Thermal Rheological Fluid Properties of Particle Dispersion Systems using Side Chain Crystalline Block Copolymer III.

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We recently developed a new dispersant which can decrease the viscosity of concentrated polyethylene (PE) particle dispersions significantly. This dispersant is a block copolymer constructed with side chain crystalline monomers and solvent compatible monomers (Side Chain Crystalline Block Copolymer: SCCBC). Also the viscosity of this dispersion shows reversible temperature dependence that the viscosity increases with increasing temperature up to almost the original value of the dispersion without the dispersant. This phenomenon is named as “Thermal Rheology” and the fluid is named as “Thermal Rheological (TR) Fluid”. In the previous report, we found this TR Fluid effect depends on the randomness of the copolymer and solvent species qualitatively.

In this investigation we researched about copolymer molecular composition and weight dependence on the TR Fluid effects. We also researched about deformation mode dependence. From this research, the TR Fluid effects strongly depend on the molecular weight, especially on the molecular weight of side chain crystalline composition. Also the TR Fluid effects are significant in low shear rate region and dynamic deformation mode.

Key Words: Thermal rheology / Thermal rheological fluid / Side chain crystalline block co-polymer /
Living radical polymerization / Concentrated particle dispersion system

1. INTRODUCTION

Polymeric particle dispersions are used for paint, cosmetics, and various oils for engineering to modify viscosity and surface properties. In these usages, however, when we increase the particle content, the viscosity increases rapidly and become uncontrollable. So we use the dispersions only in a narrow content range in many cases. And when we want to use high concentrated dispersion, we usually use a dispersant which can control the viscosity. In the case of polyethylene (PE) particle, however, the crystallinity of the particle is so high and the particle does not have any polar functional groups. There is few good dispersant which has an ability to interact with PE particle and can control the viscosity of the dispersion.

Recently, we found a block copolymer constructed with side chain crystalline monomers and solvent compatible monomers (Side Chain Crystalline Block Copolymer: SCCBC), which can be used as a good dispersant for the concentrated PE particle dispersion. In the case of the concentrated small high density PE particle dispersion system (diameter is 7.4 μm), that 40 wt% of PE particle is dispersed in acetic acid n-butyl ester, the viscosity has decreased from 1340 mPa•s to 6.2 mPa•s (about 0.5 % of the original value).1) Table I shows viscosity changes of various polymeric particle dispersions after addition of the SCCBC. From this table, the ratio of the change mainly depends on the crystallinity of particles and chemical structure of crystals.

In the previous paper, we showed that this dispersant mechanism can be extended to various kinds of particle dispersion systems.2)

The schematic mechanism of this dispersant is shown in Fig. 1. The long side chain (n≥10: n means the number of carbons in a side chain) has an ability to crystallize by

Fig. 1. Schematic assumption of adhesion mechanism of SCCBC on the PE particle.
themselves according to their interaction. For the side chain crystalline component of the block copolymer, stearyl acrylate (STA) monomer, which has a long side chain, was used. The chemical structure of the long side chain component is composed of alkane units (-CH₂-) and therefore we can assume that this long side chains have an ability to construct a PE like crystal structure. Then this long side chain can be adsorbed on the crystalline surface region of PE particle.

This phenomenon has been suggested by Yamamoto with using computer simulation. Actually, from the fact that the viscosity of the PE particle dispersion decreased to about 0.5 % of the original viscosity with use of this block copolymer, the above concept is acceptable. From this concept, by changing the structure of long side chain, we can make various block copolymer that can interact other crystalline and/or amorphous particles. From Table I, we can find that the decreasing ratio of viscosity also decreases with decreasing the crystallinity of PE particle. In the case of Polyamide12 (PA12), it is surprising that viscosity decreased to about 87.1 % of the original viscosity. The reason of this phenomenon is probably that PA12 has long alkane (-CH₂-) sequence and the structure of the crystal of this sequence is similar to that of PE crystal structure. In the case of Polypropylene (PP) particle, viscosity does not change. These results showed that the adhesion force comes from the structural and conformational similarity of involved chemical units between crystalline polymeric particle and SCCBC side chain.

Furthermore, the interaction mechanism we found in this time is attributed to molecular arrangement of crystal. We can think that side chains of the SCCBC construct a PE crystal-like quasi-crystal structure on the surface of the particle. When temperature increases up to the melting point of this quasi-crystal, the SCCBC separates from the surface of the particle. At that time, particles lost dispersant and the viscosity increases largely. When temperature decreases under the crystalline (melting) point of the quasi-crystal, the SCCBC attach on the particle surface, construct the arrangement, and can act as the dispersant again. So this function of SCCBC comes from the temperature reversible phenomenon. In the result of the previous report, the viscosity of the dispersion increased to 901 mPa·s at 60 °C. When the temperature returned to 25 °C, the viscosity reversibly returned to 6.2 mPa·s. The mechanism and appearances are shown in Fig. 2. The same phenomena were found for other various dispersion systems.

This reversible phenomenon is named “Thermal Rheology (TR)”, and the dispersion we used in these investigations and other fluids that will show this phenomena are collectively referred to as “Thermal Rheological (TR) Fluid”.

“Electro Rheological (ER) Fluid” and “Magneto Rheological (MR) Fluid” are known that their viscosity and viscoelastic properties can be controlled by the external stimulation. When compared to those fluids, however, this “TR Fluid” is excellent at those following properties.

1. There is no direction of the external stimulation.
2. There is no need to provide a special electrical circuit.
3. There is no need to set a gap clearance.
4. There is no need to use special particle or solvent.
5. We can use TR Fluid in the circumstance where we can not use electric or magnetic devices such as in the hospital or airplane.
6. In the especially case, TR Fluid can control its viscosity by self-considering the environment condition.

From these advantages, TR Fluid is a new intelligent material, and can be used as a dumper fluid, actuator, intelligent paint, and in other various areas.

The properties of TR Fluid strongly depend on various

| Table I. The viscosity changes of various dispersed particle case. The dispersant is SENSPER 1266. Numbers in brackets in cases of PE show the densities of the particles. |
|---|---|---|---|---|
| Particle | Polymer | Content (wt%) | Viscosity (mPa·s) | Changed ratio(%) |
| | Original | Resulted | |
| Ceridust 3620 | HDPE (0.96~0.98) | 40 | 1360 | 6.2 | 99.5 |
| MIPELON PM200 | HDPE (0.94) | 50 | 830 | 15 | 98.2 |
| ME 0520 | LDPE (0.93~0.94) | 40 | 311 | 15 | 95.2 |
| GPA-500 | Polyamide12 | 52 | 734 | 95 | 87.1 |
| Propylmat 31 | PP | 45 | 536 | 554 | -3.4 |

1) Clariant International Ltd, 2) Mitsui Chemical, 3) INC. DEUREX Micro-Technologies GmbHAdress, 4) Ganz Chemical Co., Ltd., 5) Micro Powder
factors listed in Table II. In this study, we investigated mainly about the influence of the block copolymer structure.

2. EXPERIMENT

2.1 Synthesis of Block Copolymer

The block copolymers we used in this research are listed in Table III. “SENSPER” is a code name of these copolymers of Gifu Shellac Mfg. For the side chain crystalline component, we used stearyl acrylate (STA) monomer. For the solvent compatible component, we used n-butyl acrylate (nBA) monomer. The polymerization method was living radical polymerization. The initiator was 3,7-Dioxa-4-aza-6-phosphanonoic acid, 4,5- bis(1,1-dimethylethyl)-6-ethoxy-2,2-dimethyl-6-oxide, which is sold by Arkema Inc. named as “Blocbuilder®”. The polymerization temperature was controlled at 118 °C and the atmosphere was nitrogen. SENSPER N1156 was made by Gifu Shellac Mgd. Others were polymerized in FUKUOKA University. Molecular weights were measured by gel permeation chromatography (GPC). These molecular weights are standard polystyrene equivalent molecular weight.

2.2 Preparation of Dispersion

For the PE particle we used was Ceridust®3620 (Clariant International Ltd). The number averaged diameter of this particle was 7.4 μm. For the dispersion solvent, we used acetic acid n-butyl ester. The content of the particle was 40 wt%. The concentration of the block copolymer was 1 wt% of the dispersion particle.

Table II. The examples of factors influencing to the TR Fluid effects.

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Monomer type</th>
<th>Structure</th>
<th>Molecular weight</th>
<th>Stress loading condition</th>
<th>Shear rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed particle</td>
<td>Crystallinity</td>
<td>Solubility</td>
<td>Diameter and distribution</td>
<td>Shear rate</td>
<td></td>
</tr>
<tr>
<td>Dispersed solvent</td>
<td>Crystal structure</td>
<td>Viscosity</td>
<td>Frequency</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table III. The molecular weights of each component and weight ratio of various SCCBC used in this research.

<table>
<thead>
<tr>
<th>Code name</th>
<th>Molecular weight of side chain crystalline block (STA)</th>
<th>Molecular weight of solvent compatible block (nBA)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SENSPER N1156</td>
<td>~5000</td>
<td>~6000</td>
<td>1.3</td>
</tr>
<tr>
<td>SENSPER N0633</td>
<td>~3000</td>
<td>~3000</td>
<td>1.7</td>
</tr>
<tr>
<td>SENSPER N0321</td>
<td>~1600</td>
<td>~1000</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.3 Measurement of Viscosity and Viscoelastic Properties

For the measurement of viscosity and viscoelastic properties of the dispersion, Rheogel-G2000W (UBM Co., Kyoto, Japan) was used. The Cone-Plate type fixture with solvent trap was used. The measured temperature was 35, 45, and 55 °C (sometimes we also measured at 65 °C).

The measured viscosities were steady state viscosity. And all the viscoelastic measurement points in this article, to confirm the linear response, we have controlled the strain ratio from 0.5 % to 10 %.

3. RESULTS AND DISCUSSION

Shear rate and temperature dependence of steady flow viscosity (η) of SENSPER N1156 dispersion system is shown in Fig. 3. At 35 °C, the flow curve shows almost Newtonian in low shear rate region and η shows shear thinning behavior with increasing the shear rate. At 45 °C and 55 °C, the viscosities increase about two orders larger than the viscosity at 35 °C. Above these temperatures, the SCCBC separates from the surface of the particle. The particles lost the dispersant, and the viscosity increases largely.

The shear rate dependence of these temperatures on the viscosity is also very complex. Once viscosities decrease slightly, and then they increase to approximately twice values of the minimum value. After that, they suddenly show large shear thinning behaviors and decrease more than two orders. We think more detailed investigations are necessary.

Fig. 4 shows frequency dependence of storage modulus (G') and loss modulus (G'') of SENSPER N1156 dispersion system. At 35 °C, the torque was very low and we could not
measure these values. From this figure, at 45 °C and 55 °C, the $G'$ and $G''$ slightly depend on the frequency and the slope angles are about 1/2 in each case. These results show that the inner structures of the dispersion systems of these temperatures are gel like network structure. When temperature was raised to 65 °C, $G'$ and $G''$ discontinuously increased about four order and lose the frequency dependence. In the concentrated polymer particle dispersion, when the dispersed particle lost the solvent compatibility and increase of the interaction strength between particles, similar phenomenon has been reported by Matsumoto et. al.\textsuperscript{10)

Fig. 5 shows frequency dependence of complex viscosity ($|\eta^*|$) of SENSPER N1156 dispersion system. In the $|\eta^*|$ vs $\omega$ curves at 45 °C and 55 °C, we can observe a slight shoulder region. But not the same as the case of steady flow viscosity, these flow curves depend on the frequency and the $\omega$ dependences of $|\eta^*|$ show those of typical non-Newtonian fluid. In the low frequency region, as indicated by the slope values $|\eta^*|$ vs $\omega$ curves are almost -1. From the results, these systems seem to have yield values.

In Fig. 6, we compared the temperature dependence of $\eta$ at 1 sec$^{-1}$ and $|\eta^*|$ at 1 rad·sec$^{-1}$. From this figure, $\eta$ increased about two orders as temperature increased 35 °C to 45 °C. From 45 °C to 65 °C, the viscosity monotonically increased about one order. The $|\eta^*|$ values at 45 °C and 55 °C are about one order lower than $\eta$ values due to the shear thickening behavior. But the tendency is very similar to the case of $\eta$. $|\eta^*|$ rapidly increases about four orders at 65 °C.

Above 45 °C, almost the quasi-crystal structure melted and the SCCBC removed from the surface of particle. At that time the particles lost dispersant and may construct an aggregation structure and then the system lost fluidity. In the case of dynamic measurement, the deformation is small, and the aggregation structure may not be destroyed. But in the steady flow, the deformation is large, and this aggregation structure thought to be destroyed. This may be the result that the temperature dependence effect is much remarkable in dynamic measurements.

Fig. 7 shows shear rate dependence of $\eta$ of SENSPER N0633 dispersion system. Same as Fig. 3, the flow behaviors are very complex. At 35 °C and 45 °C viscosities decrease slightly in the low shear rate region, and then increase to

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Frequency and temperature dependence of (a) storage modulus ($G'$) and (b) loss modulus of SENSPER N1156.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{Frequency and temperature dependence of SENSPER N1156 complex viscosity.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6}
\caption{Temperature dependence of SENSPER N1156 viscosity at $\gamma = 1$ sec$^{-1}$ and complex viscosity at $\omega = 1$ rad·sec$^{-1}$.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig7}
\caption{Shear rate and temperature dependence of SENSPER N0633 viscosity.}
\end{figure}
approximately twice values of the minimum value. After that, they suddenly show large shear thinning behaviors. With increasing temperature, the viscosity values increased and the data at 65 °C and 75 °C show the existence of yield values. The magnitude of viscosity increased about two orders in low shear rate region and almost one order in the middle shear rate region. In this case, the degree of the viscosity change depends on the shear rate.

Fig. 8 shows frequency dependence of $G'$ and $G''$ of SENSPER N0633 dispersion system. The frequency dependences at 35 °C and 45 °C are almost same and the system showed slightly flow behavior. But the slope angles are smaller than 1/2. This may show the aggregation structure is more rigid compared to the case of N1156. This result also shows that the dispersant effect of N0633 is weaker compared to N1156.

When temperature was raised to 55 °C and 65 °C, same as the case of N1156, $G'$ and $G''$ discontinuously increased about one order and they show weak frequency dependence.

Fig. 9 shows frequency dependence of $|\eta^*|$ of SENSPER N0633 dispersion system. Almost all flow curves show monotonically decreasing frequency dependence (non-Newtonian). Same as the N1156 system, these flow curves seem to have yield values. When compared the results of Fig. 7, the values are about one order larger than the steady flow viscosity. The results show the aggregation structure of dispersion particles does not destroy in the dynamic deformation. On the other hand, the aggregation structures of these systems destroy by steady shear deformation.

In the case of N0633, the effect of viscosity change is much smaller compared to the case of N1156. As the molecular weight of N0633 is about half of N1156 and the numbers of N0633 molecule in the system is about twice, the PE particles are modified more densely. But from the results, we can consider that the chain length of solvent compatible component in this case is not enough to be a good dispersant.

Fig. 10 shows shear rate dependence of $\eta$ of SENSPER N0321 dispersion system. In this case the flow curve behavior at 45 °C is also similar to the results of N1156 and N0633 systems. In the low shear rate region, the viscosities show temperature dependence but the dependence is very small. Even in high shear rate region, the viscosities slightly increased with increasing the temperature.

Fig. 11 shows frequency dependence of $G'$ and $G''$ of SENSPER N0321 dispersion system. From this figure, the system lost frequency dependence gradually with increasing
the temperature. With increasing the temperature, $G'$ and $G''$ increased about half order. The increasing ratio is higher compared to the shear rate dependence. But when compared to the other SENSPER system, the ratio is very small.

Fig. 12 shows frequency dependence of $|\eta^*|$ of SENSPER N0321 dispersion system. Almost all flow curves show shear thinning behavior but the degree of reduction are not so steep compared to the case of N1156 and N0633. But when compared the results of Fig. 10, the complex viscosities show temperature dependence and they increase with temperature increase at all frequencies.

From the results of these experiments, when whole molecular weight was above 10,000 and the molecular weight of the STA component is also above 5,000, the steady flow viscosity of the tested system decreased significantly and we could observe the dispersant effect. When we increased temperature, the viscosity increased about three orders. This phenomenon was remarkable in low shear rate region. This means that the viscosity increasing effect shows shear rate dependence. In the dynamic measurement, both $G'$ and $G''$ increased significantly about four orders with increasing the temperature, and lost frequency dependence. We could consider that in this case particles construct rigid aggregation structure in the system. From these results, the TR Fluid effect is thought to be significant in low shear rate and more significant for the dynamic deformation mode.

When we decreased the whole molecular weight about 6,000, as the composition ratio is almost same, the dispersant effect and the viscosity increasing effect became smaller. This shows that not the component ratio but the molecular weight is more effective for both phenomena.

In the system of molecular weight of 3,000, the phenomena were almost same as the 6,000 system in the dynamic measurement. But in the steady shear measurement, we hardly observed the viscosity increasing effect.

### 4. CONCLUSION

In this study we investigated about the temperature, shear rate, and frequency dependence of viscosity and viscoelastic properties of PE particle dispersions of various SCCBC by steady flow and dynamic measurement.

About the viscosity increasing effects and viscoelastic property changing effects, they depend significantly on the whole molecular weight of SCCBC and side chain crystalline component length. In the previous research, we found that random copolymer showed a slight TR Fluid effect. The results also indicate that we need a certain length of side chain crystalline block component to exhibit enough TR Fluid effect. From this research, we found that molecular weight may be also large factor for TR Fluid effect.

About the dependence of deformation mode, the viscoelastic property changing effects are more significant than the steady flow viscosity increasing effect. In the case of steady shear deformation, the viscosity increasing effect is larger in low shear rate region. From these results, we can consider that the attached amount of SCCBC depends on the shear rate and deformation mode. From a different perspective, the TR Fluid effect can control by changing the molecular weight and molecular conformation of SCCBC.

From these results, the properties of steady flow viscosity at the low temperature are very complex. We need more detailed investigation. And we think more quantitative researches about molecular conformation and composition of SCCBC, the solvent species dependence, deformation mode dependence and deformation history dependence are necessary to understand the functional expression mechanism of TR Fluid.

### REFERENCE