SHEAR THINNING BEHAVIOR AND MICROSTRUCTURES OF MWCNT/EPOXY AND CNF/EPOXY SUSPENSIONS UNDER STEADY-STATE SHEAR

T. Yokozeki[1*], S. C. Schulz[2], S. T. Buschhorn[3], K. Schulte[3]

[1]*Department of Aeronautics and Astronautics, University of Tokyo, 7-3-1 Hongo Bunkyo-ku Tokyo, 113-8656 Japan*
[2]*Institut für Optische und Elektronische Materialien, Technische Universität Hamburg-Harburg, Eissendorfer Str. 38, D-21073 Hamburg, Deutschland*
[3]*Institut für Kunststoffe und Verbundwerkstoffe, Technische Universität Hamburg-Harburg, Deinicke Str. 15,D-21073 Hamburg, Deutschland*
**yokozeki@aastr.t.u-tokyo.ac.jp*

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Abstract
This report investigates the steady-state viscosities of multiwall carbon nanotube (MWCNT)/epoxy and carbon nanofiber (CNF)/epoxy suspensions with varying filler concentrations under different shear rates at various temperatures. In-situ observation of filler networks suggests the build-up of shear induced MWCNT and CNF agglomerates at low shear rates, which correlates with the measured shear thinning behavior. The agglomeration process in MWCNT/epoxy suspensions is enhanced at lower shear rates in the case of higher temperatures, whereas, at high shear rates, both nano-fillers show good dispersion. Shear thinning behavior is observed for both types of fillers, and shear thinning exponential parameters are evaluated as a function of filler content. The shear thinning exponent increases in conjunction with increase in filler content, but it is found to saturate at a specific value, independently of filler material.

1 Introduction
Extensive attention has been paid to research activities on the use of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) for high-performance and multi-functional reinforcements of engineering polymers [1]. Enhancement of matrix-dominated mechanical properties of fiber-reinforced plastic (FRP) using nanoparticle-dispersed polymer (e.g. compressive strength, interlaminar fracture tougness, residual strength) has been also widely recognized [2,3]. When using nanoparticle modified polymer for FRPs, prepreg-based fabrication, resin transfer molding (RTM), and resin film infusion (RFI) are widely used. Therefore, the rheological properties of nanoparticle-dispersed polymer suspensions prior to curing are one of the key factors to control the quality and performance of the fabricated composites.
Nanoparticles are ideally expected to be isolated individually in the matrix, while in reality, they interact closely with each other and entangle. This results in the formation of nanoparticle agglomerates in the final products. The evolution of nanoparticle microstructure in the presence of shear flow has been widely reported [4,5], and, in general, low shear forces induce agglomerates whereas high shear forces break up agglomerates. The susceptibility of

network formation under shear depends on shear rates, filler contents, processing methods, surface treatment of fillers, etc [4]. The microstructures or network formation of nanoparticles are closely related to the rheological properties of suspensions, which was clearly indicated by viscosity measurement and in-situ optical observation of nanoparticle-dispersed suspensions under shear flow [4,5]. These results indicate the importance of systematic rheological characterization of nanoparticle-dispersed suspensions under various shear rates, various filler contents, etc.

As suggested by the previous investigations [6], shear flow history influences dispersion state of nanoparticles, and subsequently, the rheological properties of suspensions. Prior to the complete understanding of this transient viscous behavior, we should understand the steady-state viscous behavior of nanoparticle-dispersed suspensions, because the controlled steady-state properties give the basic knowledge for manufacturing processes in industry. In general, the addition of fillers into a suspending medium tends to increase the base viscosity. This viscosity enhancement effect decreases in conjunction with increase in shear rates, which is denoted as "shear thinning". The shear thinning behavior is observed in various suspensions, and is influenced by the various parameters as described in the previous paragraph on the agglomerations or network formation of nanoparticles.

Although the shear-thinning behavior has been widely reconginzed in various suspensions, the derived conclusions sometimes depend on filler material, resin viscosity, filler contents, etc. The authors want to derive a comprehensive representation of the non-Newtonian viscosity or shear-thinning behavior of non-dilute nanoparticle-dispersed polymer suspensions. Such understanding is useful for manufacturing process of nanoparticle-dispersed polymer composites.

In the present paper, we systematically investigate the steady-state viscosities of nanoparticle-dispersed suspensions by changing the filler material, filler content and temperature (i.e. viscosity of the base suspension) with the in-situ observation of nanoparticle microstructures in suspensions. Additionally, we focus on the shear thinning parameter and the steady-state viscosities at higher shear rates and characterize the viscous properties of suspensions.

2 Experimental

2.1 Preparation of Suspensions

Epoxy suspensions filled with different contents of multiwalled carbon nanotubes (MWCNTs) or carbon nanofibers (CNFs) were prepared by mixing the epoxy resin and MWCNTs or CNFs. The matrix used in this study is bisphenol-A-based epoxy resin (Araldite LY 556) obtained from Huntsman Advanced Materials. The used filler particles are "NC 7000" MWCNT supplied by Nanocyl S.A. and "Pyrograph" CNF supplied by Applied Science Inc.

The suspensions were produced with a high shear mixing process using a lab-scale three-roll-mill (Exakt 120E, Exakt Advanced Industries GmbH). First, the nano-fillers were manually stirred in the resin, and then, the pre-dispersed suspension was given onto the rolls. In this work, the suspensions were produced by using a three cycle program with decreasing distances between the rolls for each cycle. The speed for the apron roll was set to be 300 rpm, and the smallest gap size used was 5 μm. Details about the dispersion technique can be also found in the earlier publication [7]. Suspensions at different filler concentrations were produced as summarized below.

MWCNT/epoxy: 0.1 wt%, 0.3 wt%, 0.5wt%, 1wt%
CNF/epoxy: 0.5wt%, 1wt%, 2wt%, 3wt%, 5wt%

Neat epoxy (i.e. 0 wt% suspension) was testes as reference.

2.2 Measurement of Steady-state Viscosity

Rheological measurements with different filler contents were carried out using a stress-controlled rheometer (StressTech HR, Rheologica Instruments) in steady mode with a 30 mm parallel plate geometry. All viscosity measurements were carried out with a gap size of 1 mm. All suspensions were pre-sheared with 100 s-1 for 5 min before the measurement to guarantee a uniform shear history. Afterwards, decreasing stepwise shear rates were applied.

$$100\ s^{-1}\ (20min) \rightarrow 10s^{-1}\ (20min) \rightarrow 1s^{-1}\ (20min) \rightarrow 0.1s^{-1}\ (30min)$$

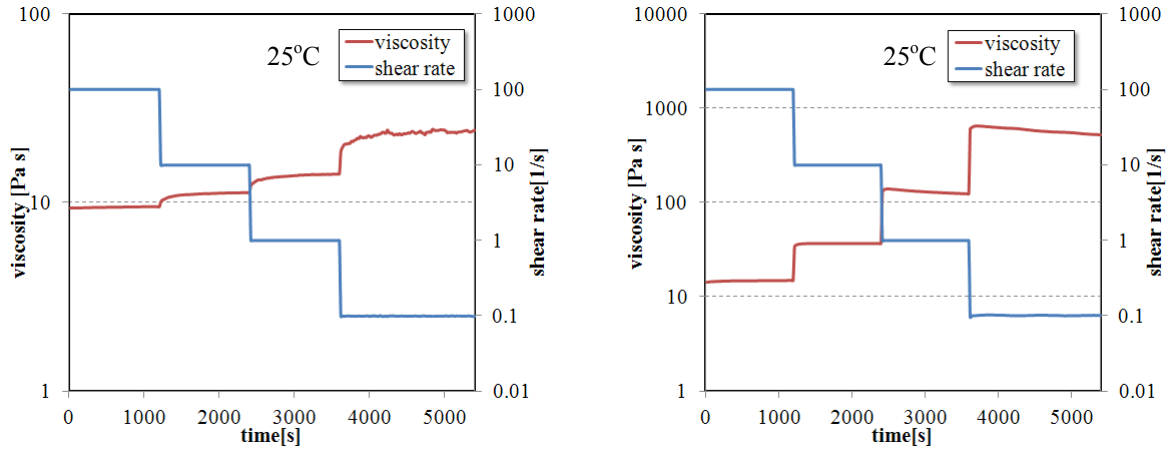
The parentheses indicate the hold time which is necessary to obtain steady-state shear flow as confirmed in the preliminary measurement. Viscosity measurements were carried out at 25 °C, 40 °C, and 60 °C.

This experimental system allows in-situ optical microscopic observation of suspensions under shear flow as described in the previous publication [6]. Optical observations were conducted only for 0.1wt% MWCNT/epoxy and 0.5wt% CNF/epoxy suspensions at 25 °C and 60 °C, because higher filler contents cannot allow us to observe the suspensions optically. For image capture, the gap was decreased to 0.5 mm for 0.1wt% MWCNT/epoxy and 0.2mm for 0.5wt% CNF/epoxy to achieve better depth resolution.

3 Results and Discussions

3.1 Viscosity

The rheological histories of 0.1wt% and 0.5wt% MWCNT/epoxy suspensions at 25 °C are shown in Figure 1(a) and (b). Additionally, applied shear rates are also plotted. CNF/expoy suspensions exhibited similar behavior. Viscosity increases as the shear rate decreases. Typical shear thinning behavior was observed for all cases except for pure epoxy, which behaves as Newtonian fluid. It should be noted that suspensions with higher filler contents exhibit some "overshoot" behavior during the stepwise measurement as can be seen in Figure 1(b). Gradual filler alignment to the flow direction after the shear rate change is the main mechanism of the transient overshoot behavior. It is considered that the effect of filler or agglomerate alignment on the transient viscosity is enhanced in the cases of higher filler contents.



(a) 0.1wt% MWCNT/epoxy (b) 0.5wt% MWCNT/epoxy

Figure 1. Time history of steady-state viscosity measurement of MWCNT/epoxy suspensions at 25 °C

Due to the above-mentioned transient behavior, the steady-state viscosities at the applied shear rates were determined by averaging the measured viscosities during the last five minutes in each step. The steady-state shear viscosities are summarized as a function of the applied

shear rate in Figure 2 for MWCNT/epoxy suspensions and Figure3 for CNF/epoxy suspensions. Viscosity enhancement was more pronounced for suspensions with higher filler contents and at higher temperatures. Comparison of the MWCNT/epoxy and CNF/epoxy with the same contents (i.e. 0.5 wt% and 1 wt%) suggests that MWCNT suspensions tend to show a much stronger shear thinning effect compared with CNF suspensions. This more pronounced effect is attributed to the comparatively high aspect ratio of the MWCNTs.

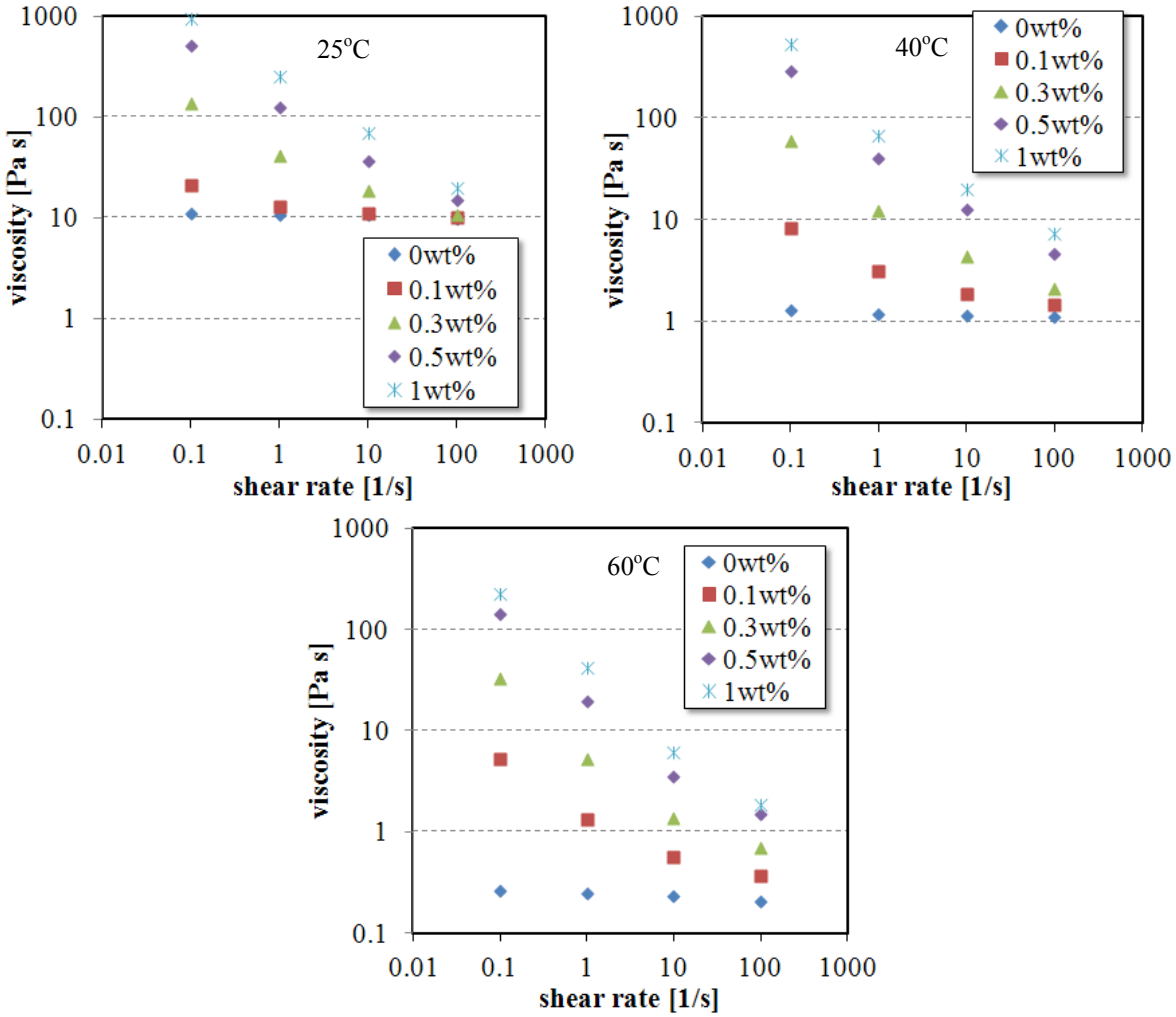


Figure 2. Steady-state viscosity as a function of applied shear rate of MWCNT/epoxy suspensions

3.2 Optical Observation

In order to investigate the microstructures of suspensions under the steady shear flow, in-situ microscopic observation was performed. Microscopic images of 0.1 wt% MWCNT/epoxy suspensions at 25 °C are shown in Figure 4 in conjunction with the measurement history (identical to Figure 1(a)). These images were captured at the last instances of each step. The suspension contains well distributed small agglomerates for the shear rate of 100 s^{-1}. Further shearing at lower shear rates creates bigger agglomerates, especially at the shear rate of 0.1 s^{-1}. It is concluded that this CNT network formation at lower shear rates results in the increase in the measured viscosities. In Figure 5, microscopic images of 0.1 wt% MWCNT/epoxy suspensions at 60 °C are summarized. More clearly defined and separate agglomerates are

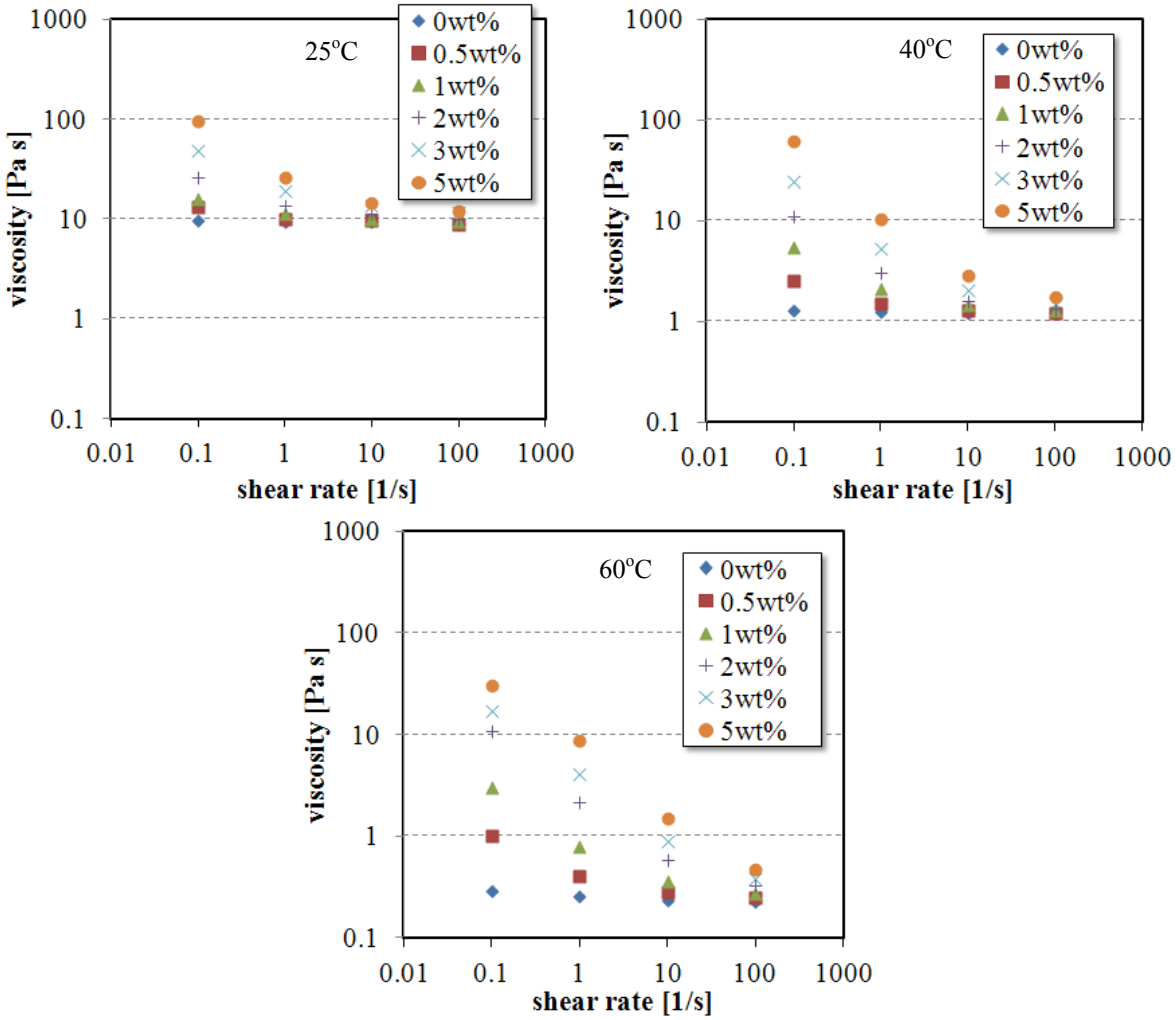


Figure 3. Steady-state viscosity as a function of applied shear rate of CNF/epoxy suspensions

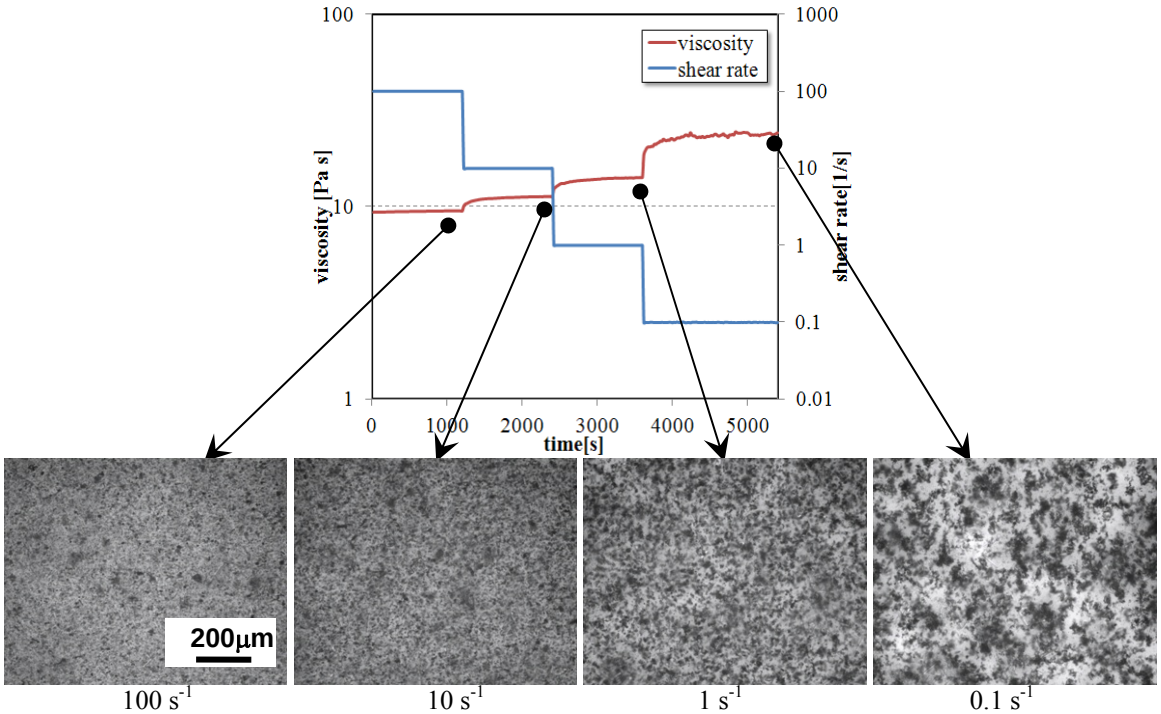


Figure 4. Optical microscopy images of 0.1 wt% MWCNT/epoxy suspension at 25°C

induced at 60 °C. Temperature increase (i.e. decrease in matrix viscosity) induces more clearly defined agglomerates of fillers, and thus stronger viscosity enhancement of the whole system as indicated in the previous section.

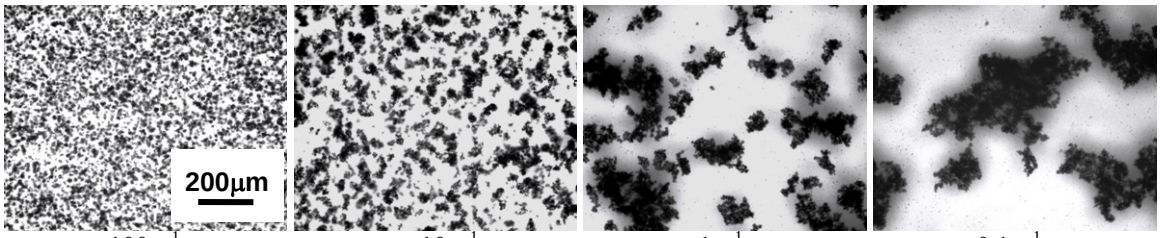
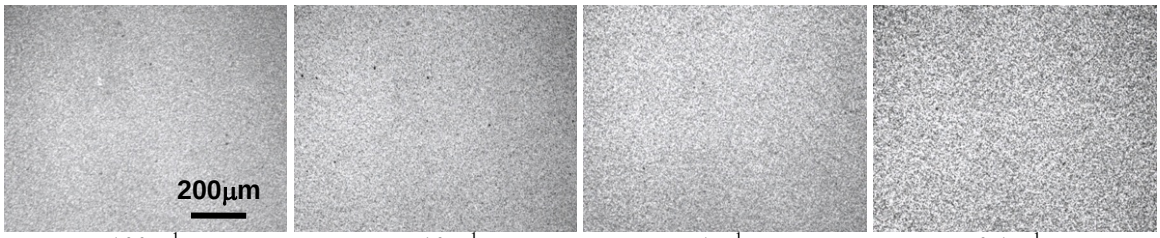
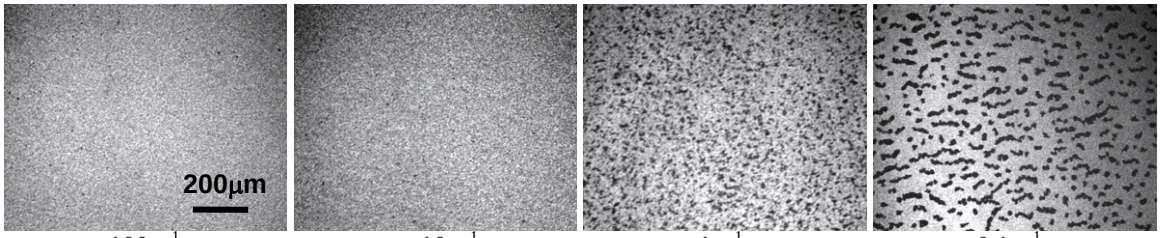


Figure 5. Optical microscopy images of 0.1 wt% MWCNT/epoxy suspension at 60°C



(a) 25°C



(b) 60°C

Figure 6. Optical microscopy images of 0.5 wt% CNF/epoxy suspension at (a) 25°C and (b) 60°C

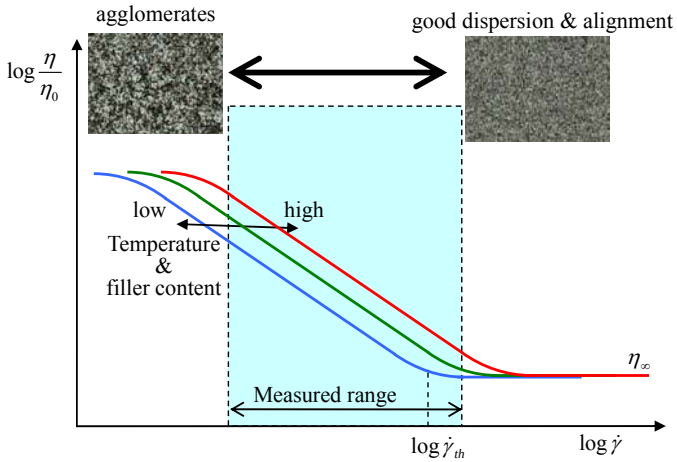


Figure 7. Schematic of the relationship between steady-state viscosity and shear rate

In-situ microscopic observation was also conducted for 0.5wt% CNF/epoxy suspensions at 25 °C and 60 °C. The microscopic images are summarized in Figure 6. 0.5 wt% CNF/epoxy suspension exhibits less agglomerates at lower shear rates compared with 0.1 wt% MWCNT/epoxy, even though the former includes higher filler content. This observation

supports the experimental result that MWCNT suspensions showed a much stronger affinity to entangle and thus a more pronounced shear thinning effect compared with CNF suspensions. It should be noted that 0.5 wt% CNF/epoxy suspension at 60 °C at the shear rate of 0.1 s^{-1} contains many small agglomerates like "helical bands" as reported by Ma et al.[4]. Helical bands are considered to be induced in the case of CNF suspensions at lower shear rates, as a result of the constraint by the upper and lower plates.
Based on the rheological measurements and the optical observations, schematic explanation on the shear thinning behavior of MWCNT/epoxy and CNF/epoxy suspensions is described in Figure 7. The applied shear rate is plotted against the viscosity normalized by that of pure resin. Measured viscosities approach to that of pure resin at higher shear rates, whereas viscosities increase linearly in logarithmic scale in conjunction with decreasing shear rates. This shear thinning tendency correlates with the microscopic formation/destruction of agglomerates. The measured shear thinning curves seem to shift horizontally, sometimes with a change of slope, depending on the temperature and the filler content.

3.3 Shear Thinning Exponent
In this study, shear thinning behavior is expressed as exponential law as described by the following equation.:

$$\eta = \eta_{\infty}\left(\frac{\dot{\gamma}}{\dot{\gamma}_{th}}\right)^{-n} \tag{1}$$

In this equation, η and $\dot{\gamma}$ express the viscosity and the shear rate, η_{∞} denotes the asymptotic viscosity at higher shear rates, $\dot{\gamma}_{th}$ is the threshold shear rate that represents the intersection with the bilinear model, and n is the exponent describing the shear thinning behavior.

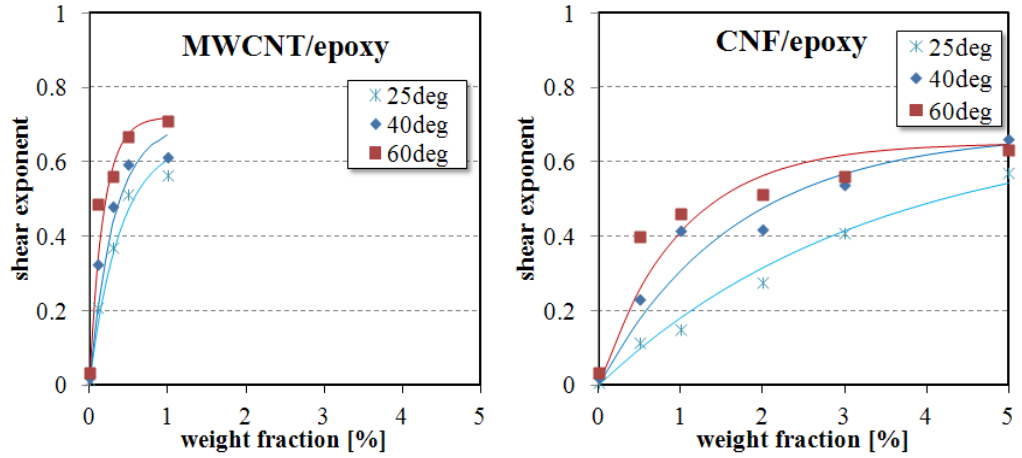


Figure 8. Shear thinning exponent as a function of filler content

Using the experimental data, the exponential parameter (shear thinning exponent, n) was evaluated. In the cases of suspensions with lower filler contents at lower temperatures (e.g. see 0.1wt% MWCNT suspension in Figure 2), the applied shear rates correspond to the transient region, and thus, the bilinear representation may not be suitable. In such cases, we used the partial data that fit the linearity of shear thinning (e.g. the data between the shear rates of 0.1 s^{-1} and 1s^{-1} were used in the case of 0.1wt% MWCNT suspension at all temperatures). The evaluated shear thinning exponents are summarized in Figure 8. Shear thinning exponent increases as a function of filler content, and is slightly influenced by

temperature. It is noted that, in the case of CNF/epoxy suspension at 25 °C, the measured data may not include the linear region, which may result in underestimation of the shear thinning exponents. MWCNT suspensions have higher shear thinning exponents compared with CNF suspensions. This coincides with the arguments based on the optical observation. At higher contents, shear thinning exponents seem to be saturated for both suspension systems. Interestingly, the saturated value is about 0.6-0.7 independently of filler types and temperatures.

4 Conclusions

In the present paper, we systematically investigate the steady-state viscosities of MWCNT/epoxy and CNF/epoxy suspensions with different shear rates, filler content and temperature with the in-situ optical observation of microstructures. The shear thinning behavior of thermoset suspensions and the steady-state viscosities at higher shear rates are specifically focused on, and the following conclusions can be drawn:

- Viscosity increase was more pronounced for suspensions with higher filler contents and at higher temperatures. Optical observation suggested that more MWCNT and CNF agglomerates are induced at higher temperature. This observation supported the experimental tendency of viscosity.
- MWCNT suspensions tended to show a much stronger shear thinning effect compared with CNF suspensions. This more pronounced effect was attributed to the comparatively high aspect ratio of the MWCNTs. The optical observation also confirmed that MWCNT suspensions exhibit more agglomerates under shear.
- Shear thinning behavior was evaluated for MWCNT and CNF suspensions using an exponential law. Shear thinning exponent was an increasing function of filler contents, and was somewhat influenced by temperatures. MWCNT suspensions exhibited higher shear thinning exponents compared with CNF suspensions, which was correlated with the optical microscopic observation. At higher contents, shear thinning exponents converged to about 0.6-0.7 independently of filler types and temperatures.

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