STUDY ON THE RHEOLOGICAL CHARACTERISTICS OF NANO-FILLERS/EPOXY SYSTEMS

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Keywords: *Rheological Characteristics, Nano-fillers, Epoxy systems*

Abstract

The influence of different kinds and contents of nano-fillers such as nano-montmorillonite (nano-MMT) , nano-fumed silica (nano-SiO_2) and multi-wall carbon nanotubes (MWCNTs) on the rheological characteristics of nano-fillers/ Bisphenol-A diglycidyl ether epoxy resin (DGEBA) systems have been studied. First, the rheological characteristics of these systems are analyzed, and we find that Casson model is the best model to describe them. Then the flow models and the viscosity models based on Casson Model are established. By comparing and analyzing parameters in the flow models, the effect of nano-fillers on the rheological characteristics of these systems is concluded in quality and quantity. The results of the research can improve preparing technologies of nanometerials by supplying theory directions in future.

1 Introduction

Fillers have been widely applied in the products of resin matrix composites. Main function of fillers is improving the fluidity and other processing properties of resin besides elevating electrical property, thermal conductivity, mechanical property, the volume of products and reducing the cost. Compared with traditional fillers, nano-fillers can obtain the same functions at much less content. Moreover, nano-fillers can improve mechanical property, gas-insulating property, non-flame property and electrical conductivity of composites. Therefore, nano-fillers have a great potential to be applied in the field of composites [1].

Recently molding technologies for nanocomposites have been developed rapidly, and the influence of nano-fillers on the rheological characteristics of polymer systems has been attracting much attention. However, the studies on the effect of nano-fillers on the rheological characteristics of resin systems are very limited [2-4].

In this work, the influence of nano-fillers such as nano-montmorillonite (call MMT for short thereinafter), nano-SiO_2 (called SiO_2 for short thereinafter) and multi-wall carbon nanotubes (MWCNTs) on the rheological characteristics of nano-fillers/DGEBA systems was studied. Through constructing the flow models, the influence of the kind and content of nano-fillers on the rheological characteristics of epoxy systems at different shear rates was analyzed quantitatively.

2 Experimental

2.1 Materials

DGEBA, whose average molecular weight is about 360-380 and viscosity is 8-11Pa·s at room temperature, is supplied by WUXI DIC EPOXY CO., LTD. Nano-fillers include MMT I30E (from Nanocor, USA), SiO_2 A-300 (from Shenyang Chemical, China), MWCNTs-3 (from Shenzhen Nanotech Port, China).

2.2 Preparation of nano-fillers/DGEBA systems

For different nano-fillers/DGEBA systems, two methods such as mechanical agitation and mechanical agitation plus ultrasonic vibration were used to blend them.

In mechanical agitation, DGEBA was firstly low-speed stirred in water bath (70-80℃ controlled) for half an hour. Then nano-fillers were gradually added during agitation, meanwhile the rotate speed was adjusted to middle speed (about 1000-1500 r/min). Finally MMT/DGEBA and SiO_2/DGEBA systems were maintained at constant temperature for 15-30min, the content of both MMT and SiO_2 were respectively 1, 3, 5, 7 and 10phr.

In mechanical agitation plus ultrasonic vibration, the mechanical agitation was moved to ultrasonic water bath. The content of MWCNTs in the MWCNTs/DGEBA system was respectively 0.5, 1, 2, 3 and 5phr, the system was maintained at constant temperature for 1-3h according to the content of MWNTs.

2.3 Measuration of the rheological curves

Steady-state flow curves and constant temperature viscosity-time curves of DGEBA systems were measured by the plate mode of rheometer.

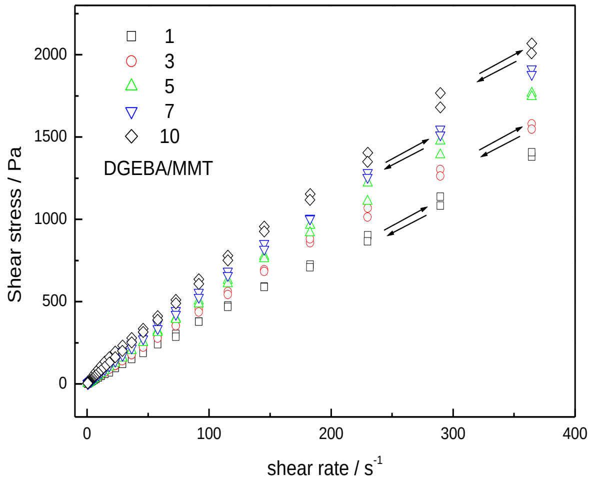
Nano-fillers/DGEBA systems were circular scanned in the range of 0.5-365s^{-1} of shear rate which was raised and dropped evenly after being taken logarithm at constant 30℃, and the shear stress-shear rate curves were obtained. Moreover, all measure points were measured until the system had reached set shear rate for 20s in order to ensure that rheological data were measured until the system reached the steady state. Constant temperature viscosity-time curves was respectively measured at 45, 60, 75, 90, 105 and 120℃, and the number of measure points was 15 so that repeatability of data could be ensured, shear rate was 10s^{-1}, thickness of the sample was 1mm, and force was clockwise.

3 Results and discussion

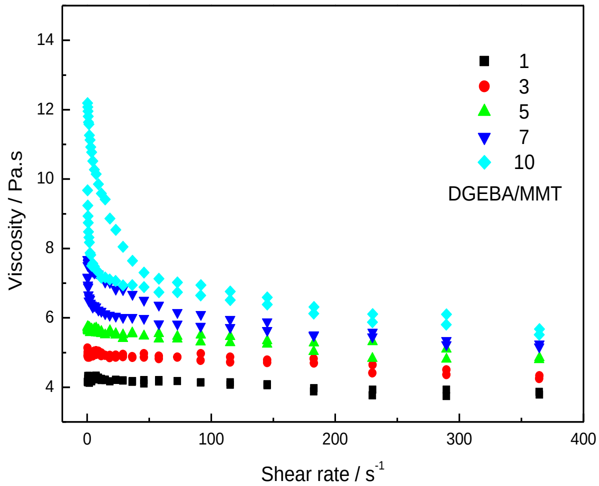
3.1 Analysis of the rheological characteristics of nano-fillers/DGEBA systems

The shear stress-shear rate curve (flow curve) of the MMT/DGEBA system is shown in Fig. 1(a). The value of $\tau/\dot{\gamma}$ on the flow curve expresses the instant shear viscosity of the system in a certain value of $\dot{\gamma}$. Therefore, according to the flow curve, the viscosity-shear rate curve (viscosity curve) can be obtained as shown in Fig. 1(b), the content of MMT φ (phr) is respectively 1, 3, 5, 7 and 10phr. In the same way, the flow curve and the viscosity curve of SiO_2/DGEBA can be obtained as shown in Fig. 2, the content of SiO_2 is respectively 1, 3, 5, 7 and 10phr. The flow curve and the viscosity curve of MWCNTs/DGEBA can be obtained as shown in Fig. 3, the content of MWCNTs is respectively 0.5, 1, 2, 3 and 5phr.

Through analyzing the data, we found that when the content of nano-particles was not very high (≤10phr), the nano-particles/DGEBA systems exhibited thixotropy at different degree and appeared yield stress, moreover, the relation between shear stress and shear rate was nonlinear, therefore, it was shown that resin system exhibited the characteristic of shear-thinning, non-Newtonian fluid along with the addition of nano-particles.

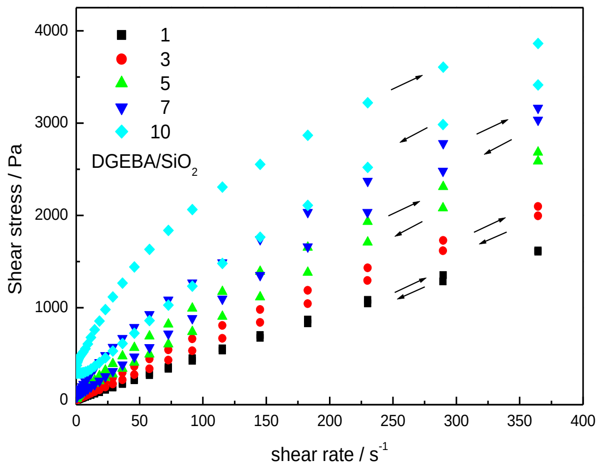


(a) $\tau - \dot{\gamma}$

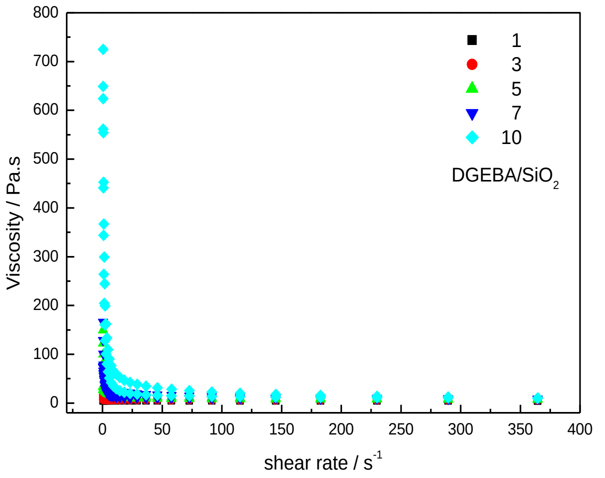


(b) $\eta - \dot{\gamma}$

Fig. 1. The $\tau - \dot{\gamma}$ and $\eta - \dot{\gamma}$ curves of the MMT/DGEBA system at different contents of MMT

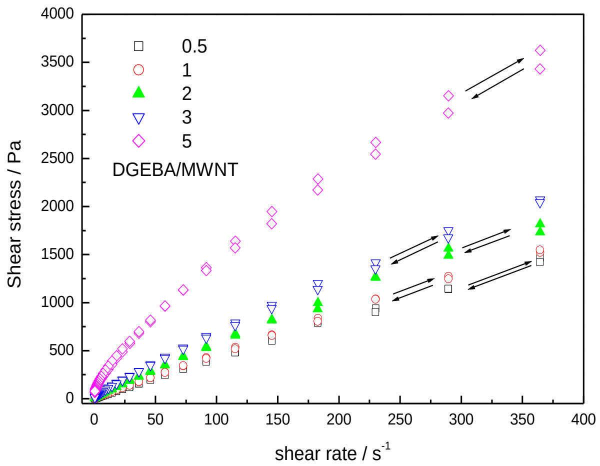


(a) $\tau - \dot{\gamma}$

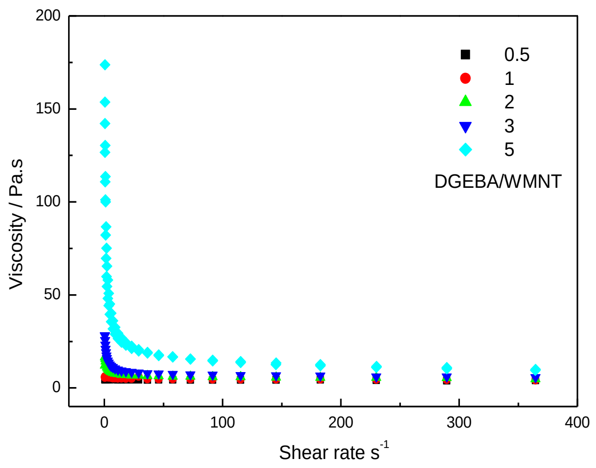


(b) η - $\dot{\gamma}$

Fig. 2. The τ - $\dot{\gamma}$ and η - $\dot{\gamma}$ curves of the SiO_2/DGEBA system at different contents of SiO_2



(a) τ - $\dot{\gamma}$



(b) η - $\dot{\gamma}$

Fig. 3. The τ - $\dot{\gamma}$ and η - $\dot{\gamma}$ curves of the MWCNTs /DGEBA system at different contents of MWCNTs

3.2 Flow models of nano-fillers/DGEBA systems

Viscosity of suspensions has been described by many equations. And the viscoelasticity of various dense suspensions is generally characterized by their viscosity and shear modulus [5, 6]. However, these theories can not describe the systems exactly which have yield stress and exhbit thixotropy, so they can not be applied in this research.

Now there are several experiential flow models (namely fluid's constitutive equations) which can be used to characterize the flow of systems which have yield stress, as shown in the following,

Bingham, $$\tau = \tau_y + K\dot{\gamma} \quad (1)$$

Casson, $$\tau^{1/2} = \tau_y^{1/2} + (K\dot{\gamma})^{1/2} \quad (2)$$

Herschel, $$\tau = \tau_y + K\dot{\gamma}^n \quad (3)$$

Vocadlo, $$\tau = (\tau_y^{1/n} + K\dot{\gamma})^n \quad (4)$$

In Eq. 1-Eq. 4, τ represents shear stress, τ_y represents yield stress, K represents viscosity factor, $\dot{\gamma}$ represents shear ratio, n represents rheological index.

Therefore, experiential models were adopted to study the rheological characteristic of systems in this work.

Through comparing four equations above, we found that Casson model was the best model to describe the disciplinarian of the shear stress-shear rate changes of that three nano-fillers/DGEBA systems such as MMT/DGEBA, SiO_2/DGEBA and MWCNTs/DGEBA systems. Then we adopted this model to construct flow models of systems respectively, and obtained shear viscosity models of systems according to these flow models.

3.2.1 The MMT/DGEBA system

Casson model was adopted to study the relation between shear stress and shear rate of the MMT/DGEBA system and construct the flow model of the system. The experimental data were minimum variance nonlinear fitted, the fitting results of model parameters such as τ_y and K are shown in Table 1, r in the table represents correlation coefficient, and the value of r is closer to 1, the error between the experimental data and the data calculated by the model is smaller. The experimental data are shown in Fig. 1(a).

Through comparing the changes of parameters value of Casson model at different contents of MMT, it was concluded that yield stress τ_y and viscosity factor K of the system increased along with the content of MMT increasing, as shown in Fig. 4. The scattering points in Fig. 4 represent the experimental data, and solid curves represent minimum variance fitting curves. Fitting equations are shown in Eq. 5 and Eq. 6, and the correlation coefficients are respectively 0.9961 and 0.9990.

$$\tau_y = 0.032 exp(\varphi / 2.47) \quad (5)$$

$$K = 6.50 - 3.01 exp(-\varphi / 7.59) \quad (6)$$

Table 1 Parameters value of Casson Model of the MMT/DGEBA system

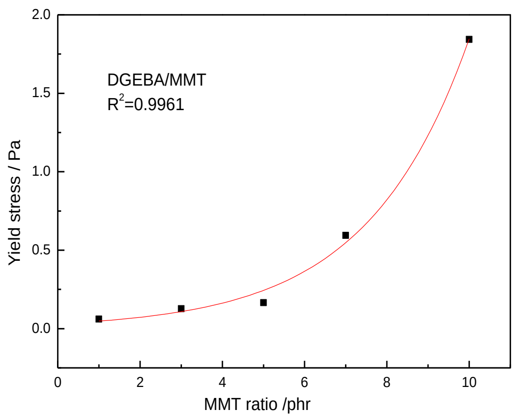
MMT ratio	τ_y	K	r
1	0.06034	3.864	0.9995
3	0.1269	4.442	0.9981
5	0.1655	4.97	0.9989
7	0.5944	5.285	0.9991
10	1.8430	5.69	0.9983

Putting Eq. 5 and Eq. 6 into Eq. 2, we could obtain the flow model of the MMT/DGEBA system at 30℃ when the shear ratio ranged from 0.5 to 365s^{-1} and the content of MMT ranged from 1 to 10phr,

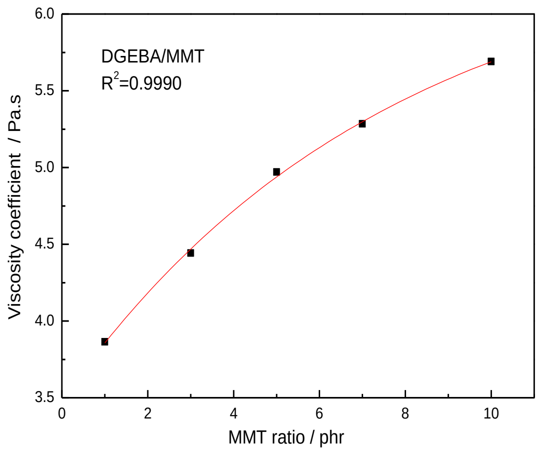
$$\tau^{1/2} = [0.032 exp(\varphi / 2.47)]^{1/2} + \{[6.5 - 3.01 exp(-\varphi / 7.59)]\dot{\gamma}\}^{1/2} \quad (7)$$

We could also obtain the viscosity model of the MMT/DGEBA system,

$$\eta = \frac{\tau}{\dot{\gamma}} = ((0.032 exp(\varphi / 2.47))^{1/2} + ((6.5 - 3.01 exp(-\varphi / 7.59))\dot{\gamma})^{1/2})^2 / \dot{\gamma} \quad (8)$$



(a) $\tau_y - \varphi$



(b) $K - \varphi$

Fig. 4. The $\tau_y - \varphi$ and $K - \varphi$ curves of the MMT/DGEBA system

3.2.2 The SiO_2/DGEBA system

Similar to the MMT/DGEBA system, Casson flow model was adopted to construct the flow model of the SiO_2/DGEBA system. In Table 2, parameters of Casson flow model of the SiO_2/DGEBA system such as τ_y, K and correlation coefficient r at different contents of SiO_2 are shown.

Table 2 Parameters value of Casson Model of the SiO_2/DGEBA system

SiO_2 ratio	τ_y	K	r
1	0.05472	4.548	0.9994
3	0.8702	5.713	0.9966
5	21.62	6.289	0.9942
7	59.78	6.542	0.9784
10	201.7	6.539	0.9258

Through comparing the changes of parameters value of Casson model at different contents of SiO_2, it was concluded that yield stress τ_y and viscosity factor K of the system increased along with the content of MMT increasing, as shown in Fig. 5. Fitting equations are shown in Eq. 9 and Eq. 10, and the correlation coefficients are respectively 0.9958 and 0.9968.

$$\tau_y = 2.565 exp(\varphi / 2.289) \quad (9)$$

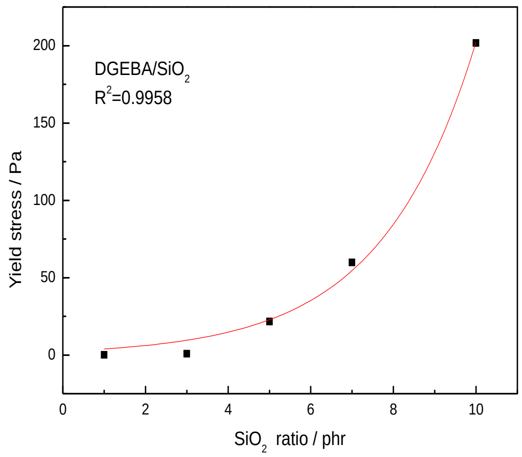
$$K = 6.64 - 3.23 exp(-\varphi / 2.31) \quad (10)$$

Putting Eq. 9 and Eq. 10 into Eq. 2, we could obtain the flow model of the SiO_2/DGEBA system at 30℃ when the shear ratio ranged from 0.5 to 365s^{-1} and the content of SiO_2 ranged from 1 to 10phr,

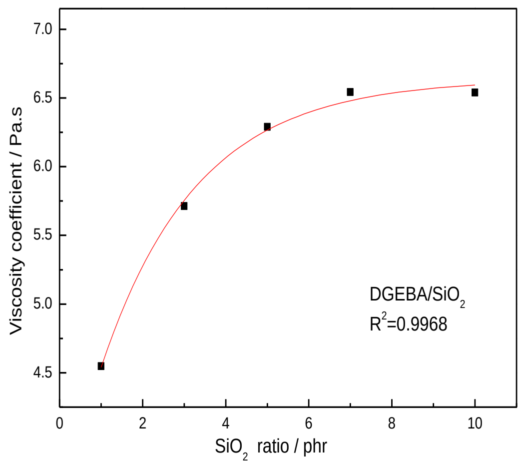
$$\tau^{1/2} = [2.565\exp(\varphi/2.289)]^{1/2} + \{[6.64 - 3.23\exp(-\varphi/2.31)]\dot{\gamma}\}^{1/2} \quad (11)$$

We could also obtain the viscosity model of the SiO_2/DGEBA system,

$$\eta = \frac{\tau}{\dot{\gamma}} = ((2.565\exp(\varphi/2.289))^{1/2} + ((6.64 - 3.23\exp(-\varphi/2.31))\dot{\gamma})^{1/2})^2/\dot{\gamma} \quad (12)$$



(a) $\tau_y - \varphi$



(b) $K - \varphi$

Fig. 5. The $\tau_y - \varphi$ and $K - \varphi$ curves of the SiO_2/DGEBA system

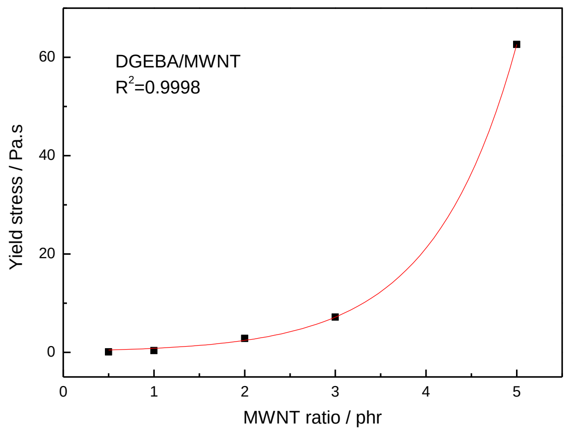
3.2.3 The MWCNTs/DGEBA system

In the same way, Casson flow model was adopted to construct the flow model of the MWCNTs/DGEBA system. In Table 3, parameters of Casson flow model of the MWCNTs/DGEBA system such as τ_y, K and correlation coefficient r at different contents of MWCNTs are shown.

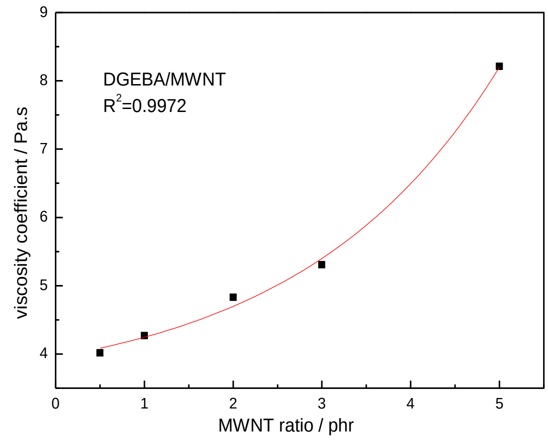
Table 3 Parameters value of Casson Model of the MWCNTs/DGEBA system

MWNTs ratio	τ_y	K	r
0.5	0.08393	4.015	0.9992
1	0.3712	4.269	0.9994
2	2.828	4.829	0.9984
3	7.148	5.307	0.9989
5	62.62	8.211	0.9961

Through comparing the changes of parameters value of Casson Model at the different contents of MWCNTs, it was concluded that yield stress τ_y and viscosity factor K of the system increased along with the content of MWCNTs increasing, as shown in Fig. 6. Fitting equations are shown in Eq. 13 and Eq. 14, and the correlation coefficients are respectively 0.9998 and 0.9972.



(a) $\tau_y - \varphi$



(b) $K - \varphi$

Fig. 6. The $\tau_y - \varphi$ and $K - \varphi$ curves of the MWCNTs/DGEBA system

$$\tau_y = 0.279\exp(\varphi / 0.9237) \qquad (13)$$

$$K = 3.44 - 0.518\exp(\varphi / 2.254) \qquad (14)$$

Putting Eq. 13 and Eq. 14 into Eq. 2, we could obtain the flow model of the MWCNTs/DGEBA system at 30℃ when the shear ratio ranged from 0.5 to 365s^{-1} and the content of MWCNTs ranged from 1 to 10phr,

$$\tau^{1/2} = [0.279\exp(\varphi/0.9237)]^{1/2} + \{[3.44 + 0.518\exp(\varphi/2.254)]\dot{\gamma}\}^{1/2} \qquad (15)$$

We could also obtain the viscosity model of the MWCNTs/DGEBA system,

$$\eta = \frac{\tau}{\dot{\gamma}} = ((0.279\exp(\varphi/0.9237))^{1/2} + ((3.44 + 0.518\exp(\varphi/2.254))\dot{\gamma})^{1/2})^2 / \dot{\gamma} \qquad (16)$$

3.3 Comparison and analysis of parameters value of flow models

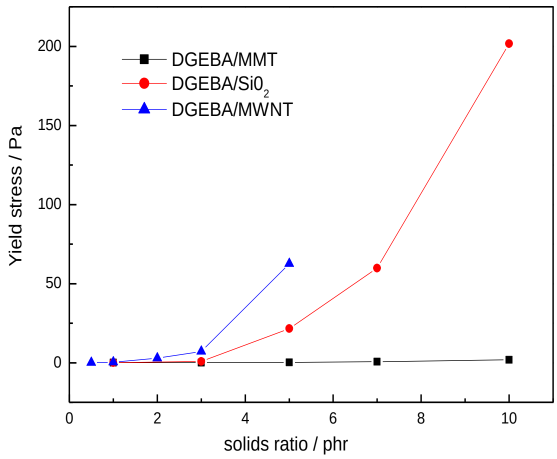
From the results above, it was concluded that Casson model could describe the flow characteristic (namely the shear stress-shear rate relation) of nano-particles/DGEBA systems very well. Therefore, flow models and viscosity models based on Casson model was used to analyze the influence of the content of nano-fillers on parameters of the models. Detailed parameters are shown in Table 4, we can see that both yield stress τ_y and viscosity factor K of the systems trend to increase when the content of nano-fillers increases, which is shown in Fig. 7.

Table 4 Parameters value of Casson Model of nano-fillers/DGEBA systems

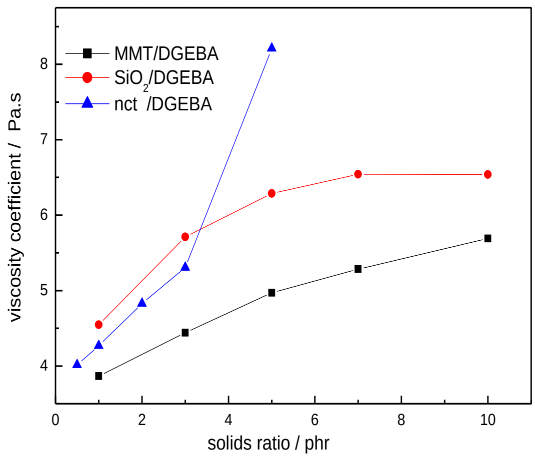
Ratio/phr	τ_y			K		
	MMT	SiO_2	MWCNTs	MMT	SiO_2	MWCNTs
0.5	---	---	0.08393	---	---	4.015
1	0.06034	0.05472	0.3712	3.864	4.548	4.269
2	---	---	2.828	---	---	4.829
3	0.1269	0.8702	7.148	4.442	5.713	5.307
5	0.1655	21.62	62.62	4.97	6.289	8.211
7	0.5944	59.78	---	5.285	6.542	--
10	1.8430	201.7	---	5.69	6.539	---

The existence of yield stress indicated that temporary three-dimensional network structure was formed in the nano-fillers/DGEBA systems. If the stress value of systems is lower than that of yield stress τ_y, this network can resist the shear stress, that is mean the systems are solid and the relation between stress and deformation is linear. In the other hand, if the stress value is higher than that of yield stress, the network will break up and the systems will begin to flow. Therefore, the higher is yield stress of the systems, the steadier is the three-dimensional network structure.

By analyzing Fig. 7, we found that yield stress of different nano-fillers/DGEBA systems was different at the same content of nano-fillers, which indicated that the interaction among nano-particles was different along with the different kinds of nano-particles. It was also concluded that yield stress of the systems increased at the same kind and the increasing content of nano-fillers, which indicated that the interaction among nano-particles increased and the stability of the network structure improved when the content of nano-fillers increased.



(a) $\tau_y - \varphi$



(b) $K - \varphi$

Fig. 7. The $\tau_y - \varphi$ and $K - \varphi$ curves of nano-fillers/DGEBA systems (Casson Model)

The relation of τ - $\dot{\gamma}$ was described by flow models, and if the two sides of the flow equation were both divided by $\dot{\gamma}$, viscosity models of the systems related to shear rate could be characterized. For Casson model, viscosity factor K represents shear viscosity of the systems when $\dot{\gamma}$ trends to be positive infinity, so K can be used to characterize the interaction among components of nano-fillers/DGEBA systems at high shear rate, and the value of K increases when the content of nano-fillers increases.

4 Conclusions

The nano-fillers/DGEBA systems exhibit thixotropy at different degree and appear yield stress when the content of nano-fillers is not very high (≤10phr), moreover, the relation between shear stress and shear rate is nonlinear. Therefore, DGEBA systems exhibit the shear-thinning characteristic with the addition of nano-fillers, and their constitutive equations can be expressed by Casson model. According to the flow models and viscosity models based on Casson Model, yield stress of different nano-fillers/DGEBA systems is different at the same content of nano-fillers, which indicates that the interaction among nano-particles is different along with the different kinds of nano-particles. In addition, yield stress of the same systems increases at the increasing content of nano-fillers, which indicates that the interaction among nano-particles augments and the stability of the formed network structure improves when the content of nano-fillers augments.

5 References

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