In the preceding two chapters, various effects on steady shear viscous and elastic properties of filled polymer systems were discussed. The present chapter focuses on the unsteady shear viscoelastic properties of these systems. The unsteady shear characteristics are mainly discussed with respect to small-amplitude oscillations, namely, dynamic rheological data. In some cases, the thixotropic sweep responses and the stress relaxation behavior are also included because they bring out the rheological characteristics in some situations in a much better manner. The extensive literature [1-85] on the rheology of filled polymer systems, however, contains quite limited information on the unsteady shear data [1,8,43-45,54,61,62,64,68,71,72,74,91,92].

The reason for this is because unsteady shear data were normally not used when dealing with low loading levels of fillers where the bulk of information is available. For highly filled systems, this is the only mode of obtaining reliable rheological data, but since the work on highly filled polymer systems is not extensive, the information on unsteady shear data is naturally limited.

With higher filler loading, it becomes increasingly difficult to gap set in a cone and plate arrangement of the rheogoniometer; whereas through the use of the parallel-plate arrangements, it is possible to obtain rheological data at any level of loading. The use of steady shear in the case of highly filled systems is not recommended because the material trapped between the plates of the rheometer during data generation normally tends to hang outside the plate dimensions, thereby giving erroneous results. On the other hand, when dealing with unsteady shear data generation, small-amplitude dynamic oscillation keeps the material between the plates of the rheometer intact and hence gives much more reliable and reproducible data. Thus, dynamic data are often the preferred mode for viscoelastic information of highly filled polymer systems. Of course, it need not be restricted only to high filler loadings.
Unsteady shear viscoelastic properties

as it would certainly provide reliable information even in low filler loadings as well.

As a matter of fact, the most reliable rheological data on filled polymer systems can be obtained through the use of dynamic oscillatory measurements. The dynamic rate sweep and the dynamic strain sweep would be most suitable for assessing the internal structure of the system. During a strain sweep, a plot of storage modulus vs. percentage strain at low frequency would be the best indicator of the level of homogeneity in the system. A decrease in storage modulus with percentage strain would be an indicator of the occurrence of the structural breakdown in the system. During a frequency sweep, it is best to maintain the strain as low as possible within the system constraints, in order to be in the linear viscoelastic region of the material. The response of complex viscosity, storage modulus, loss modulus and tangent delta that is then obtained would give a measure of the dispersion of the filler in the matrix. A highly agglomerated system would show the existence of a yield at low frequency, the storage modulus would be high and vary minimally with frequency giving a more solid like response and the tangent delta would be lower. However, generation of reliable and consistent data in case of filled systems depends to a large extent on the preparation of the sample for the rheological test. Premolding samples under high pressure to a shape and size as would be used for the parallel-plate rheometer test, would ensure that the variation in the observed rheological response is related to the filled system characteristics and is not an experimental artifact.

During generation of dynamic data, it is important to use a fixed low amplitude when collecting data for comparison on various systems. The effect of the amount of strain during dynamic data measurement on filled polymer systems has been brought out by Bigg [44]. Figure 8.1 shows the strong effect of strain on the complex viscosity and storage modulus for low density polyethylene filled with 50 vol% of spherical stainless steel particles at 160°C. It can be seen that the difference between the complex viscosity at $10^{-3}$ rad/s with a 1% strain ($\eta^* = 10^6$ Pa.sec) to that with a 25% strain ($\eta^* = 2 \times 10^4$ Pa.sec) is almost two orders of magnitude. Much greater differences are observed in the storage modulus response with increasing strain. When the unfilled low density polyethylene is tested using different levels of strains, it is seen from Figure 8.2 that the complex viscosity remains unaffected by strain and remains so at all temperatures. Thus, for unfilled polymers, it may be all right to determine dynamic data at any level of strain. However, for filled systems, because of the sensitivity of the dynamic response to the level of strain, it is always important to determine the dynamic viscoelastic properties at a strain that is low enough not to affect the material response. As the filler loading increases, the level of strain...