

ABS-카본블랙 복합재의 유성학적 성질

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Rheological Properties of ABS-Carbon Black Composite

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요약 : 본 연구에서 ABS (acrylonitrile-butadiene-styrene)에 전도성 카본블랙을 충전시킨 전도성고분자복합재료의 여러가지 제 성질들을 항복응력을 중심으로 고찰하였다. ABS-카본블랙 복합재의 겔보기 점성도는 카본블랙의 양이 증가함에 따라 증가하였으며, 온도가 상승함에 따라 감소하였다. 또한 power law 지수는 온도가 증가함에 따라 감소하였다. 그리고, 복합재의 겔보기 점성도는 카본블랙의 구조에 큰 영향을 받으며, 구조가 발달되어 있을수록 높은 값을 나타내고 있었다. 또한 일정한 shear rate에서의 활성화에너지는 shear rate가 증가함에 따라 감소하였다. Die swell ratio는 사용되는 용액의 종류에 관계가 없었으며, 카본블랙의 양이 증가함에 따라 감소하였다. Casson의 식에 의한 항복응력은 최소자승법으로 계산하였으며, 온도가 상승함에 따라 감소하였고, 카본블랙의 함량이 증가함에 따라 증가하였다. 특히 항복응력은 사용된 rheometer의 capillary에 무관하며, 오직 plunger의 cross head speed에만 영향을 받았으며, 0.1-0.15cm/min의 범위에서 항복응력이 나타남을 알았다.

Abstract : The properties of ABS(Acrylonitrile-Butadiene-Styrene) and conductive carbon black composite have been studied based on yield stress. The apparent viscosity of ABS-carbon black composite was found to be increased with increasing carbon black content and with decreasing temperature. The Power Law index was decreased with increasing temperature. The apparent viscosity of the composite was affected by the structure of carbon black. The value of apparent viscosity has been found to be higher in the developed filler structure. The activation energy at the constant shear rate was found to be decreased with increasing shear rate. The die swell ratio was not affected by the various medium, however, the die swell ratio was decreased with increasing carbon black content of the composite. The yield stress which was calculated by Casson's equation was decreased with increasing temperature. The yield stress was decreased with decreasing carbon black content of the composite. The yield stress of the composite was observed when the cross head speed was 0.1 to 0.15 cm/min, however, the yield stress was not affected by changing the capillary of the rheometer.

INTRODUCTION

It is well known that the mechanical properties of polymer can be varied by the addition of various fillers.¹ Many polymeric composite materials which are filled with carbon black were prepared and suggested different mechanical properties.²

Conductive polymers have various excellent properties such as lightening the weight, thermal and electric insulations, corrosion resistancy, and good absorption.

ABS is one of the typical engineering plastics which has good tensile strength and chemical durability. ABS-conductive carbon black composites are used in discharging static electricity, heat conduction, EMI (Electromagnetic Interference), electrical heating, converting the mechanical signals to electrical signals, and electroplating plastics.^{3,4}

The rheological properties of polymer and filler systems have been studied for a long time. It is generally accepted that the problems are occurred by mutual interactions between polymer and filler when they are mixed together. Watson⁵ reported that the viscosity was increased with decreasing particle size of carbon black in the rubber and carbon black system. Smaller particles exhibit the similar behavior discussed above due to the greater surface areas. The viscosity was affected by the structure of carbon black. The structure of carbon black is a coagulated state of fine carbon black particles.⁶ In the mixture of carbon black and rubber, viscosity, η , is known to increase with increasing degree of carbon black structure.

In this study, the shear stress and die swell ratio as a function of shear rate were investigated, and the apparent viscosity, yield stress and activation energy with various carbon black contents were also calculated. The effects of filler on the rheological properties of the ABS and carbon black system were also determined in order to investigate the viscosity of the ABS and carbon black system.

EXPERIMENTS

Materials

ABS (HF-350, Lucky Co. Ltd.) and carbon black (Ketjenblack EC furnace black and Vulcan XC-72, Cabot Corp.) were used in this study. Carbon black and ABS were sieved in order to get reasonable particle sizes. (ASTM No. 30 and No. 12, respectively) ABS was dried at 60°C for 30 minutes and carbon black was dried at 150°C for 2 hrs. The characteristics of the samples used in this study are given in Table 1.

In order to determine the effect of mixing time, the weighed samples were mixed for 4, 8, 12, 24 and 48 hrs. Micron photosizer (SKA-5000, Japan) was employed to measure the particle sizes of carbon black. Ethanol as medium and supersonic dispersor were used in this study.

Measurement of Rheological Properties

The rheological properties were measured by using Instron Capillary Rheometer (Model 3211, USA). The ratios of L/D of capillaries used here were 20, 33.3 and 40, and the experimental conditions are given in Table 2.

The moisture of samples was completely removed to prevent bubble formations during the measu-

Table 1. Composition of Sample, in Parts by Weight

Sample Number	1	2	3	4	5	6	7	8	9
ABS	100	100	100	100	100	100	100	100	100
EC Carbon Black	—	3	5	10	20	—	—	—	—
Vulcan XC-72	—	—	—	—	—	3	5	10	20
Weight Fraction (%)	—	2.91	4.76	9.09	16.67	2.91	4.76	9.09	16.67
Volume Fraction (%)	—	1.70	2.81	5.46	10.36	1.70	2.81	5.46	10.36
Density	1.040	1.062	1.076	1.109	1.167	1.062	1.076	1.109	1.167

Rheological Properties of ABS-Carbon Black Composite

Table 2. Experimental Condition

Sample Number	Temperature (°C)	Capillary Size(L / D)
1	180, 190, 200, 210, 220, 230	20, 33.3, 40
2	180, 190, 200, 210, 220	"
3	"	"
4	"	"
5	"	"
6	180, 190, 200, 210	33.3
7	"	"
8	"	"
9	"	"

rements. The apparent viscosity was calculated by the following equations,⁷

$$\dot{\gamma} = (2D_p^2 / 15D^3) V_C$$

$$\tau = (D / \pi D_p^2 L) F$$

$$\eta = \tau / \dot{\gamma}$$

where, η is the apparent viscosity, D is the diameter of capillary, D_p is the diameter of plunger, F is the force on the plunger, L is the length of capillary, V_C is the cross head speed, $\dot{\gamma}$ is the shear rate, and τ is the shear stress.

Die swell ratio was measured under the frozen states in water bath, silicon oil bath, and air.

To measure the die swell, round filament was collected in length of about 5 cm. The round filament diameters were measured with a micrometer at points around the circumference about 2.5 cm from the leading end of the sample.

RESULTS AND DISCUSSION

Mixing time is important in filled system.⁸ According to White and Crowder,⁹ the apparent viscosity was increased with decreasing particle size. The comparison between particle size and mixing time is shown in Table 3. From Table 3, it can be seen that the particle size of carbon black was almost independent of mixing time when carbon black was mixed for more than 12 hours. From Fig. 1, the viscosity of the composite was also independent with mixing time of 12,

Table 3. Average Particle Size by 50 Weight Percent (Ketjenblack EC)

Mixing Time(hr)	0	4	8	12	24	48
Particle Size(micron)	0.30	0.32	0.34	0.38	0.41	0.39

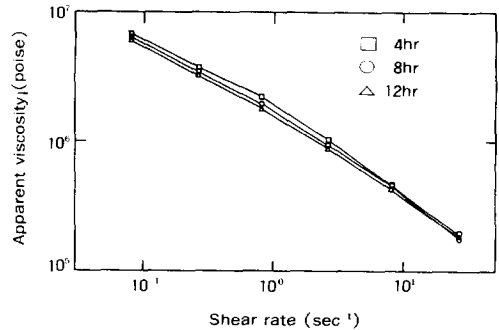


Fig. 1. Apparent viscosity as a function of shear rate for various mixing time (sample 2, capillary diameter : 0.03 inch and length : 1 inch).

24 and 48 hrs. Therefore, all samples were mixed for 12 hours in ball mill.

Apparent viscosity is known to be increased with increasing filler content and decreased with increasing temperature.¹ As well known, the fluid obeys Rabinowitsch equation which is based on Power Law. The Rabinowitsch equation was modified by Metzner¹⁰ and the modified equation is given by

$$n = \frac{d \log(R \Delta P / 2L)}{d \log(4Q / \pi R^3)}$$

$$\log(R \Delta P / 2L) = n \log(4Q / \pi R^3) + \log K$$

$$\dot{\gamma}_{true} = \left(\frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3}$$

where, K is the constant, n is the Power Law index, R is the radius of capillary, ΔP is the pressure drop in capillary, $\dot{\gamma}_{true}$ is the true wall shear rate, and Q is the flow rate.

The surface analysis mapping which shows the relationship between temperature and carbon black content is shown in Fig. 2. The value of n was decreased with increasing carbon black content and with decreasing temperature.

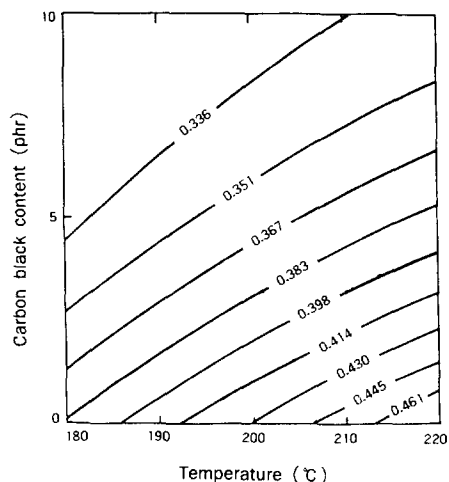


Fig. 2. Effect of temperature and carbon black (ketjenblack EC) on power law index (capillary diameter : 0.05 inch and length : 1 inch).

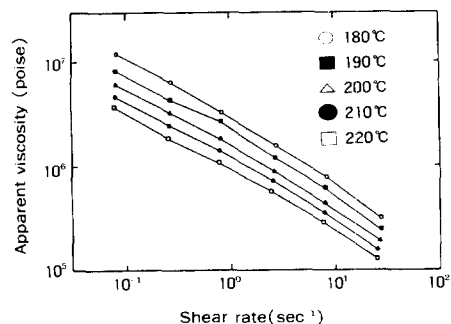


Fig. 3. Apparent viscosity as a function of shear rate for various temperature (sample 2, capillary diameter : 0.05 inch and length : 2 inch).

The relationship between apparent viscosity and shear rate at different temperatures is shown in Fig. 3. As temperature increases the value of apparent viscosity decreases. The effects of temperature on the relationships between apparent viscosity and shear rate for two different carbon blacks which are Vulcan XC-72 and Ketjenblack EC are shown in Fig. 4. Under the same conditions, the apparent viscosity with the Ketjenblack EC is greater than with the Vulcan XC-72.

On the other hand, the structure of Ketjenblack

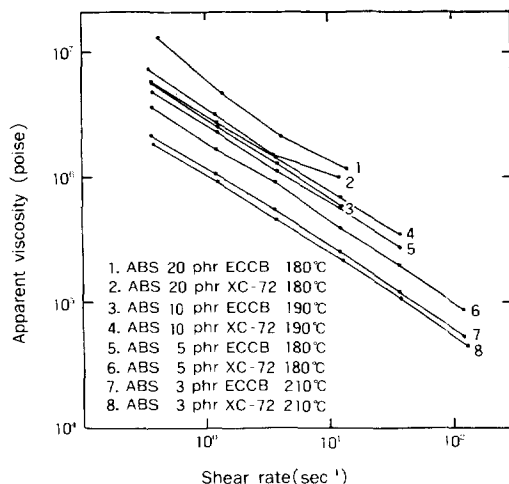


Fig. 4. Apparent viscosity as a function of shear rate.

EC is more developed than the structure of Vulcan XC-72. Generally, carbon black having developed structure is called as conductive carbon black. The particle size of carbon black and the values of DBP(Dibutyl Phthalate) and BET(Brunauer-Emmett-Teller) are important to define structure. The reason that the structure of Ketjenblack EC is more developed than one of Vulcan XC-72 is believed as Ketjenblack EC has larger value of BET and DBP than the structure of Vulcan XC-72, White and Crowder¹ reported the same results.

Activation Energy

There are two kinds of caillary rheometers : one is imposed rate viscometer which has constant shear rate and the other is imposed pressure viscometer which has constant shear stress.¹¹ Activation energy obtained using Instron Capillary Rheometer under constant cross head speed can be expressed by Arrhenius equation.

$$\eta = A \exp(E\dot{\gamma} / RT)$$

where, A is the constant, R is the gas constant, T is the absolute temperature, and $E\dot{\gamma}$ is the activation energy under constant shear rate.

The variation of the activation energy on carbon black content with various shear rates is shown in Fig. 5. As the carbon black content or shear rate increased the activation energy decreased. The carbon black content having 3 phr or 5 phr shows low activation energy under low shear rate. The activation energy of ABS without filler decreased with increasing shear rate for all the sizes of capillaries. Philippoff and Gaskin¹² also observed the similar results for polyethylene which did not contain filler.

Die swell ratio as a function of temperature with various carbon black contents is shown in Fig. 6. Die swell ratio was decreased when the temperature and carbon black content were increased.

Yield Stress

When filler particles float in the polymer solution or melt, the viscoelasticities of non-Newtonian behavior are observed.¹¹ The melt flow with filler and polymer system exhibits yield point. This behavior is called as "critical value of shear stress"

or "yield value of yield stress".

A non-linear viscoelasticity is observed within a few percent of strain while pure polymer or melt exhibits a non-linear viscoelasticity under large strain.¹³ A non-Newtonian behavior is observed above yield stress. Therefore, the transition phenomena such as thixotropy or rheopexy are predominant in a filled system. It is due to the aggregations of filled particles during flow.

In the case of pure polystyrene, the slope of (shear stress)^{1/2} vs. (shear strain)^{1/2} curve is 1.

Yield stress is the minimum stress at which fillers come to flow and can be obtained from the intercept point between the shear stress and

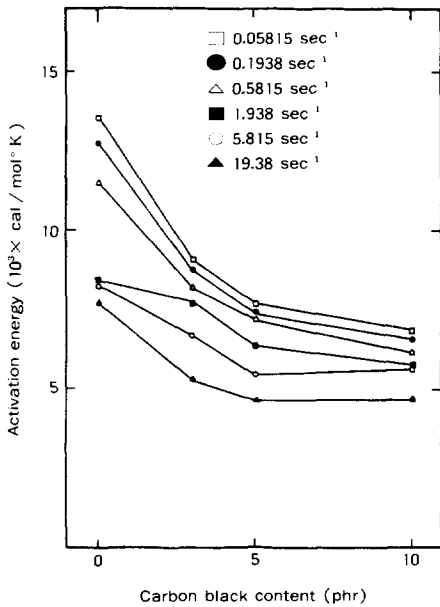


Fig. 5. Activation energy as a function of carbon black (Ketjenblack EC) content for various shear rate (Capillary diameter : 0.05 inch and length : 1 inch).

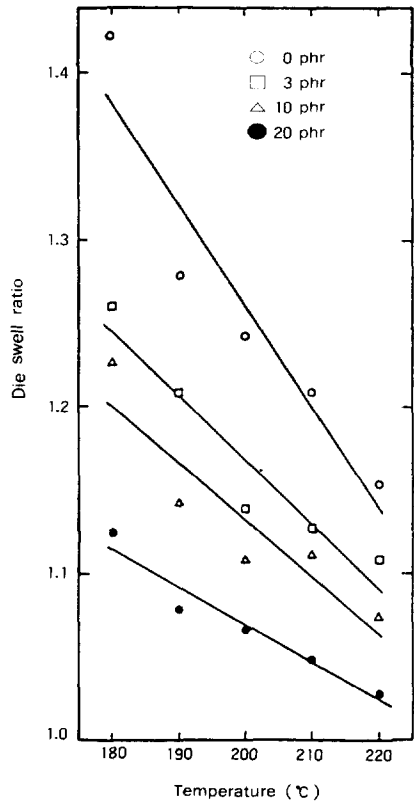


Fig. 6. Die swell ratio as a function of temperature for various carbon black(Ketjenblack EC) content at air frozen (Capillary diameter : 0.03 inch and length : 1 inch, shear rate 8.921 sec⁻¹).

the shear rate curve. More accurate value can be obtained from the linear relationship between shear stress and shear rate. The study about yield stress was conducted by Casson,^{14,15} and it is expressed by the following equation,

$$\frac{1}{\tau^2} = K_0 + K_1 \dot{\gamma}^{\frac{1}{2}}$$

where, K_0 and K_1 are the constants. The yield stress obtained using the above equation is in good agreement with the experimental results when solid particles are floated.¹⁴

Onogi et al.¹⁶ considered the value of K_1 in Casson's equation as a function of shear rate. The equation can be written by

$$\tau^{\frac{1}{2}} = K_0 + K_1 (\eta_a \dot{\gamma} / \eta_0)^{\frac{1}{2}}$$

where, η_0 and η_a are the zero shear viscosity and the apparent viscosity, respectively. The yield stress is determined by the square of K_0 in Casson's and Onogi's equations.

Under the constant shear stress, zero shear viscosity can be obtained by extrapolating the results which are observed from the relationship between shear stress and apparent viscosity. Apparent viscosity can not be obtained using capillary rheometer under the constant shear stress. Therefore, yield stress was calculated using Casson's equation.

The relationship between yield stress and temperature is shown in Fig. 7. The yield stress

based on Casson's equation was calculated by using least square method. The yield stress is decreased with decreasing carbon black content or increasing temperature. The similar behavior was observed from the experiment of the apparent viscosity.

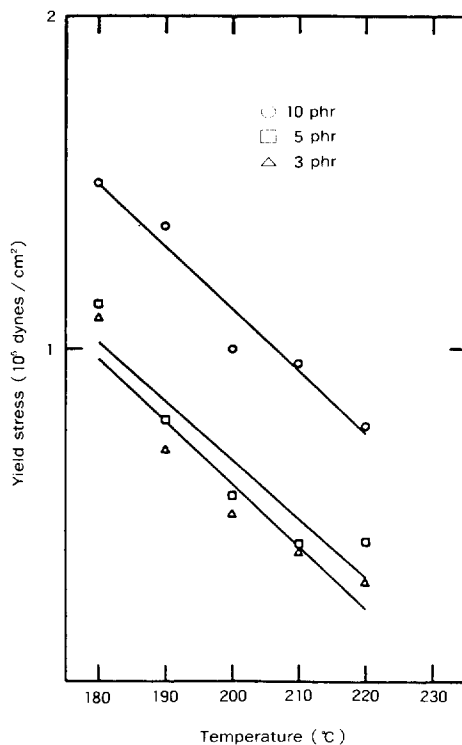


Fig. 7. Yield stress as a function of temperature for various carbon black(ketjenblack EC) content (Capillary diameter : 0.06 inch and length : 2 inch).

Table 4. Shear Rate and Cross Head Speed having Yield Stress

Carbon Black	Capillary Diameter (inch)	Capillary Length (inch)	Shear Rate ^a (μcm^{-1})	Cross Head Speed (cm / min)
Ketjenblack EC	0.03	1	0.55 - 0.62	0.1233 - 0.1390
"	0.06	2	0.068 - 0.077	0.1211 - 0.1372
"	0.05	2	0.11 - 0.14	0.1135 - 0.1445
"	0.05	1	0.11 - 0.14	0.1135 - 0.1445
Vulcan XC-72	0.03	1	0.55 - 0.62	0.1233 - 0.1390

a : Shear rate having yield stress.

The value of yield stress was obtained from the relationship between (shear stress) $^{\frac{1}{2}}$ and (shear rate) $^{\frac{1}{2}}$.¹⁷ The yield stress which was estimated by Casson's equation was used to calculate shear rate by using Metzner's expression. The shear rate which was calculated by Metzner's expression using both yield stress and Power Law index is shown in Table 4.

The shear rate was affected by the capillary diameter but the shear rate was not affected by the capillary length or the value L/D from Table 4. However, the shear rate was not affected by the carbon black type. By using Instron Capillary Rheometer, the yield stress in terms of cross head speed in the range of 0.1-0.15 cm/min was calculated by the Casson's equation. In this study, it was found that (the yield stress) was not affected by the capillary diameter but the yield stress was affected by the cross head speed of plunger from 0.1 to 0.15 cm/min.

CONCLUSIONS

The rheological properties of ABS-carbon black melts were studied using Capillary Rheometer. The apparent viscosity of ABS-carbon black melts was found to be increased with increasing the amount of carbon black, and decreased with increasing temperature. The apparent viscosity was increased by the structure factor when the structure of carbon black was developed. The activation energy under the constant shear rate was decreased with increasing shear rate. The die swell ratio was independent of medium used when the sample was frozen, but it was decreased with increasing the content of carbon black. The yield stress was found to be decreased with increasing temperature or with decreasing the amount of carbon black. Particularly, the cross head speed of plunger influenced to the yield stress which was found to be independent of capillary size. The yield stress was observed when the cross head speed was 0.1 cm/min to 0.15 cm/min.

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