MOLECULAR DYNAMICS AND THE CORRESPONDING RHEOLOGICAL RESPONSE OF POLYMER NANOCOMPOSITES

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1 Introduction
Nanocomposites usually shows the outstanding improvements in tensile strength and modulus, heat resistance, gas and liquid permeability, biodegradability, ionic conductivity, and so on [1-6]. The improved properties of nanocomposites are realized only when the nanoparticles are homogeneously dispersed throughout polymer matrix and close interactions between nanoparticles and polymer molecules exist. Nanocomposites show different rheological behaviors with respect to the degree of dispersion of nanoparticles [7]. The rheological properties are improved by achieving strong interfacial bonding as well as homogeneous dispersion. Since the characteristic rheological behaviors of nanocomposites are caused by nanoscale interaction between nanoparticles and polymer molecules, molecular-level modeling is suitable to study the nanocomposite system.

In this study, molecular modeling using Brownian dynamics simulation are used to model rheological behavior of the nanocomposites. Dynamic behavior of molecule in nanocomposite were predicted by a newly proposed molecular model and Brownian dynamics simulation with stochastic process was used to simulate the model effectively.

2 Theory
2.1 Molecular modeling
The new model proposed in this study incorporates the ideas from both the thermodynamically admissible single segment reptation model and the full chain geometry. The evolution equation of the thermodynamically admissible reptation model is used to incorporate double reptation, convective constraint release, and chain stretching of the individual chain segments [8-9]. Full chain geometry composed of the multiple chain segments having the above information is considered to investigate dynamics of the realistic polymer molecular chain. The proposed model is used to predict rheological characteristics of the linear polymer and its nanocomposite and also to understand the characteristic rheological behaviors on the molecular level.

2.2 Simulation procedure
Model evaluation starts from construction of the realistic multiple chain geometry composed of L beads and (L-1) connectors which is represented in the Fig.1. The geometrical description is represented as follows.

\[ x_{i+1} = x_i + u_i' \]  \hspace{1cm} (1)
\[ u_i' = \lambda_i u_i \]  \hspace{1cm} (2)

where \( x_i \) is the position of the \( l \)-th bead, \( u_i \) is the connector vector connecting from \( x_i \) to \( x_{i+1} \), and \( \lambda_i \) is the chain stretch ratio of the \( l \)-th connector vector which is defined as ratio of the present chain length to the equilibrium one.

Fig.1. Molecular geometry of polymer chain

The individual chain segment follows the evolution equations of the thermodynamically admissible reptation model [9]. The diffusion equation for the
configurational distribution function, \( f \), is given by the configurational variables, \( u \) and \( s \), because terms for the anisotropic variables, tube cross-sections are neglected in this model.

\[
\frac{Df}{Dt} = -\frac{\partial}{\partial u} \left[ \left( 1 - \frac{u u}{|u|^2} \right) \kappa \cdot u f \right] - \frac{\partial}{\partial s} \left( \frac{1}{2} \left( s - \frac{1}{2} \right) \lambda_{\text{max}} f \right) - \frac{\lambda_{\text{max}} f}{\lambda} f
\]

\[
+ \frac{1}{\pi \tau_s} \frac{Df}{ds} + \frac{\partial}{\partial u} D \left( 1 - \frac{u u}{|u|^2} \right) \frac{\partial f}{\partial u}
\]

(3)

The variable \( u \) is the unit vector representing orientation of the polymer chain segment and \( s \) represents the relative position within a chain segment. The scalar variable \( s \) is in the range of \([0,1]\) and \( s=0,1 \) represents both ends of the chain segment. \( \kappa \) is the transpose velocity gradient tensor, \( \tau \) is the reptation time and \( D \) is the orientational diffusion constant.

Stress tensor of the model is expressed as the following equation.

\[
\tau = 3NkT \left[ 1 + \frac{\lambda_{\text{max}}^2 (\lambda^2 - 1)}{\lambda_{\text{max}}^2 - \lambda^2} \right] \sum_{i=1}^{N} \frac{u_i u_i \kappa}{|u_i|^2}
\]

(4)

where \( \lambda \) is stretch ratio of chain segment and \( \lambda_{\text{max}} \) is maximum possible stretch ratio. The angular bracket \( \langle \rangle \) represents the ensemble average over the trajectories of the reptation processes.

The evolution equations of the full chain reptation model are evaluated by utilizing Brownian dynamics simulation with stochastic processes. The new configurations are constructed by the following equation.

\[
u(t + \Delta t) = \frac{\nu(t) + \kappa \cdot u(t) \Delta t + \sqrt{2D \Delta W}}{|\nu(t) + \kappa \cdot u(t) \Delta t + \sqrt{2D \Delta W}|}
\]

where \( W \) is the three dimensional Wiener process representing Brownian diffusion of polymer chains.

4 Results and discussion

4.1 Experimental results

Rheological behaviors in shear and elongational flows of polymer nanocomposites with the different dispersion states were investigated by observing the dispersion state and measuring the corresponding rheological properties. Dispersion states and internal structure of polyamide 6/organoclay nanocomposites were verified by using SAXS and TEM as shown in Fig.2 and Fig.3. Characteristic diffraction peaks corresponding to the interlayer distance of nanoclays disappeared in the cases of nanocomposites containing 1, 3, 5, 7 wt% of the nanoclay as shown in Fig. 2, which means that the layered clay structure...
is fully broken. The nano-scale dispersion of silicate layers in the nanocomposite is shown by the TEM pictures in Fig.3. The polyamide 6/organoclay nanocomposite has the exfoliated structure with homogeneous dispersion and superior interaction between nanoclays and polymer molecules are achieved. On the other hands, the composite with unmodified clay shows the poor dispersion state and weak interaction between clays and polymer molecules.

Fig.3. Dispersion state of nanocomposites with respect to surface treatment of nanoclay.

Rheological behavior of the two kinds of nanocomposites with different dispersion state is represented in the Fig.4. In shear flow, the exfoliated nanocomposites show solid-like plateau behavior in storage modulus and strong shear thinning behavior in shear viscosity. In elongational flow, only fully exfoliated nanocomposites show strain hardening behavior which is caused by the interaction between nanoparticles as well as the interaction between polymer molecules and nanoparticles.

Fig.2. Small angle X-ray scattering peaks of the nanocomposites containing 1, 3, 5, 7 wt% of (a) montmorillonite (MMT) and (b) organoclay.
Elongational viscosity

Fig. 4. Rheological behaviors of nanocomposites with respect to dispersion state. (a) Storage modulus, (b) shear viscosity, and (c) elongational viscosity

4.2 Numerical results

Numerical results are compared with the experimental data of polyamide 6/clay nanocomposites to study the rheological behavior of polymer nanocomposites. Effects of maximum chain stretch and constraint release on dynamics of macromolecular chain in polymeric nanocomposites are the main concern of this study. Steady shear and uniaxial elongational flow behaviors are investigated by varying the maximum chain stretch (\(\lambda_{\text{max}}\)) and parameters of constraint release (\(\delta_1\), \(\delta_2\)). Molecular motion of a polymer chain exposed to the applied flow is traced and chain characteristics are denoted by calculated total contour length \(L_t\) and molecular orientation factor \(M_f\) defined by the following equation.

\[
M_f = \frac{1}{L_t} \sum_{i=3}^{L-1} |\mathbf{u}_i \cdot \mathbf{u}_1| \quad (6)
\]

where \(\mathbf{u}_0\) is the unit vector along the main flow direction.

Fig. 5 shows shear rate dependence of the steady shear viscosity predicted by the full chain reptation model with various parameters of constraint release and experimental results of polyamide 6/clay nanocomposites. The model predicts non-Newtonian power law behavior of nanocomposites at a low shear rate region, which shows a good agreement with the experimental results. However, the model predicts excessive shear thinning at high shear rate regions when values of \(\delta_2\) are not as large as about \(100/\lambda\). It is known that excessive shear thinning is caused by extremely strong orientation of molecular chains along the flow direction and such molecular conformations do not produce significant resistance to flow. When the value of \(\delta_2\) is much larger than \(\delta_1\), probability of constraint releases from chain stretch and retraction is increased. It means that more chain segments do not follow the external flow field but are randomly oriented. As increasing the portion of randomly oriented chain segments, it is expected that the resistance to flow is increased and resulting stresses become higher. In conclusion, excessive decrease in shear viscosity is alleviated by increasing the portion of constraint release and is nearly independent of chain extensibility.

(a) Shear viscosity of nanocomposite

(b) Dynamic behavior of polymer chain in shear flow

Fig. 5. Dynamic behavior of polymer chain in the corresponding viscosity in shear flow

Strain hardening of the nanocomposite melts is predicted successfully and dynamic motions of polymer chain in the elongational flow are visualized in the Fig. 6.
5 Conclusions

A new molecular model was proposed from the idea of the thermodynamically admissible reptation theory to describe more realistic chain dynamics and predict rheological properties of polymers and polymeric nanocomposites. Brownian dynamics simulation was utilized to calculate the model without any significant approximations and the proposed stepwise Wiener process was applied to obtain more improved curves of rheology, especially at uniaxial elongational flow with low elongation rates. The model predicted the characteristic rheological behavior of polymeric nanocomposites, e.g., strong non-Newtonian behavior from low shear rates in shear flow and nonlinear strain hardening in elongational flow. Elongational flow properties were strongly affected by chain extensibility and constraint release, while shear flow properties were almost independent of chain extensibility but affected by constraint release of chain retraction. Polymer molecular chains showed different deformation in shear and elongational flows, the former was dominated by molecular orientation and the latter was strongly affected by chain stretch as well as orientation.

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References