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SUPERPOSED STEADY SHEAR AND OSCILLATORY FLOWS OF FIBER FILLED POLYMER MELTS

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ABSTRACT
In this work, low density polyethylene (PE) and its compounds with carbon fiber (CF) undergo the parallel superposed steady and oscillatory shear flows. The effect of the steady shear on the viscoelastic properties and the effect of the oscillatory perturbation on the shear viscosity as well as the effect of fiber content on the superposed flow properties were discussed. Overall, superposed flow conditions enhanced viscoelastic response (dynamic viscosity, storage modulus) of filled systems. The critical angular frequency, where phase angle becomes 90° and storage modulus decreases sharply to zero, was found to be largely dependent on the volume fraction of fiber, regardless of the superposed shear rate. Specific attention was paid to comparison of the superposed flow properties of unfilled polymer melts with those of filled systems.
Keywords: superposed flow, steady shear flow, oscillatory flow, fibre filled system

1. INTRODUCTION
Filled polymer melts, prone to conform the three-dimensional network structures, are often moulded under a variety of complex deformations (flows), which are far from simple steady or oscillatory shears. Therefore, superposition experiments of steady shear flow on dynamic oscillatory flow is thought to be one of the useful flow patterns providing new information about the structure of polymer fluids.
Generally, there are two types of superposed flow: a parallel superposition of steady shear and oscillatory flows, and an orthogonal superposition of the two flows. However, the study reported by Mewis et al. [1] has shown that the analyses of the orthogonal superposed flow are rather easier, the parallel superposition was chosen in the study presented here.
Constitutive equations have to be applicable to analyse the various flow fields, and the superposed behaviour might prove their versatility. The total shear rate and shear stress under the superposed shear flow are given by simple superposition of steady and oscillatory shear flows:

$$\dot{\gamma} = \dot{\gamma}_0 + \mathrm{Re}(\dot{\gamma}_0^0 e^{i\omega t}) \tag{1}$$

where $\dot{\gamma}_0$ stands for the steady shear rate superposed on oscillatory flow, ω is the angular frequency of oscillatory flow, and $\mathrm{Re}(\dot{\gamma}_0^0 e^{i\omega t})$ represents the real part of the shear rate dependent on angular frequency, where $\dot{\gamma}_0^0$ is the amplitude of shear wave.

$$\tau = \eta\,\dot{\gamma}_0 + (\eta' / \dot{\gamma}_0^0 \sin\delta)\sin(\omega t + \delta) \tag{2}$$

where η represents the steady shear viscosity and η´ corresponds to the dynamic viscosity obtained from the simple oscillatory flow measurement.

However, these relations are successfully used only for simple fluids. For the materials showing remarkable non-linear flow properties (filled polymers), their applicability has not been confirmed yet, and therefore, it is an important subject for discussion.

2. EXPERIMENTAL

Low density polyethylene (PE, Flowthene G701, MFR 7.8 g/10min, powder, Seitetsu Kagaku Ind. Co.Ltd.) and carbon fibre (CF, Beshight 12 000, diameter of 7 μm, 3 mm chopped strand, Toho Rayon Co.Ltd.) were compounded in an elastic extruder (designed and constructed at the National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan).

Superposed rheological properties of pure and fibre filled polyethylene melts were determined in a cone-plate type rheometer (Weissenberg Rheogoniometer, Carri-Med R21). The cone had radius of 1.25 cm and angle of 2°. All the measurements were performed at 200°C. The angular frequency for the dynamic measurements varied from 0.02 to 60 rad/s, and strain amplitude in a shear unit was 1.75 %. The superposed shear rate was selected between 0.05 and 5 s^{-1}.

Steady shear rate and angular frequency are the variables in this experiment, and influence of these parameters on viscoelastic properties, such as dynamic viscosity and storage modulus, is investigated. The superposed flow measurement was carried out in a mode, where oscillatory shear flow is superposed on steady shear flow, which is kept at constant shear rate; angular frequency is changed stepwise.

The procedure was as follows: the unidirectional shear flow with a fixed shear rate was started, torque gradually increased, and then approached to a stable state at low shear rate (at high shear rates it has to overcome a stress overshoot first). When the stable shear flow was reached, an oscillatory shear flow was superposed on it. After the superposition, time-dependent torque varied sinusoidal with a phase lag (difference) to the oscillatory displacement.

3. RESULTS AND DISCUSSION

In the low shear region steady shear viscosity slopes of composites (*Figure 1*) differ much from that of PE, which is Newtonian; the curves become steeper as the fibre content is increased. However, at high shear rates they approach the curve of the pure matrix, indicating that the composed fibre structure changes drastically under rather high shear as fibres tend to orient to the flow direction.

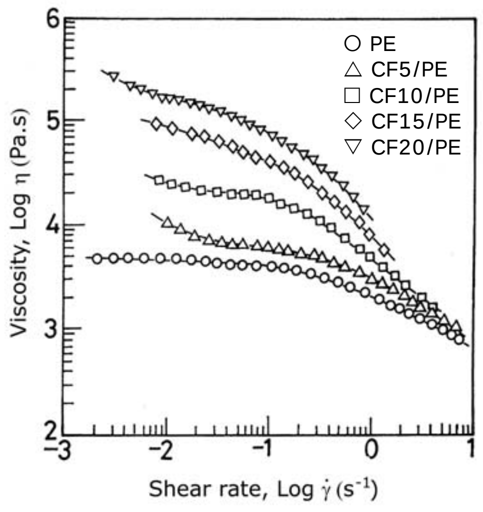

Figure 1. Relationship between shear viscosity and shear rate of unfilled PE and CF/PE melts.

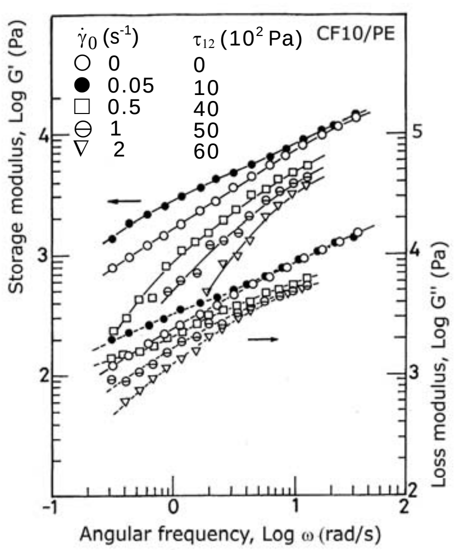

Figure 2. Storage and loss moduli versus angular frequency curves of CF10/PE system as a parameter of the superposed shear rate.

Accordingly, complex viscosity of all tested materials decreases monotonously with angular frequency, and the discrepancy between complex and steady shear viscosities increases with increase of the fibre content. These rheological phenomena are generally observed for various heterogeneous systems, and it seems that the change of the structure composed by fibres under simple steady shear deformation differs from that under oscillatory flow field.

For pure matrix both storage and loss moduli decrease with the increase of superposed shear rate. The degree of their decrease is relatively larger in the low angular frequency region, and it is more pronounced for storage modulus. This behaviour is in a good agreement with the results obtained for polymer melts and solutions in the previous works [2-4].

In case of the composites these variables do not change monotonously, but instead increase once and then decrease with rising superposed shear rate, see *Figure 2* for CF10/PE composite as an example. This trend is even stronger for higher content of CF in PE matrix.

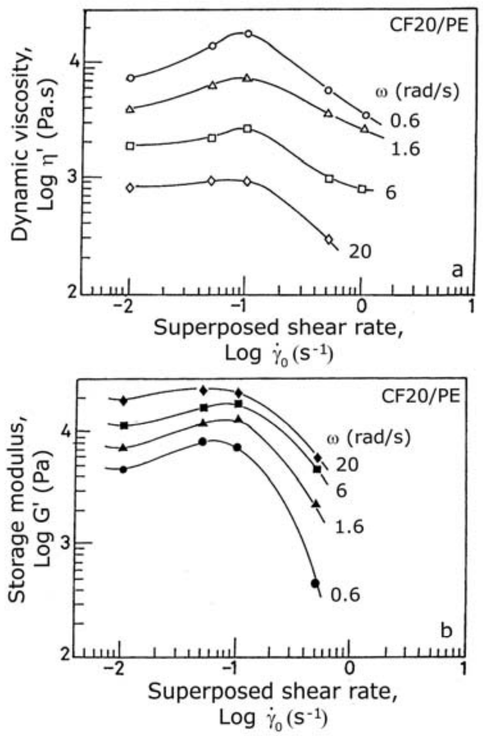

Figure 3. Dynamic viscosity (a) and storage modulus (b) as functions of the superposed shear rate for CF20/PE system at various angular frequencies.

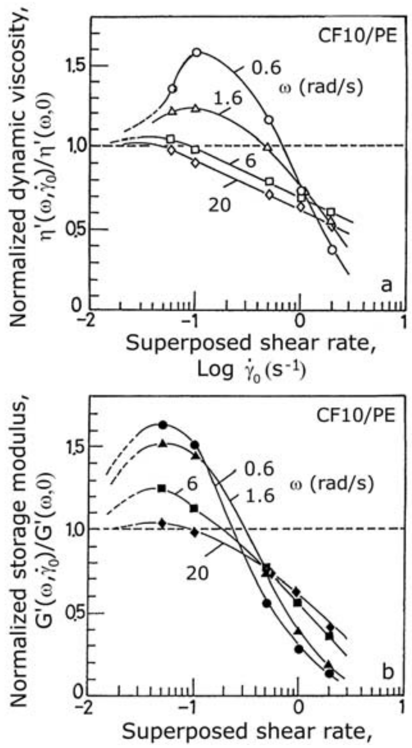

Figure 4. Normalized dynamic viscosity (a) and normalized storage modulus (b) as functions of the superposed shear rate for CF10/PE system at various angular frequencies.

Relationship between dynamic viscosity and superposed shear rate as well as storage modulus dependence on superposed shear rate at various angular frequencies is illustrated in *Figure 3* for CF20/PE system. For composites it is found that dynamic viscosity at low angular frequency increases with superposed rate, and then decreases after overcoming maximum. However, at high angular frequency this value decreases monotonously with superposed shear rate. Similar shear rate dependent behaviour is observed for storage modulus.

In order to demonstrate the superposed shear rate dependence on the dynamic viscosity and the storage modulus at various angular frequencies more clearly, the normalized plots of these variables were derived (*Figure 4* for CF10/PE system). The normalized functions have maxima at high angular frequency, and the superposed shear rate, in which dynamic viscosity shows the maximum, is higher than that of the maximum storage modulus.

These maximum values are generally increased by addition of CF fibres. However, as functions of volume fraction of fibre, both values show distinct pattern due to the different effect of the superposed shear flow on dynamic viscosity and storage modulus, especially for high fibre content systems.
It is well known that when measuring sinusoidal oscillatory flow properties of a viscoelastic material, the phase difference occurs between oscillatory displacement and corresponding torque (shear stress). The phase angle of the viscoelastic material is a function of angular frequency, and gradually increases toward 90° with declining angular frequency. Additional aspect of this work was to investigate whether the phase angle of the composite materials will change under the superposition of the oscillatory flow on the steady shear, and if the degree of the phase angle change will depend on the superposed steady shear rate.
For pure PE the phase angle at each angular frequency increases with the increase of the superposed steady shear rate. From the comparison with CF10/PE and CF20/PE composites it is found that the phase angles at zero or low superposed shear rate for fibre filled systems are generally lower than those of unfilled PE over a wide range of angular frequency. This is reasonable since the elastic properties are highly affected by the addition of fibres. From the rheological point of view it is very interesting that the fibre filled systems show higher dynamic elastic properties under the superposition of the shear flows at some critical conditions.
From the extrapolation of the curves it may be possible to determine the critical angular frequency, ω_c, in which the phase angle becomes 90°. The following relationship between critical angular frequency and superposed shear rate was obtained for various polymer solutions and melts in the previous studies [e.g. 4]:

$$\omega_c = \frac{1}{2}\dot{\gamma}_0 \qquad (3)$$

Concerning our data, it is found that ω_c of both pure PE and CF/PE melts are lower than $0.5\dot{\gamma}_0$, especially at high superposed shear rates. Furthermore, the CF/PE data at each superposed shear rate decrease once with increasing fibre content, and after passing a minimum they increase with rising fibre content. The character of the dependency is the same regardless of the superposed shear rate level. The critical angular frequency normalized by that of unfilled PE as a function of fiber concentration plots may be superimposed into a single curve, supporting the idea that the ω_c change of the CF filled systems is dependent largely on the volume fraction of fibre in the compound.

4. CONCLUSION

Both storage modulus and dynamic viscosity of the composites under the superposed steady shear flow show higher values than those obtained under simple oscillatory flow, especially at the low superposed shear rate region. The degree of the increase of these viscoelastic functions is dependent on the superposed shear rate, angular frequency and fibre content. The critical angular frequency is dependent largely on the volume fraction of fibre, but independent of the superposed shear rate.
Fibre filled systems show, in comparison to simple shear, higher dynamic elastic properties under the superposition of the shear flows at some critical conditions.

5. ACKOWLEDGEMENT

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