of talc added. Any level of talc addition improved the polymer's resistance to reprocessing but the optimum conditions were at low concentrations of filler.

9.11 YIELD VALUE

The yield value of a filled system depends on its filler and the matrix.^{23,27,58,72-3} On the filler side, yield value depends on particle size and on the functional groups which interact with the matrix to form easily recoverable bonds. For carbon black

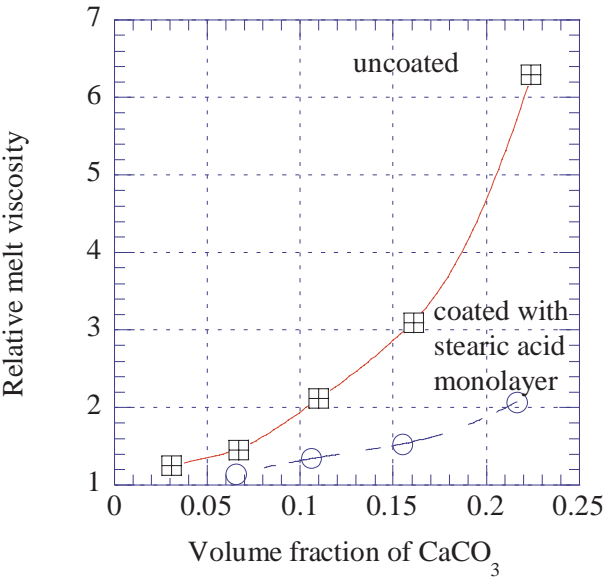


Figure 9.31. Relative melt viscosity vs. fraction of calcium carbonate in LDPE. [Data from Bomal Y, Godard P, *Polym. Engng. Sci.*, **36**, No.2, 1996, 237-43.]

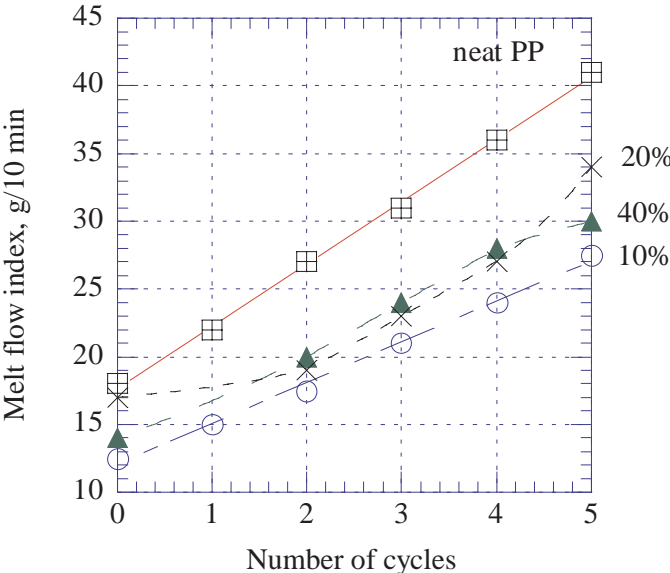


Figure 9.32. Melt flow index of PP filled with talc vs. number of processing cycles. [Data from Guerrica-Echevarria G, Eguiazabal J I, Nazabal J, *Polym. Degradat. Stabil.*, **53**, No.1, 1996, 1-8.]

in PPS, yield values range between 15 and 90 kPa. Smaller values were found for calcium carbonate in PPS (1.5 to 40 kPa). Fillers dispersed in PE usually resulted in low yield values.

Figure 9.9 shows that yield stress increases with a filler volume fraction.²³ Polymer type does not play a significant role here since neither polymer interacts with filler. Small additions of carbon black increase yield stress rapidly. Several equations are used to describe yield stress. The Casson equation is the most frequently used. In this equation the yield stress of a filled system depends on the yield stress and the viscosity of the matrix and on the applied shear rate.⁵⁸

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