Microstructural Observation and Simulation of Micro Damage Evolution of Ternary Polypropylene Blend with Ethylene-Propylene-Rubber (EPR) and Talc*

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Abstract
An attempt has been made to study the microstructural deformation and micro damage evolution process in the thermoplastic polypropylene (PP) blended with the ethylene-propylene rubber (EPR) and talc. The in situ observation is conducted during uniaxially stretching within TEM step by step to investigate the deformation events depending on the elongation of samples. In addition, the microstructural deformation and damage evolution process were simulated by coarse-grained molecular dynamics (MD). The experimental result shows that the micro damage initiates at the interface between PP matrix and talc particle. Then, the micro void is generated there, leading to the fibrils of the PP matrix and EPR particles. The similar trend of the micro damage evolution process is obtained by MD simulation. Finally, the effects of the interfacial strength of PP-EPR and PP-talc on the microstructural damage evolution and macroscopic mechanical properties are investigated. It is indicated that increasing the interfacial strength between PP-EPR is more effective for improving the stiffness and the maximum stress, compared to the PP-talc interfacial strength. In addition, to enhance the material ductility, it is important to increase the interfacial strength of PP-EPR.

Key words: Polymer, Blends, Tensile Behavior, Cavitation, Polypropylene, Ethylene Propylene Rubber (EPR), Talc; Molecular Dynamics (MD)

1. Introduction
Polymers are widely used in the fields of automobiles, aerospace and electric devices because of light weight, ease of molding and resistance to corrosion. Especially in the automobiles, Polypropylene (PP) has been extensively used for many applications such as interior and exterior automotive parts(1,2).

Blending PP with inorganic fillers, such as silica(3-5), calcium carbonate(6-15), talc(16-19), clay(20) and wollastonite(21,22), is a useful way to improve physical and mechanical properties of polypropylene composites. The effects of inorganic fillers on the mechanical and physical properties of the PP composites strongly depend on the filler size, shape, aspect ration, interfacial adhesion, surface characteristics and degree of dispersion(15,13,23,24). Talc is one of the most commonly used in-organic fillers in PP matrix for improving the stiffness of PP blends. Talc fillers induce a significant increase in the starting crystallization temperature of PP and affect the crystallization behavior of talc-filled PP composites(16,25,26).
This crystallinity effect changes the mechanical and physical properties of PP matrix\(^{(27)}\).

The introduction of inorganic fillers to PP leads to an increase in stiffness but a decrease in toughness and ductility\(^{(18)}\). The detail analyses of the damage evolution in talc-filled PP has been studied by Hadal and Misra\(^{(21,22)}\). The damage evolution in talc-filled PP is characterized by wedge, ridge-tearing, fibrillation, and brittle fracture with debonding of talc-fillers from the PP matrix, while the damage process of neat PP is characterized by craze-tearing followed by brittle fracture. From their observations, it is considered that the lack of craze formation in talc-filled PP is one reason for the loss of toughness and ductility of the neat PP.

It is well known that most semicrystalline polymers can be effectively toughened by incorporation of well-dispersed secondary phase(s) in the matrix. Blending PP with rubber particles is an attractive way to improve toughness. Stamhuis\(^{(28)}\) has shown that talc filler can significantly increase the impact resistance of PP if it is physically blended with either an Styrene-Butadiene-Styrene (SBS) or an Ethylene-Propylene-Diene-Monomer (EPDM) elastomer. The toughening mechanism of rubber-blended PP is the cavitation of rubber particles followed by crazing and shear-band formation in PP matrix. Rubber particles play a role as an initiator of the craze formation. In addition, the distance between particles improves the toughness of Styrene-Ethylene-Butadiene-Styrene (SEBS) blended PP composites\(^{(29,30)}\). However, the significant drawback of rubber toughening is loss of stiffness and strength. Therefore, blending inorganic fillers in elastomer-blended PP is one solution to achieve the simultaneous improvement of both the stiffness and toughness of the polymer matrix.

The compatibility between the surfaces of the inorganic fillers and polymers is also the important factors to improve the physical and mechanical properties\(^{(31,32)}\). Velasco et al.\(^{(33)}\) showed that PP/talc composite with silane coupling agents had a pronounced effect on the crystallization behavior of the PP/talc composites. Gonzalez et al.\(^{(9)}\) improved Young’s modulus and elongation at break of PP/ High Density Polyethylene (HDPE) blends by using CaCO\(_3\) particles treated by different coupling agents. In those studies, coupling agent between inorganic fillers and matrix is critical to enhance the toughness of PP/HDPE/CaCO\(_3\). Wah et al.\(^{(34)}\) investigated the effect of titanate coupling agent on the mechanical properties of talc-filled polypropylene. These results indicate that the interfacial strength between fillers and matrix is key parameter to enhance the mechanical properties. However, there are few studies about Ethylene Propylene Rubber (EPR) blended PP with inorganic fillers and, hence, the detail understanding about the effect of the interfacial strength on the damage evolution process and overall mechanical properties have not been clarified. Therefore, in this study, the attempt has been made to explain the effect of interfacial strength on the damage evolution and the toughening mechanism of EPR blended PP with talc through molecular dynamics (MD) simulation. The obtained results are valuable and contributed to design interfacial coupling agents in order to achieve simultaneously improve both the stiffness and toughness of the polymer matrix.

In this study, the in situ microstructural deformation process under tensile loading was observed by transmission electron microscope (TEM) in order to clarify the microstructural damage evolution in EPR blended PP with talc fillers. Next, MD model was constructed based on the morphological observation by TEM. Then, the tensile deformation was simulated by coarse-grained MD simulation and the numerical results were compared with experimental observation. In order to investigate the interfacial role in the improvement of stiffness and toughness, the interfacial strength of PP-EPR and PP-talc were changed parametrically and the effects of interfacial strength on the microstructural deformation and damage evolution process, and overall mechanical properties were studied.
2. Experimental Procedure and Results

2.1 Material

Isotactic polypropylene (i-PP) was used as a matrix polymer in this study. It has a melt flow rate (MFR) = 30 g/10 minute (230 °C). The blended elastomer was ethylene propylene rubber (EPR), whose blend ratio was 35 wt %. The talc was blended at the blend ratio of 8 wt %. Detail of the blend is shown in Table 1. Table 2 shows the detail of EPR.

<table>
<thead>
<tr>
<th></th>
<th>Weight ratio</th>
<th>Volume ratio</th>
<th>Density (kg/m$^3$)</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>57%</td>
<td>58.9%</td>
<td>910</td>
<td>190000</td>
</tr>
<tr>
<td>EPR</td>
<td>35%</td>
<td>38.3%</td>
<td>860</td>
<td>320000</td>
</tr>
<tr>
<td>Talc</td>
<td>8%</td>
<td>2.8%</td>
<td>2700</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Detail of EPR

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Weight ratio</th>
<th>Number of monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene -C$_2$H$_4$-</td>
<td>84.0%</td>
<td>9567</td>
</tr>
<tr>
<td>Propylene -C$_3$H$_6$-</td>
<td>16.0%</td>
<td>1219</td>
</tr>
</tbody>
</table>

2.2 In situ Observation of Microstructural Morphology and Deformation Process by TEM

Transmission electron microscope (JEM 4000 FX (JEOL)) operating at 400keV was used to investigate the phase morphology. After staining of samples with OsO$_4$, ultra-thin sections were prepared by using an ultra microtome equipped with a diamond knife. The samples for the morphological investigation were taken from the plate specimen which was made by the injection molding.

The thin sections were prepared with the thickness of about 300 nm by means of ultra microtome equipped with a diamond knife. The thin specimen for observing the deformation process was not stained with OsO$_4$ but directly observed during deformation. The thin sections were fixed between two adhesive metal-tapes with a hole of about 1mm as shown in Fig. 1. To allow deformation of free-standing sample, the both sides of metal-tape were cut before stretching starts. Thin sections were uniaxially stretched by single tilt straining holder (Gatan, 654) within TEM step by step to investigate the deformation events. Based on the microstructural observation during stretching, one can understand the quasi-static deformation process. It is expected that the microstructural deformation observed by TEM investigation during stretching might be the same deformation mechanism as that at the deformation rate which is slower than the ductile-brittle transition deformation rate.

Figure 1: Photograph of in situ tensile stage of TEM
2.3 Experimental Result

Figure 2 shows the phase morphology taken by TEM. The EPR particles were elliptical shape oriented to the same direction as the injection direction. The mean diameter of the EPR particles was about 0.7 \( \mu \)m based on the image analysis.

![Figure 2 Morphological pictures of PP/EPR/talc blend](image_url)

Figure 3 shows the micrographs of the \textit{in situ} observation of the thin specimen taken by TEM. As mentioned above, the thin specimen for \textit{in situ} observation was not stained with OsO\(_4\), leading that the PP and EPR phases were not clearly identified. In Fig. 3, the black-color region indicated talc and the grey-color area meant the phases of PP and EPR blends. Deformation structures taken during \textit{in situ} tensile tests revealed the well-developed micro void formation in the plastically deformed specimen. It is clearly seen that the larger voids have been mostly formed around the talc aggregates, see in Fig. 3(a). Also, the smaller voids appeared randomly in the whole area of the uniaxially deformed specimen. Upon stretching specimen, the intensive void formation was activated by the cavitation of EPR particles. The matrix strands between EPR particles were highly stretched to the tensile direction, of which the deformation structure resembled to the craze-like fibrillation.

From the present TEM observation, it is summarized that the mechanism of damage evolution is as follows. First, the debonding between PP matrix and talc occurs mainly due to the high stress concentration. Next, the EPR particles cavitate and the micro-void are formed, and then, the fibril nucleates at the PP matrix. In the present \textit{in situ} TEM observation, the stress state was plane stress because the specimen was thin although the realistic case would cause the three-dimensional stress states inside the materials. However, according to the references\(^{35,36}\), it is reported that the plastic deformation and extensive cavitation of PP elastomer blend were caused by debonding of the in-organic filler particles and PP matrix. Thus, it is considered that the presently observed damage evolution process should be similar to the realistic cases.
3. Numerical Procedures and Results

3.1 Microstructural Phase Separation Simulation

The material focused in this study was polypropylene blended with EPR and talc. Before simulating the tensile deformation process in such a blend system, one has to conduct the phase separation simulation for constructing the initial simulation model of tensile deformation in the coarse-grained MD.

In this study, the interface simulator SUSHI\(^{(36)}\) inside an integrated simulation system for soft materials OCTA\(^{(37)}\) was used. SUSHI calculates the equilibrium and non-equilibrium structures in polymer blends by solving the self-consistent Edwards equation. The static simulations were carried out by SUSHI based on Self Consistent Field Theory (SCF)\(^{(38)}\).

In the SCF theory, the minimum unit, that constitutes the polymer system, is called a segment. The polymers are composed of several kinds of segments specified by the index \(K\). The volume fraction distribution \(\phi_K (r)\) of \(K\)-type segments is calculated by taking the chain confirmations into account using the path integral formalism. The self consistent field, \(V_K (r)\) is a potential field that accounts for the external conditions such as the interaction between segments and the incompressible conditions, and has the following form in this study

\[
V_K (r) = W_K (r) - \mu_K (r),
\]

where \(W_K (r)\) and \(\mu_K (r)\) are the mean field resulting from the interaction between segments and the chemical potential respectively, and are given by

\[
W_K (r) = \sum_\kappa \chi_{K\kappa} \phi_\kappa (r),
\]

Figure 3 Photographs of micro deformation process by TEM

(a) Initial stage of damage; Debonding between talc and PP/EPR matrix

(b) Fibrillation of PP/EPR matrix
acting on a \( K \)-type segment at position \( r \). Here, \( Z_{KK} \) is the interaction strength between the \( K \)-type segment and \( K' \)-type segment and \( \Gamma \) is the free energy in the system. For calculating the full equilibrium state of the distribution of the segment volume fraction, the only constraint condition is the following local incompressible condition.

\[
\sum_k \phi_k(r) = 1.
\]

In this study, a homo-polymer chain was considered. Then, all the \( \mu_k(r) \) given by Eq. (3) should be equal irrespective of the segment type \( K \).

\[
\mu_k(r) = \mu(r) \quad \text{for all } K.
\]

Let introduce the path integrals, \( Q_k(i, r) \) and \( \bar{Q}_k(i, r) \) as follows.

\[
Q_k(i, r) = \int d\mathbf{r}_0 Q_k(0, \mathbf{r}_0, i, r)
\]

\[
\bar{Q}_k(N_K - i, r) = \int d\mathbf{r}_0 Q_k(N_K, \mathbf{r}_0, i, r).
\]

where \( N_k \) is the total number of segments compositing the \( K \)-type polymer.

Then, the path integrals \( Q_k(i, r) \) and \( \bar{Q}_k(i, r) \) are obtained by solving the evolution equations

\[
\frac{\partial}{\partial t} Q_k(i, r) = \left[ \frac{b^2}{6} \nabla^2 - \beta V_k(r) \right] Q_k(i, r)
\]

\[
\frac{\partial}{\partial t} \bar{Q}_k(i, r) = \left[ \frac{b^2}{6} \nabla^2 - \beta V_k(r) \right] \bar{Q}_k(i, r)
\]

using the following the initial conditions.

\[
Q_k(0, r_0) = \bar{Q}_k(0, r_0) = 1.
\]

By using the path integrals obtained from Eqs. (8) and (9), the segment density at the position \( r \) is given as follows.

\[
\phi_k(r) = C_k \sum_i Q_k(i, r) \bar{Q}_k(N_K - i, r)
\]

where \( C_k \) is the normalization constant. In this study, the statistical ensemble of the chains is the canonical ensemble where the total number of chains in the system is fixed and is given as follows.

\[
C_k = \frac{M_k}{\int d\mathbf{r}_0 \int d\mathbf{r}_1 Q_k(0, \mathbf{r}_0; N_K, \mathbf{r}_1)}
\]

Static calculation is conducted for finding a set of self consistent solutions for \( \{V_i(r)\} \) and \( \{\phi_k(r)\} \) that satisfy Eqs. (1), (8), (9) and (11), the local incompressible condition Eq. (4), and the constraint force given by Eq. (5) simultaneously. The basic scheme is shown in Fig. 4. These solutions are numerically obtained in SUSHI. The more detail of SUSHI can be found in Ref. (37).
The main objective of the present phase separation is to obtain the spatial density distribution of the two types of polymers, which looks like the sea-island phase morphology. Then, the spatial density distributions were obtained by simulating the phase separation in the PP and polyethylene (PE) diblock copolymer blend system. Here, the diblock copolymer means the polymer system consisting of two blocks of polymers. The present PP/PE blend consisted of 13 PP segments and 7 PE segments as illustrated in Fig. 5. Here, talc was modeled as one segment. The phase diagram of diblock copolymer is reported by Matsen, et al. (40), where four types of well known equilibrium mesophases such as spheres, cylinders, gyroid and lamellae are shown. In the phase diagram, the dominant parameters for determining the phase type are the volume fraction $f$ of a segment, the interaction strength $\chi$ between the segments, and the number of segments $N$. In the present study, the target equilibrium phase type was the hexagonal cylindrical shape between PP and PE segments. Then, the interaction strengths were set as shown in Table 3 focusing on the condition $\chi N = 20$. The interaction parameter between PP segment and talc segment and that between PE segment and talc segment were determined by try and error approaches so that the final phase separation should be similar to TEM morphological picture. The unit length $L$ was determined based on the lattice constants of PP/PE diblock copolymer, leading that the lattice constants were 8.0$L$ in the $x$ direction and 14.0$L$ in the $y$ direction in the two-dimensional $x$-$y$ plane. The diameter of PE cylindrical domain was about 5$L$. In this study, EPR particles had approximately the diameter of 700 nm. Thus, the unit length $L$ was defined as 140 nm. The system size was $56L \times 32L$ as shown in Fig. 6(a). The geometry of talc was $3L \times 7.5L$. As shown in Fig. 5(a), the distribution of the volume fraction of each segment was intentionally applied in the initial phase separation model. The total number of calculation steps was 1,000,000. During calculation, the iteration procedure was finished when the maximum updated amount of $\phi_k(r)$ during a single iteration step becomes less than $10^{-6}$. Figure 6(b) shows the result of phase separation simulation. As shown clearly, the hexagonal cylindrical phase was obtained. In addition, the two talc segments were separated from PE segments without constructing the core-shell structures. The obtained distribution of the volume fraction of each segment was used so as to construct the initial structural model for the coarse-grained MD as described in next section.
3.2 Simulation Method of Tensile Deformation by Coarse-Grained Molecular Dynamics

In this study, the prototypical system was a dense glass of bead-spring polymer chains filled with soft bead-spring rubbers and stiff talc-like bead-spring inclusions. The system contains three types of particles; PP monomers, PE monomers and inclusion monomers; they were treated as point masses. Reduced units were used throughout while all reduced units were converted to SI units and shown in one table for references. \( L \) is the base unit for length, \( \rho \) is the reduced density, \( P \) is the reduced pressure, \( \rho = \frac{\rho L^3}{M} \) is the base unit for mass, \( A v \) is Avogadro’s number, \( u_0 = \frac{P A L}{\varepsilon} \) is the base unit for energy and \( T = \frac{u_0}{R} \) is the reduced temperature where \( R \) is the gas constant. The reduced stress will be later mapped to engineering units for parametric study of the interfacial strengths of PP-EPR and PP-talc. Because of the coarse-grained nature, there is no one-to-one mapping of the model system to the actual system. In this coarse-grained simulation, the goal is to understand the model system self-consistently. In relating the simulation results to the current PP/EPR/talc blend, the emphasis is on the qualitative microstructural deformation and damage evolution mechanisms.

The dynamics was performed using a Langevin thermostat. MD numerically solves Newton’s equations of motion for each particle; particles interact according to a potential energy function \( U \). We employed a set of potentials to model the polymer chains which are standard for dense bead-spring glasses.

Beads separated by a distance \( r \) interact via a truncated Lennard-Jones potential \( U_{LJ} \):

\[
U_{LJ}(r) = \begin{cases} 
4\epsilon \left( \frac{\sigma_0}{r} \right)^{12} - \left( \frac{\sigma_0}{r} \right)^{6}, & r \leq r_c \\
0, & r \geq r_c 
\end{cases} 
\]  

\[ r_c = \sigma_0 \]  

\[ U_{LJ}(r) = 0 \]  \( r \geq r_c \)  

In this article, \( \sigma_0 \) represents the diameter of LJ sphere and \( \epsilon \) means the strength of the interaction between beads, \( r_c \) is the cutoff distance, which means that the beads separated by the distance larger than \( r_c \) does not interact. The bonded interactions along each polymer chain are modeled via a simple harmonic potential \( U_{bond} \):

\[
U_{bond}(r) = \frac{1}{2} k (r - r_0)^2 
\]  

Table 3 Parameters of segment interaction

<table>
<thead>
<tr>
<th></th>
<th>( \chi_{PP/PE} )</th>
<th>( \chi_{PP/Talc} )</th>
<th>( \chi_{PE/Talc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6 Result of phase separation simulation

(a) Initial model

(b) Result of phase separation
where $k$ is a parameter representing the bond strength, $r_0$ is a parameter representing the equilibrium bond distance.

The initial structures of chains were generated from the spatial distribution of segments obtained by the phase separation simulation. The SCF calculation gave the spatial distribution of segments in the phase separated state. In the numerical calculation, the local volume fraction of segment $n: \phi_n(\mathbf{r})$ is given as $\phi_n(i, j, k)$, where $(i, j, k)$ is the index of the lattice point and $\phi_n(\mathbf{r})$ is calculated by the interpolation from the values of $\phi_n(i, j, k)$ of the nearby lattice points. For generating the initial chain configuration, the chains are grown using the density biased Monte Carlo procedure. The detail of the density biased Monte Carlo procedure can be found in Ref. (37). The initial MD model for tensile simulation was developed by replacing the spatial density distribution of PE segment obtained by the phase separation simulation to that of EPR. The spatial density distributions of PP and talc were the same as those obtained in the phase separation simulation.

For structural relaxation by dynamics simulation, the excluded volume effect is introduced gradually by scaling the forces acting on atoms. The maximum force allowed to act on atoms is given and if the forces become larger than the maximum force, the force is scaled to that value. Then the maximum force for scaling is increased gradually, if the averaged force and the maximum force acting on each atom decrease in the relaxation process, and if the forces acting on all atoms become smaller than the initial maximum force for scaling, the relaxation is completed.

The simulation domain was a hexahedron $(56L \times 32L \times 14L)$. The length of $z$ direction was set as $14L$ so that it should be larger than the inertial radius of the system. The polymer models are shown in Fig. 7. In this study, the polymer chain length of PP was set as 20 segments, leading to about 200 propylene monomers in one PP segment and about 340 ethylene monomers in one PE segment as shown in Table 4. In addition, talc was modeled as one talc segment because talc did not have polymer chains. Here, EPR was modeled as triblock copolymer in order to make the interaction between PP and EPR strong. The number of polymer chains was determined such that the system density was 1.0. This resulted in 802 for polypropylene, 307 for EPR and 630 for talc, respectively. All the reduced units converted to SI units are shown in Table 5. Here, firstly, the unit length $L$, the unit density $\rho$ and the unit pressure $P$ were determined so that the simulation model should be similar to the actual PP/EPR/talc blend system, leading to the rest of the reduced units.

![Figure 7 PP/EPR/talc polymer models](image)

Table 4 PP/EPR/talc polymer models

<table>
<thead>
<tr>
<th></th>
<th>Number of monomers</th>
<th>Number of segments</th>
<th>Number of monomers in a segment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>4529</td>
<td>20</td>
<td>227</td>
</tr>
<tr>
<td>PP in EPR</td>
<td>1219</td>
<td>6</td>
<td>204</td>
</tr>
<tr>
<td>PE in EPR</td>
<td>9567</td>
<td>28</td>
<td>342</td>
</tr>
</tbody>
</table>
The bonding strengths of PP, PE and PP-PE segments were determined mainly based on the apparent elastic moduli of PP and EPR because the bonding strength is strongly related to the stiffness, in general. According to Ref. (41), the apparent elastic modulus of PP was about 1 GPa, and that of EPR ranged from 0.01 to 0.1 GPa. EPR consisted of both bonding connections, between PE and PE segments, and PP and PE segments, as illustrated in Fig. 7. Therefore, their bond strengths were determined as one tenth of that of PP segments. The strength of the L-J potential was identified based on the tensile strengths of PP and EPR. The tensile strength of PP ranges from 20 to 40 MPa and that of EPR are between 10 and 20 MPa(41). As a result, the strength of the L-J potential of PP segments was twice as large as that of PE segments. The strengths between PP and PE segments were determined by assuming that the interaction between the same kinds of segments should be larger than that between the different types of segments. It was also assumed that the strengths between talc and PP (or PE) segments should be smaller than that between PP and PE segments. The experimental observation(35,36), that the debonding between in-organic fillers and PP/elastomers blends caused the plastic deformation and extensive cavitation, indicates that these assumption should be reasonable qualitatively. The identified parameters are shown in Tables 6 and 7.

The monomers in the simulation domain were evolved through time using the velocity Verlet integration algorithm. The numbers of calculating steps were 10,000 for relaxation with a time step of 0.012 \( \tau \) and 1,000,000 for tensile deformation with a time step of 0.01 \( \tau \). Periodic boundaries were applied in the x, y and z directions for relaxation and in the y and z directions for tensile deformation because the affine deformation in the x direction was applied to the unit cell. The increment of strain was 10-6 in each calculating step. During the elongation, the stress was calculated based on Virial theorem.

Both relaxation and tensile simulations were conducted in the NVT ensemble using a Langevin thermostat(42,43) with a friction of 0.5 and a set-point temperature of 0.17. The tensile strain rate in the x-direction was 10^{-5} (1/\( \tau \)). Because of the coarse-grained nature, the strain rate was much faster than the quasi-static deformation. Especially, the reduced length was much larger than the conventional coarse-grained MD models, leading to very short time duration. However, it is validated that the total potential energy changed within small range (0.05 % of the total energy) during the tensile deformation, and the change of the potential energy was almost the same as that of the initial structural relaxation calculation. In addition, it is shown that the structure of the current model was relaxed fully during deformation in the snapshots of the morphological deformation. Thus, it is considered that the current model can be similar to the quasi-static deformation process qualitatively. The simulation code used in this study was the standard coarse-grained molecular dynamics code with public domain meso-scale simulation code COGNAC(44) inside an integrated simulation system for soft materials OCTA(38).

In this study, the qualitative analyses of the deformation mechanism and the damage evolution in PP/EPR/talc blend system were mainly focused. In addition, the effects of the interfacial strength of PP-EPR and PP-talc on the tensile deformation behavior were investigated. For investigating the effect of PP-EPR interface, the strengths of the

### Table 5 Reduced units in SI unit

<table>
<thead>
<tr>
<th>Reduced units</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>140 nm</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.945 x 10^3 kg/m^3</td>
</tr>
<tr>
<td>( P )</td>
<td>12.658 MPa</td>
</tr>
<tr>
<td>( M )</td>
<td>2.593 x 10^{-24} kg</td>
</tr>
<tr>
<td>( \tau )</td>
<td>1.21 ps</td>
</tr>
<tr>
<td>( u_0 )</td>
<td>2.091 x 10^{10} J/mol</td>
</tr>
<tr>
<td>( T )</td>
<td>2.515 x 10^9 K</td>
</tr>
</tbody>
</table>
interaction between PP and EPR were changed as 0.075\(u_0\), 0.1875 \(u_0\), 0.375 \(u_0\), 0.5625 \(u_0\), 0.75\(u_0\), 0.9\(u_0\), 1.05\(u_0\), 1.2\(u_0\), 1.35\(u_0\) and 1.5 \(u_0\) while the rest of the parameters were kept the same as what were shown in Tables 6 and 7. In the case of studying the effect of PP-talc interface, the strengths of PP-talc interface were changed as 0.01\(u_0\), 0.025 \(u_0\), 0.05 \(u_0\), 0.075 \(u_0\), 0.1 \(u_0\), 0.12\(u_0\), 0.14\(u_0\), 0.16\(u_0\), 0.18\(u_0\) and 0.2\(u_0\) with the same parameters as shown in Tables 6 and 7, where the indexes A, B and C mean PP, PE and talc segments, respectively.

<table>
<thead>
<tr>
<th>Bonding pair</th>
<th>Bond strength (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A A</td>
<td>(30u_0/L^2)</td>
</tr>
<tr>
<td>B B</td>
<td>(30u_0/L^2)</td>
</tr>
<tr>
<td>A B</td>
<td>(30u_0/L^2)</td>
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</table>

Table 6 Bonding strengths

<table>
<thead>
<tr>
<th>Bonding pair</th>
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<th>(\sigma_0)</th>
<th>(r_c)</th>
</tr>
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<tbody>
<tr>
<td>A A</td>
<td>2(u_0)</td>
<td>1(L)</td>
<td>1.3(L)</td>
</tr>
<tr>
<td>B B</td>
<td>1(u_0)</td>
<td>1(L)</td>
<td>2(L)</td>
</tr>
<tr>
<td>C C</td>
<td>20(u_0)</td>
<td>0.891(L)</td>
<td>1.3(L)</td>
</tr>
<tr>
<td>A B</td>
<td>0.75(u_0)</td>
<td>1(L)</td>
<td>2(L)</td>
</tr>
<tr>
<td>A C</td>
<td>0.1(u_0)</td>
<td>1(L)</td>
<td>2(L)</td>
</tr>
<tr>
<td>B C</td>
<td>0.1(u_0)</td>
<td>1(L)</td>
<td>2(L)</td>
</tr>
</tbody>
</table>

Table 7 Strengths of interaction and cut-off length of LJ potential

3.3 Result of Tensile Simulation

Figure 8 shows the initial phase morphology of the coarse-grained MD model after relaxation where the blue-color area is PP, the green-color area is EPR and the red-color area is talc particles, respectively. In the same as the actual morphology, it is clearly shown that the EPR particles and talc are the islands and the PP matrix is the sea. This result indicates that the phase separation could be done successfully.

Figure 9 shows the snap shots of deformation process simulated by coarse-grained MD. Figure 10 shows the magnified snapshot of deformation process at the tensile strain of 0.04. At the beginning of elongation, the elongations in the PP matrix and the EPR particles are uniform. Then, at the tensile strain of 0.04, the debonding between the PP matrix and the talc occurs, leading to voids around talc particles as indicated by red arrows in Fig. 10. Next, the voids around the talc particles induce the cavitations of the adjacent EPR particles. Finally, the molecular chains of PP are fibrillated. The simulated deformation and damage evolution mechanisms are similar to the in situ microstructural observation during tensile loading in TEM as shown in Fig. 3. This indicated that the micro-damage evolution process was successfully captured by coarse-grained MD model, leading to the clear understanding of the micro-damage evolution in the PP/EPR/talc blend system.

Figure 8 Initial phase morphology before tensile deformation
3.4 Effects of Interfacial Strength of PP-EPR and PP-talc on Mechanical Properties

The effects of the interfacial strengths of PP-EPR and PP-talc were investigated by changing the strength parameter of interaction $\varepsilon$. Figure 11 shows the stress strain curves of various $\varepsilon$ values between PP and EPR. As shown clearly, the stiffness and the maximum stress increased with the decreasing yield strain. Here, the yield strain was defined as the strain when the stress reached the maximum value in this study. At the yield strain, the debonding occurred along the interface between PP and talc phases. As the interfacial strength of PP-EPR increased, the deformation was localized at the interface of PP-talc, leading to the decrease of the yield strain. Figure 12 shows the stress-strain curves with various $\varepsilon$ values of the PP-talc interface. On the contrary to Fig. 11, the trend of stress strain curve is similar in each case. It is clear that the effect of the interfacial strength of PP-EPR is stronger than that of PP-talc interface in the present material.

Figure 9 Snapshots of deformation process

Figure 10 Magnified snapshot of deformation process at the nominal strain of 0.04
Figure 11 Stress strain curves by changing the interfacial strength between PP and EPR

Figure 12 Stress strain curves by changing the interfacial strength between PP and talc
Figure 13 shows the apparent elastic modulus plotted against various normalized interfacial strengths of PP-EPR and PP-talc. The apparent elastic modulus was defined as the slope of the stress-strain curve at the strain between 0.01 and 0.02. Here, the interfacial strengths of PP-EPR and PP-talc were normalized by $0.75\mu_0$ and $0.1\mu_0$, respectively. Figure 14 shows the snapshots of the cases where the normalized interfacial strengths of PP-EPR are 0.1, 1.0 and 1.4 at the tensile strain of 0.03. As the interfacial strength of PP-EPR increased, the strain localized at the PP-talc interfaces, leading to early debonding between PP and talc. The apparent elastic modulus decreased as the normalized strength of interface of PP-EPR was above 1.6 because the micro damage occurred at the tensile strains between 0.01 and 0.02. The effect of PP-talc interfacial strength was much smaller than that of PP-EPR interfacial strength, indicating that the tendency would not change even though both the interfacial strengths of PP-EPR and PP-talc were changed parametrically at the same time.

![Figure 13](image1)

**Figure 13 Effects of the interfacial strengths of PP-EPR and PP-talc on the elastic modulus**

![image2](image2)

(a) 0.1 (b) 1.0 (c) 1.4

**Figure 14 Snapshots of the deformation of various normalized interfacial strengths of PP-EPR at the tensile strain of 0.03**

Figure 15 shows the maximum stress plotted against various normalized interfacial strengths of PP-EPR and PP-talc. Here, the interfacial strengths of PP-EPR and PP-talc were normalized by $0.75\mu_0$ and $0.1\mu_0$, respectively. Figure 16 shows the snapshots of the deformation when the normalized interfacial strengths of PP-EPR are 0.1, 1.0 and 2.0 at the maximum stress. As shown clearly, the PP-EPR interface had stronger contribution on the maximum stress than PP-talc interface. The maximum stress was obtained when the debonding occurred at the interface between PP and talc. Since the deformation behavior at the PP-EPR interfacial strength of 1.4 was similar to that at the PP-EPR interfacial strength of 2.0, it is considered that the maximum stress would saturate at the PP-EPR interfacial strength above 1.4. In the same as Fig. 13, it is expected that the maximum stress would not change when both the PP-EPR and the PP-talc interfacial strengths are changed parametrically at the same time because the maximum stress is not sensitive to the interfacial strength of PP-talc.
Figure 15 Effects of the interfacial strengths of PP-EPR and PP-talc on the maximum stress

Figure 16 Snapshots of the deformation of various normalized interfacial strengths of PP-EPR at the stress is the maximum

Figure 17 shows the strain energy up to the strain of 1.0 plotted against various normalized interfacial strengths of PP-EPR and PP-talc. Here, the interfacial strengths of PP-EPR and PP-talc were normalized by $0.75 u_0$ and $0.1 u_0$, respectively. Figure 18 shows the snapshots of the micro damage when the normalized interfacial strengths of PP-EPR are 0.25, 1.0 and 1.6 at the tensile strain of 0.6. As shown in Fig. 17, the interfacial strength of PP-EPR had stronger contribution on the strain energy than that of PP-talc interface. On the contrary to the maximum stress, the effect of PP-talc interface on the strain energy was relatively large. This is because the resistance against the debonding propagation got larger as the interfacial strength of PP-talc increased, leading to the slight stress reduction after reaching the maximum stress. The maximum value of the strain energy up to strain of 1.0 was obtained when the normalized strength of PP-EPR was 1.6. With the increasing interfacial strength of PP-EPR, both the PP and the EPR phases were fibrillated in the same bundles, as shown in Fig. 18 (c), while the EPR were only fibrillated with the small interfacial strength of PP-EPR as shown in Fig. 18 (a). However, the further increase of PP-EPR interfacial strength localized the deformation at the PP-talc interface, and then caused the interfacial debonding there, leading to the large stress reduction after reaching the maximum stress. This is the reason why the strain energy decreased when the interfacial strength of PP-EPR was above 1.6. In the realistic case, it is very hard to get the larger interfacial strength between PP and talc compared to that between PP and EPR. Thus, it is considered that the increasing the interfacial strength of PP and EPR should be very important task for improving the material ductility in the PP/EPR/talc blend system.
Figure 17 Effects of the interfacial strengths of PP-EPR and PP-talc on the strain energy at the tensile strain of 1.0

Figure 18 Snapshots of the micro damage evolution of various normalized interfacial strengths of PP-EPR at the tensile strain of 0.6

4. Conclusion

In this study, we observed the in situ microstructural deformation process under tensile loading by TEM in order to clarify the microstructural damage evolution in PP blended with EPR and talc fillers. Next, MD model was constructed based on the TEM morphological observation. Then, the tensile deformation was applied to the morphological MD model and the simulated micro damage evolution process was compared with experimental observation qualitatively. In order to investigate the interfacial roles in the improvement of stiffness and ductility, the interfacial strengths of PP-EPR and PP-talc were changed parametrically and the effects of the interfacial strengths on the microstructural damage evolution process and the overall mechanical properties were studied. The following conclusions were obtained.

1. From the in situ observation of damage evolution process by TEM, the debonding between PP matrix and talc firstly occurred due to the high stress concentration. Next, the EPR particles cavitate and the micro-void are formed, and then the fibril nucleates at the PP matrix.

2. The present MD simulation can catch the microscopic damage evolution process under tensile loading.

3. To improve the stiffness and the maximum stress, it is more effective to increase the interfacial strength between PP-EPR than PP-talc.

4. To enhance the material ductility, it is important to increase the interfacial strength of PP-EPR.
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