The effect of dynamic deformation on moldability and the Clinging structure of polymer chains

Theoretical consideration for Molecular weight between Clinging

Shigeru Yao

1. Introduction

Regarding the reason why the physical properties of recycled plastics are significantly lower compared to virgin products, we proposed the "Physical Degradation and Physical Regeneration Theory" shown in Fig. 1, and have fundamentally demonstrated that physical properties can be restored through physical processing, and have also practically demonstrated this by designing an extruder equipped with a resin reservoir.

This theory suggests that the deterioration in physical properties is caused by a decrease in the number of entanglements due to excessive shear during molding, which in turn reduces the number of tie chains between crystalline lamellar layers. On the other hand, it shows that the number of entanglements can be restored by statically holding the material in a molten state, thereby restoring the physical properties.

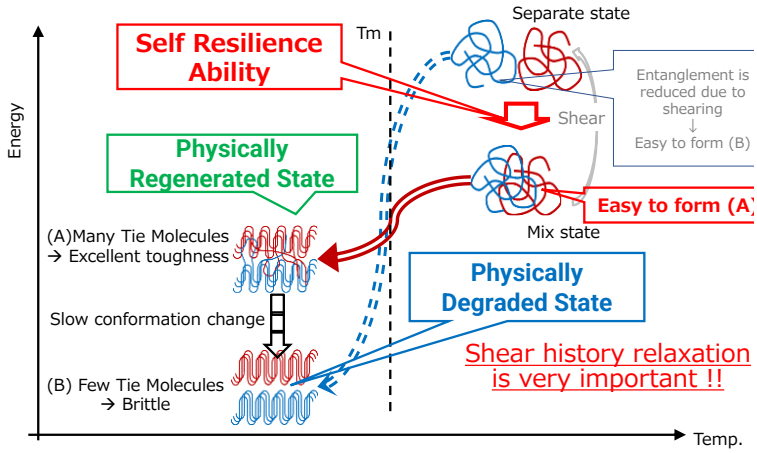

Fig.1 Physical Degradation and Physical Regeneration Theory

On the other hand, when dynamic deformation is applied, Kanemoto et al. showed, as shown in Fig. 2, that applying strains with relatively large

amplitudes, such as 100% or 200%, significantly restores the tensile properties that had deteriorated greatly due to shearing, and that applying dynamic deformation to virgin material also improves its elongation properties.

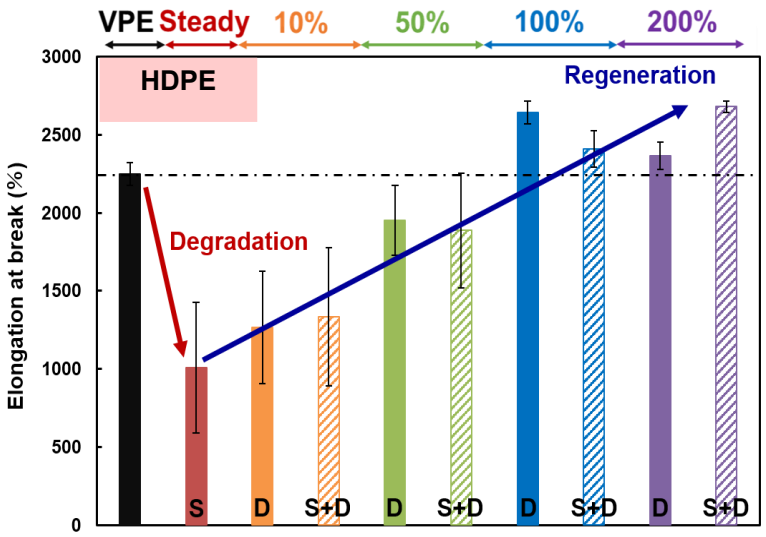

Fig.2 Effects on the Tensile Properties of Various Deformation Modes. S:Shear deformation, D:Dynamic deformation, S+D: Dynamic deformation after Shear deformation. % means strain ratio

This suggests that dynamic deformation with large amounts of strain has the effect of increasing the number of entanglements between polymers. In fact, by devising ways to reproduce this flow, it has been confirmed that good restoration can be observed in recycled plastics whose physical properties have deteriorated greatly due to their shearing history.

On the other hand, this study shows that at strain levels of 10% to 50%, the tensile properties deteriorate, though not to the same extent as when a steady-state shear history is applied. In other words, it is suggested that dynamic deformation at small strain levels reduces the number of entanglements.

Therefore, we measured the dynamic viscoelastic properties of polyethylene or polypropylene when subjected to dynamic deformation of various strain amounts for a certain period of time, as well as the frequency dependence of the dynamic viscoelasticity after the deformation.

Furthermore, we conducted a theoretical study on the Clinging structure of the polymer chain inferred from these results.

2. Experiment

The samples used were high-density polyethylene (J320, manufactured by Asahi Kasei Corporation) and homopolypropylene (J700GP, manufactured by Prime Polymer Co., Ltd.). These were molded into tablets 4 mm thick and 20 mm in diameter by hot pressing to be used as samples for viscoelasticity measurements. These were subjected to dynamic deformation at various strains for 10 minutes at a temperature of 210°C and a fixed frequency of 1 rad/sec, and the changes in G' and G over time were measured. Subsequently, the strain was reduced to 0.2%, and the frequency dependence was measured in the range of 10^{2} to 10^{-2} .

3. result

Figure 3 shows the time dependence of G' at J320. The vertical axis represents the ratio to the value at 10 seconds. From the figure, it can be seen that the value of G' increases with time, and this tendency is stronger as the amount of strain increases. A similar dependence was observed for G'' , although the proportion was lower. Figure 4 shows the frequency dependence of G '

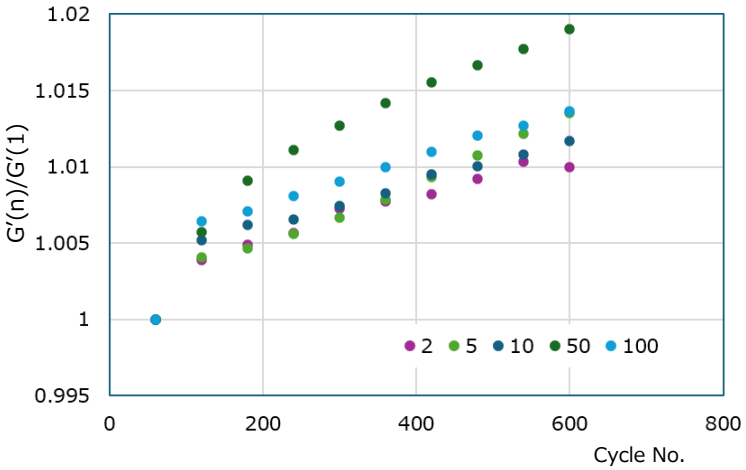

Fig.3 Cycle-dependent storage modulus. The vertical axis shows the ratio to the initial value.

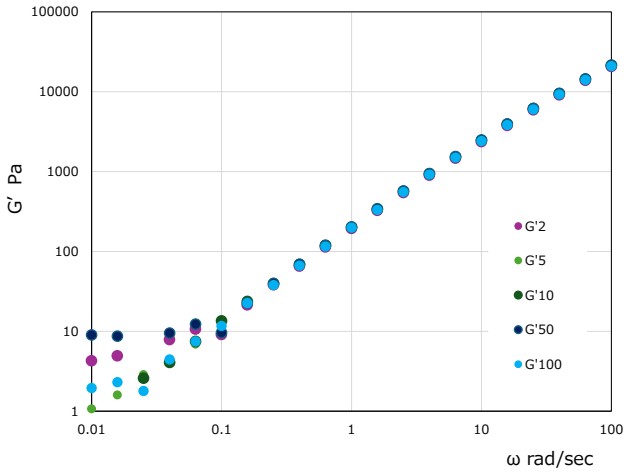

Fig.4 Frequency Dependence of the Storage Modulus After Dynamic Deformation.

measured thereafter. From the figure, it can be seen that it exhibits a flat region in the low-frequency range. Furthermore, since the zero-shear viscosity in these steady-state flow measurements remained unchanged, it is considered that the molecular weight did not change.

Similar results have been obtained from polypropylene.

The results suggest that applying dynamic deformation with relatively large strains increases the number of entanglements between polymers in the system, and that this effect is reflected in G' on the low-frequency side in frequency-dependent measurements.

4. About the Clinging structure

Based on the above characteristics, it is thought that the entanglement between polymer chains changes even with dynamic deformation. From these characteristics, it is considered that the conventional entanglement shown in Fig. 5(A) takes the form of a clinging structure like (B) .

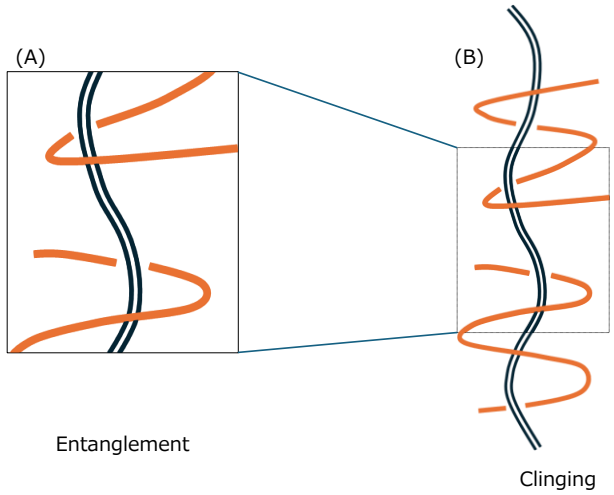

Fig.5 The Difference in “Entanglement” and “Clinging”.

Figure 6 is a model diagram for theoretically solving the clinging structure at the smallest unit. Here, N_x is the

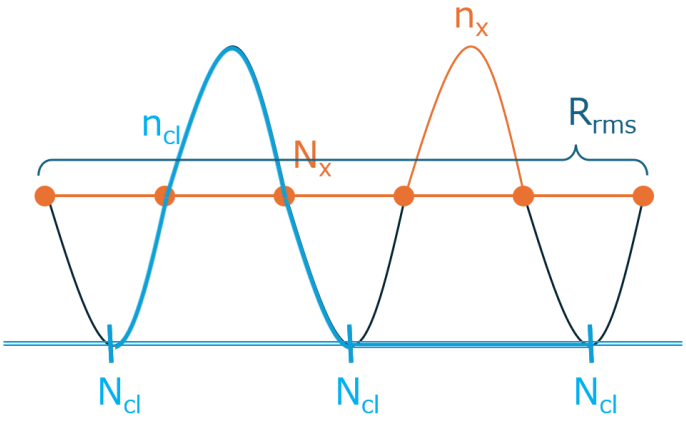

Fig.6 Unit-Chain Structures in Clinging

number of intersections, n_x is the number of molecules between intersections, N_{cl} is the clinging number, n_{cl} is the number of molecules between clinging points, and R_{rms} is the end-to-end distance. The flexibility of the polymer chain is related to the characteristic ratio (C_∞) and depends on the number of molecules, as shown in equation (1).

$$C_n = C_\infty \left(1 - \frac{A}{n}\right) \qquad (1)$$

Here, A is a constant, and in the case of polyethylene, it has been reported to be 5.2 (W.L. Mattice, et.al., Macromolecules, 2003, 36 (26), 9924–9928).

Furthermore, since the end-to-end distance is expressed by equation (2), the number of intersections is given by equation (3).

$$R_{rms} = l \times \sqrt{n} \times \sqrt{C_n} \qquad (2)$$

$$N_x = {nl}/{R_{rms}} - 1 \qquad (3)$$

For clinging to occur stably, N_x must be 4 or greater. Therefore, if we let the total number of atomic groups when $N_x = 4$ be n_{4x}, then equation (4) holds.

$$4 = \frac{n_{4x}}{\sqrt{n_{4x}} \times \sqrt{C_{4x}}} - 1 = \frac{\sqrt{n_{4x}}}{\sqrt{C_{4x}}} - 1 \qquad (4)$$

Substituting equation (1) into this, we obtain equation (5).

$$n_{4x} = 25C_{4x} = C_\infty \left(1 - \frac{A}{n_{4x}}\right) = 25 \times 6.7 \left(1 - \frac{5.2}{n_{4x}}\right) \qquad (5)$$

Solving this equation, n_{4x} becomes 162, and the molecular weight corresponding to n_{cl} (M_{cl}) is 1816.

$$M_{cl} = M_{4x} \times 0.4 = 1816 \qquad (6)$$

This value closely matches the measured value M_e, supporting the validity of this study.