

<연구논문>

입자크기와 마찰효과가 용융 과정에 미치는 영향 Part I : 회분식 혼련기

김동성[†] · 박영진 · 이봉규 · 김형수* · 이재욱**

LG전선(주) 기계부문 메카트로닉스 연구소, *단국대학교 화학공학과, **서강대학교 화학공학과
(1999년 1월 21일)

A Study of Size and Frictional Effects on the Evolution of Melting Part I : Batch Mixer

Dong Sung Kim[†], Yung Jin Park, Bong Kyu Lee, Hyung Su Kim* and Jae Wook Lee**

Mechatronics R&D Center, LG Cable and Machinery

*Department of Chemical Engineering, Dankook University
San 8, Hannam-Dong, Yongsan-Gu, Seoul, 140-714, Korea

**Department of Chemical Engineering, Sogang University
1 Shinsu-Dong, Mapo-Gu, Seoul, 121-742, Korea

(Received January 21, 1999)

요 약

폴리프로필렌(PP) 수지의 회분식 혼련기에서의 용융 거동을 입자들의 크기와 첨가제들의 마찰특성과 연관지어 연구하였다. 사용된 PP는 파우더와 펠렛 두 가지 형태였고 각각의 수지에 폴리에틸렌(PE) 왁스와 클레이(clay)를 첨가하였다. 작은 크기를 가지는 PP 파우더의 경우가 펠렛 형태의 PP보다 용융 속도가 빨랐으며 마찰효과가 큰 클레이는 PP수지의 용융속도를 효과적으로 촉진시키는 것으로 확인되었다. 한편 PE왁스의 경우는 펠렛 형태의 PP의 용융 속도를 지연시키는 작용을 하였으나 파우더 형태의 PP의 경우에는 오히려 그 속도를 촉진시키는 것으로 나타났다.

Abstract—Effects of particulate size and frictional characteristics were examined on the melting behavior of PP (polypropylene) in a batch mixer. Powder and pellet types of PP were used and each component was blended with PE (polyethylene) wax and clay, respectively. It was observed that small size particulates, i.e. powder systems exhibit accelerated melting behavior; and it was also found that the abrasive additive acts as an effective agent for fast melting of PP powder. Retardation of melting due to the reduced friction was observed in PP pellet/PE wax blends, while melting rate of PP powder was increased by addition of PE wax.

Keywords: melting behavior; PP; friction; particulate size

1. Introduction

In most compounding operations of polymeric materials, the components are fed into the machine as solid pellets, spheres or powder. During this process, a large amount of energy input is consumed to transform the solid feed into melt. Recently, the melting of the solid feed becomes one of the major task throughout the compounding process by recognizing the fact that it often determines the maximum output rate of acceptable quality extrudate. Thus, understanding the melting phenomena would no doubt help in optimizing energy consumption and the design of screw configuration. Based on this motivation, there have been a

number of studies on this area. For example, Tadmor and Gogos[1] described extensively the mechanism of melting classified by three major routes; (a) conduction without melt removal, (b) conduction with melt removal and (c) dissipative mix melting. Conduction alone is not effective because of the generally low thermal diffusivity of polymers in both solid and molten state. Thus they concluded that removing the melt as it is formed will provide better melting because it exposes a new solid layer to the hot barrel and the rolling flow generates appreciable thermal energy. They have also indicated that in the mix melting process which occurs in the first kneading elements of a twin screw extruder, heating by inter-particle friction is

more advantageous and efficient than simple heat conduction from barrel walls. Shih et al.[2] observed rheological changes in amorphous and semi-crystalline polymers during melting in a batch mixer. Four stages of melting are specified as follows; (i) Elastic solid pellets at temperature below T_g or T_m , (ii) Deformable solid pellets as the material gets softened, (iii) A transitional stage at T_g or T_m depending on the nature of the material, and (iv) A viscoelastic fluid at temperature 20 to 50°C above T_g or T_m coupled with a decrease in the measured torque. Curry [3] investigated the melting mechanism of amorphous and semi-crystalline polymers including SAN(styrene-acrylonitrile copolymer), LDPE(low density polyethylene), and PP(polypropylene) through carcass analysis using a twin screw extruder. The author identified the progression toward melting as follows; (i) loose particulates, (ii) joined structures, (iii) compressed masses, (iv) fluid poor aggregates, and finally (v) homogeneous melt. Although there are additional works[4,5] conducted to analyze melting characteristics of various polymers in a twin screw extruder, most of the previous studies were limited to melting of a single component system.

In many industrial processes, however, various kinds of additives, fillers, and other polymers are frequently introduced to enhance the performance of the base polymer. Thus, it is important to investigate and understand the effect of interplay between the components on the melting characteristics of the designated compound. In this study, it is intended to examine two main aspects: (i) effect of particulate size and (ii) addition of lubricant or abrasive additive on the evolution of melting in a batch mixer. This study is expected to provide a fundamental insight on the mechanism of melting in the kneading paddle section of a twin screw extruder, which will be published in the future.

2. Experimental

2.1 Materials

The materials used in this study are all commercially available polymers and their details are summarized in Table 1. The PP6501 is a free flowing powder with particle sizes ranging from 20 to 400 μm . The majority of the particles are of 200 to 300 μm in size. For stabilization purpose, 0.5% of Iganox 1010 powder and 0.25% of Iganox B225 have been added. The friction coefficients between barrel surface and polymer for various types of PP were measured as a function of pressure discharge following a

Table 1. Materials used in this study

Material	Designation	Maker	Form	T_g (°C)	T_m (°C)
Polypropylene	PP 6501	Montell	Powder	-20	165-175
	PP 6523	Montell	Pellet	-20	165-175
Polyethylene wax	PE wax	Frank Ross	Micro-pellet	N/A	55-60
Clay(Translink)	Clay	Engelhard	Powder	N/A	N/A

procedure proposed by Lee[6]. The friction coefficient of PP6501 was found to be ~ 0.34 . PP6523 is a stabilized grade in the form of disk-shaped pellet with 3 mm of diameter and 2 mm of height. The friction coefficient of PP 6523 was found to be ~ 0.25 . PE wax has micro-pelletized form which is in spherical shape with 1mm of diameter. Compared to PP, PE wax has a very low melting point in the range of 55-60°C and exhibit a constant viscosity of 4.0 E-3 Pa · s at 175°C. The clay used in this study is calcined kaolin, which is a very fine powder with average size of 1.4 μm .

2.2. Melting Experiments

An instrumented Brabender Plasticorder PL200 was used for this investigation. Each sample was prepared on a fixed volume basis of 90% and loaded at 180°C. The rotor speed was set to 30(low) and 90(high) rpm, respectively, to observe the effect of shear rate on melting. After loading, there was an initial fall in the measured temperature due to the introduction of the cold charge, the temperature, however, eventually continued rising steadily afterwards. Melting experiments were conducted under the nitrogen blanket to prevent material degradation. Also, these experiments were conducted 3 or 4 times at the given conditions, which produced similar trends. Hence the standard cases are presented in this paper.

3. Results and Discussion

3.1 Melting of Pure PP

The effect of particle size on melting rate of pure PP was studied using both types of powder and pellet at low shear rate(30 RPM) and at high shear rate(90 RPM), respectively. From the heat transfer point of view, solid pellets would take a longer time to be melted than homogeneous powders do, because the contact area between pellets is small and the thermal conductivity(k) of most gases is considerably less than those of polymers($k_{air}=0.026$ W/m²K; $k_{PP}=0.81$ W/m²K).[1] In addition, the heat transfer by conduction in unsteady state gives a good explanation

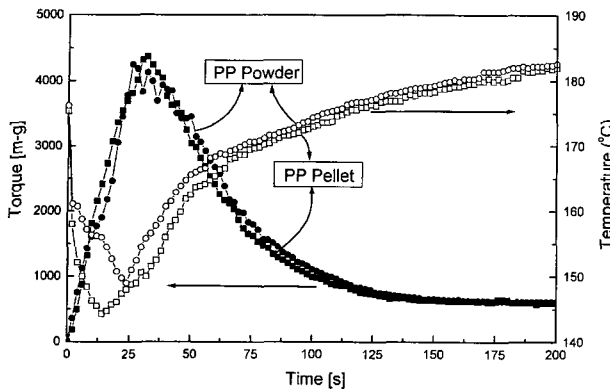


Fig. 1. Effect of particle size on melting rate of pure PP at 30 RPM.

how the particle size effects on melting when a fragment of solid is formed and it is surrounded by a sea of its own melt or melt of the other component of the blend. From the analysis given by Heisler[7], it is expected that the heat transfer by conduction is carried out by 4 times faster if the radius of particle is decreased by half. In physical point of view, size analysis and surface contact of each materials are important to understand the physical properties of materials in both batch mixer and twin screw extrusion. The calculated data relating to this issue are found elsewhere[8].

Fig. 1 represents the results obtained at 30 rpm. The torque traces of two experiments are not very different, however the temperature of the charge appears to be higher for powder than pellets. Based on the results shown in Fig. 1, the mechanical energy and thermal energy were calculated and plotted in Fig. 2 as a function of mixing time. For mechanical energy(ME) calculation, first the power can be calculated with the measured torque as follows;

$$\text{HP(horse power)} = \text{Torque(in.lb)} \times \text{Speed(rpm)} / 63000 \quad (1)$$

$$\text{Power} = \text{HP} \times 7.457 \times 10^2 (\text{W/HP}) \quad (2)$$

Then, ME per each gram of material can be calculated with this power by

$$\text{ME} = \text{Power (W)} \times \text{Time(sec)} = \text{Joules} \quad (3)$$

With this energy, the temperature change in 1 gram of the material can be predicted by using heat capacity data[5]. Since ME calculation is based on the torque evaluation, obviously it accounts for the energy required to deform the given solid particulates. Accordingly, in comparison of various ME values between different systems, it should be reminded that high ME value does not necessarily stand for effective melting of the component polymer. Nevertheless, ME can be recognized as an useful indication for

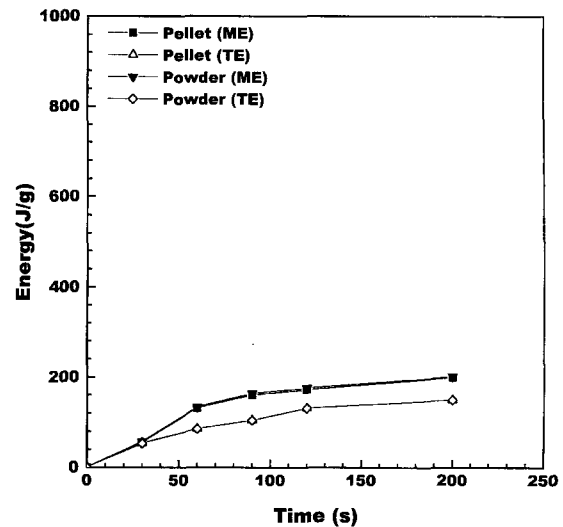


Fig. 2. Cumulative mechanical and thermal energy vs. Time for pure PP at 30 RPM.

discerning apparent status of friction in the blend system. For example, it is easy to expect reduced ME for the blend of PP with PE wax, as will be shown later.

In addition, the thermal energy(TE) by heat transfer can be estimated by

$$\text{TE} = A \times h \times \Delta T \quad (4)$$

where A = internal surface area of the mixer(112.48 cm²)

h = overall heat transfer coefficient(W/m²)

ΔT = temperature change by heating

In this calculation, the value for maximum power per area($h \times \Delta T$) is reported to be 6,000 W/m² and the heat transfer coefficient was assumed to be 60(W/m²)[4]. Since TE is basically supplied from the electrical heating unit of the mixer, little variation is expected for most of the systems considered in this study.

The calculated energy for the case of 30 RPM is represented in Fig. 2, where the mechanical energy input is relatively small and comparable with thermal energy for melting. At high speed, however, the mechanical energy input plays an important role in melting for both pure powder and pellet experiments as shown in Fig. 3.

Fig. 4 shows the data obtained at 90 RPM. The torque trace for powder appears to shift to left by 10 seconds from that of pellets, and the width of the torque trace of powder is narrower. In addition, the temperature drops lower at initial loading indicating a colder charge. As the melting progresses, the charged temperature crosses over the temperature curve for pellet and levels off at a higher temperature. These observations clearly represent that the particle size is quite important in setting the melting rate

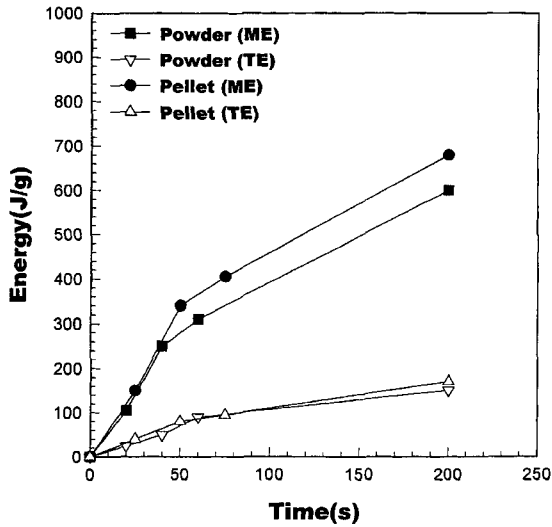


Fig. 3. Cumulative mechanical and thermal energy vs. Time for pure PP at 90 RPM.

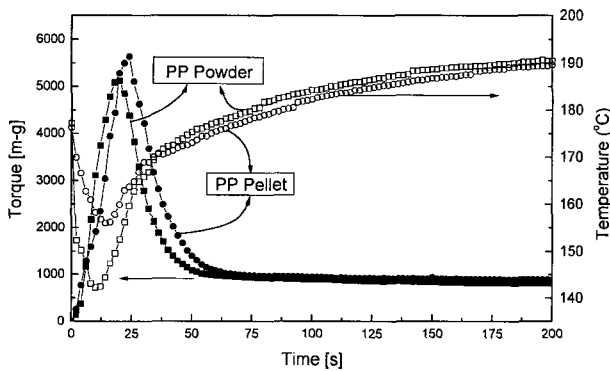


Fig. 4. Effect of particle size on melting rate of pure PP at 90 RPM.

and powders are melted faster than pellets in a high shear rate mode. The trend shown in Fig. 5 is closely related to the role of particle size based on two reasons: First, compared to pellets, powders with small size (~200 to 300 μm) should in principle, lead to faster heat transfer and consequently faster melting as previously mentioned. Second, powders can provide more chances to contact between particles themselves or particles and barrel surface, and furthermore, high frictional coefficient of PP powder also promotes high frictional heat, which in turn causes more frictional heating and faster melting of the charge.

3.2. Effect of Lubricant

When one component in a blend has a lower melting temperature, it will melt sooner than the rest of the components in melting and mixing process. An intermediate mixture composed of fluid and solid pellets is formed

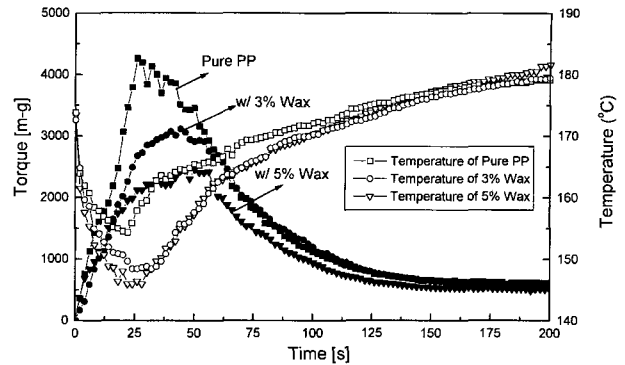


Fig. 5. Effect of lubricant addition on PP pellet at 30 RPM.

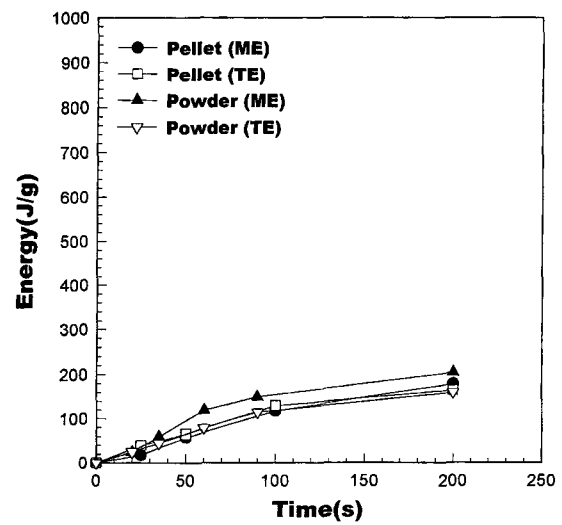


Fig. 6. Cumulative mechanical and thermal energy vs. Time for PP (95%)/PE wax(5%) at 30 RPM.

before the matrix polymer is softened. A two-component blend of PP pellet/PE wax was studied to examine the effect of earlier melting of the PE wax on the melting characteristics of PP pellets at 30 RPM(Fig. 5). The addition of 3% wax was found to retard the melting rate, and lower the torque peak. This is obviously due to the early melted PE wax, which acts as lubricant by covering the pellet surface and thus reduces friction between pellets or pellets and barrel. Increasing the amount of lubricant from 3 to 5% in the feed appears to retard more and more the melting process of the PP pellets. In addition, the mechanical energy input at 30 RPM was calculated to be smaller than that of pure component(Fig. 6).

It is important to note that the melting rates observed in a batch mixer are related to a constant volume of material which is 90% filling, which means that not much of free volume is present between the particles or particles and

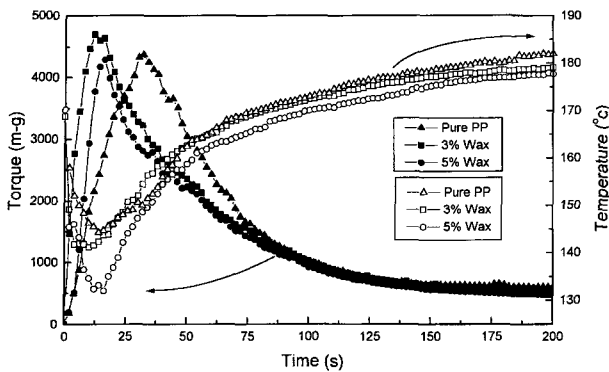


Fig. 7. Effect of lubricant addition on PP powder at 30 RPM.

the barrel surface. However, since early melted PE wax fills the void volume, better heat transfer is achieved with increasing the amount of lubricant, by which the temperature during the feed is lowered more sharply as increasing the amount of lubricant, and sharp increase in temperature after the initiation of melting to reach the melting point of PP pellets (Fig. 7).

The torque traces shown in Fig. 7 are quite different from those found in Fig. 5. When 3% of PE wax was added, the torque peak shifted to the left side and the width of the curve became narrower. In addition, the temperature decreased sharply to a lower point than for the powder and also increased sharply to reach the melting peak. A similar trend was observed when 5% of the PE wax was added. The melting rate was more accelerated in the case of PP powder/PE wax system. Two factors may be considered: First, the effectiveness of the small size on the enhanced heat conduction, which was previously mentioned, is also pertinent here. Second, the mobility of particles may be active in increasing melting rate in blend of PP powder and PE wax. Unlike the large size pellets, the small size powder particles may form compact agglomeration in the filled barrel. This state is expected to cause a tightly filled suspension which enables earlier melting by friction as well as solid deformation.

3.3. Effect of Abrasive Additive

Fig. 8 shows the results of melting experiments for pellets with two different amounts of clay at 30 RPM. This figure reveals that adding an abrasive component does not largely affect the melting rates for pellets at low shear rate. Comparison of the torque values in the viscoelastic fluid-region indicates that the viscosities of the three blends is comparable.

Fig. 9 shows the data obtained at 90 RPM. High rate of energy dissipation causes a rapid temperature rise in the

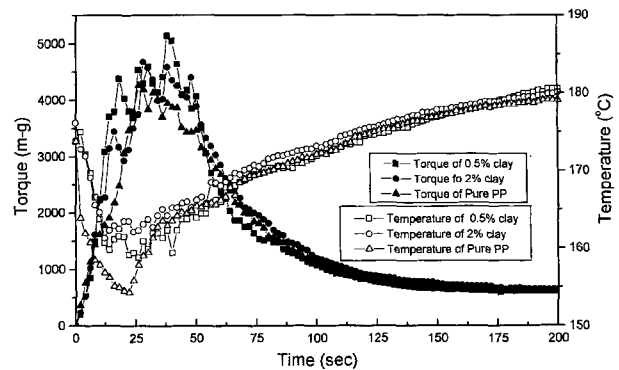


Fig. 8. Effect of abrasive additive addition on PP pellet at 30 RPM.

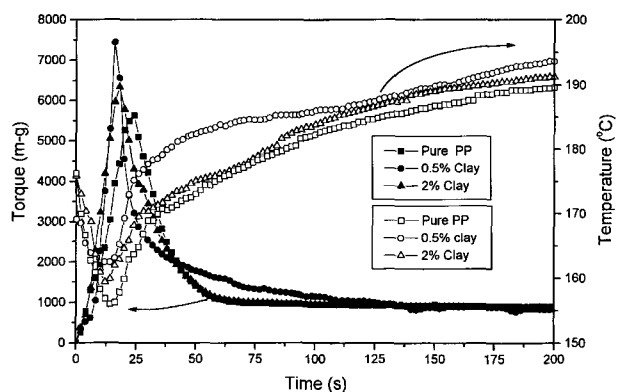


Fig. 9. Effect of abrasive additive addition on PP pellet at 90 RPM.

PP pellet/clay system which is reflected in the torque profile. Increasing the amount of clay affects the melting rates as the torque peak shifts to the left, i.e. earlier melting occurs, and the torque curves became narrower as well. This is an evidence that the melting rates have been sensitively influenced by frictional heating and the size differences between PP pellets and clay. According to the size analysis of the components [8], a single pellet is surrounded by 7.60×10^7 of clay particles and 2% of clay is pretty much enough to cover the pellets. Thus, if the clay particles are not agglomerated or even if they are agglomerated, the pellets with 2% clay blend should be able to provide more heat energy dissipation by friction.

Unlike PP pellet/clay blends at low shear rate, experiments with PP powder/clay blends show a considerable effect of the clay on energy dissipation which causes a faster melting and rapid temperature rise as shown in Fig. 10, where the torque curves of both 0.5% and 2% clay blends shift to the left for 20 seconds from the curve for pure PP powder, and they become narrower with increasing amount of clay. Again, the trends found here parallel the notion that smaller size and higher frictional coefficient of the particulate lead to larger heat dissipation

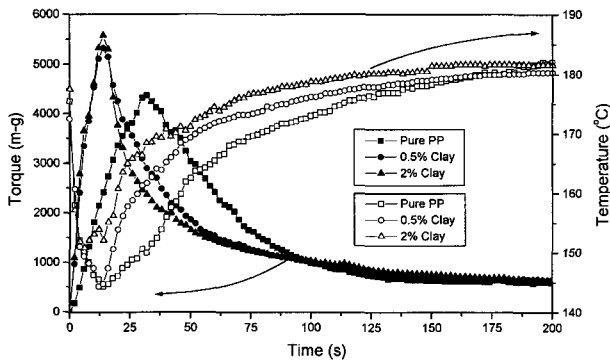


Fig. 10. Effect of abrasive additive addition on PP powder at 30 RPM.

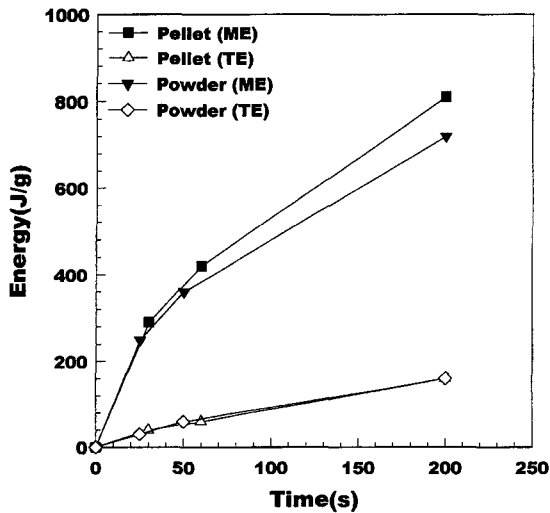


Fig. 11. Cumulative mechanical and thermal energy vs. Time for PP (98%)/Clay(2%) at 90 RPM

and hence faster melting. While previous results revealed significant difference between low and high RPM, the frictional effect on melting for PP powder/clay blends at 90 RPM was not much different, except the slightly higher torque, from the corresponding case of low RPM, which reflects the activity of clay as an abrasive ingredient over a broad range of rotor speed. From the calculation for energy input at 90 RPM, the mechanical energy turned out to be about 20% more than the each case of pure pellet and powder by introducing clay (Fig. 11).

4. Conclusions

The evolution of melting in pure PP and PP with additives appears to be strongly influenced by the particle size and frictional characteristics of the additives, especially at high RPM. Melting of PP pellet/PE wax blends has been retarded by increased amount of PE wax, which is explained by the lubrication effect of PE wax filling the void volume between solid particles. On the contrary, melting rates of PP powder/PE wax were accelerated as the amount of PE wax increased. Since about 90% by volume of the mixer is occupied, earlier melting of PE wax promotes wetting the surface of the solid particles and barrel as well. At this stage, unlike with large size pellets, small size solid powders would constitute more compact entity in the filled barrel. This environment enables to form tight suspension between particles, by which melting is expedited by enhanced compression and shearing.

Melting rates of PP pellet/clay blends have been accelerated compared to those of pure PP and PP/PE wax system. Here melting occurs with large interparticular friction due to the fact that the clay acts as abrasive additive which leads to higher frictional heat and more mechanical energy.

References

1. Z. Tadmor and C.G. Gogos, "Principles of Polymer Processing", John Wiley & Sons, New York, 1979.
2. C.K. Shih, D.G. Tynan, and D.A. Denelsbeck, *Polym. Eng. Sci.*, **31**, 1670(1991).
3. J. Curry, *SPE ANTEC Tech. Papers*, **53**, 92(1995).
4. D.B. Todd, *SPE ANTEC Tech. Papers*, **50**, 2528(1992).
5. M. Esseghir and D.W. Yu, *Proc. 11th Semiannual Meeting, Polymer Mixing Study*, PPI, May(1996).
6. B.K. Lee, PhD Thesis, Stevens Institute of Technology, May (1997).
7. M.P. Heisler, *Trans. ASME*, **69**, 227(1947).
8. D.S. Kim, Master Thesis, Stevens Institute of Technology, December(1997).