

Melt Blowing Polyoxymethylene Copolymer

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Abstract

Polyoxymethylene (POM) copolymer is one of the relatively new, high performance engineering polymers. Its high crystallinity provides this polymer with excellent properties, including great tensile strength and stiffness, high toughness, good resilience, and low surface friction. POM also possesses excellent chemical resistance to a wide range of materials, comparing favorably with many thermoplastic polymers.

Fine fibered products of POM may find applications in specialty filtration, such as hydrocarbon fuel filtration, and hydraulic fluid filtration.

This paper discusses the melt blowing process for POM with an emphasis on the effects of spinnerette setting on the fiber property. It also discusses the relationship of process/web properties for this specific polymer and compares it with that of PP in terms of processability.

Key Words

Melt blowing, Spinnerette, Polypropylene, Polyoxymethylene, Microfiber

Introduction

Polyoxymethylene (POM) is a high-molecular-weight polymer of formaldehyde with the hydroxyl ends stabilized by etherification or esterification. It is often referred to as acetal homopolymer or polyacetal, which distinguishes it from polyformaldehyde, a low molecular weight, thermally unstable, and waxy material. POM is one of the high performance engineering polymers. It is available in the market as a homopolymer or a copolymer. Its high crystallinity provides excellent properties, including great tensile strength and stiffness, high toughness, good resilience, and low friction. POM also possesses excellent chemical resistance to a wide range of materials, comparing favorably with many thermoplastic polymers [1,2].

Turning this unique thermoplastic into fine fibered products is of interest to many industry engineers and scientists. Melt blowing (MB), a process of making fibrous products directly from a polymer resin, is on the top of their selection lists. The MB process utilizes high velocity hot air to attenuate extruded molten filaments into microfibers very rapidly, almost instantly. The fibers are then deposited on a collecting surface to form a self-bonded, nearly randomly oriented nonwoven web [3].

Since the concept of MB was introduced in 1950s, especially in the past 20 years, tremendous R&D efforts had been made from both academia and industries [3]. A variety of polymers were thoroughly explored. However, very little literature is available for melt blowing POM.

Numerous products of different polymers, such as filter media, absorbent materials, wipes and battery separators, have been developed and commercialized by utilizing a melt blown technology. According to the published data on the demand of nonwoven roll goods in the U.S. [4], it is estimated that melt blown product sales could increase to \$500-600 million in 2007. Polypropylene (PP) MB products will still be the majority in the market. Although POM has great overall properties, only recently has a MB grade Acetal copolymer become available [5]. Fine fibered products of POM may find applications in specialty filtration, such as hydrocarbon fuel filtration, and hydraulic fluid filtration. Many other applications are yet to be explored. As a new member of MB-capable resins, the Acetal copolymer has a long way to go. Extensive research and development efforts are required to effectively manufacture Acetal MB products.

This paper discusses the MB process for POM with an emphasis on the effects of spinnerette settings on the fiber property. It also briefly discusses the relationship of process/web properties for this specific polymer and compares it with that of PP.

Experimental

Materials

POM pellets, under the trade name of Celcon[®], is a melt blown grade copolymer (grade FG40U01 CF2001), supplied

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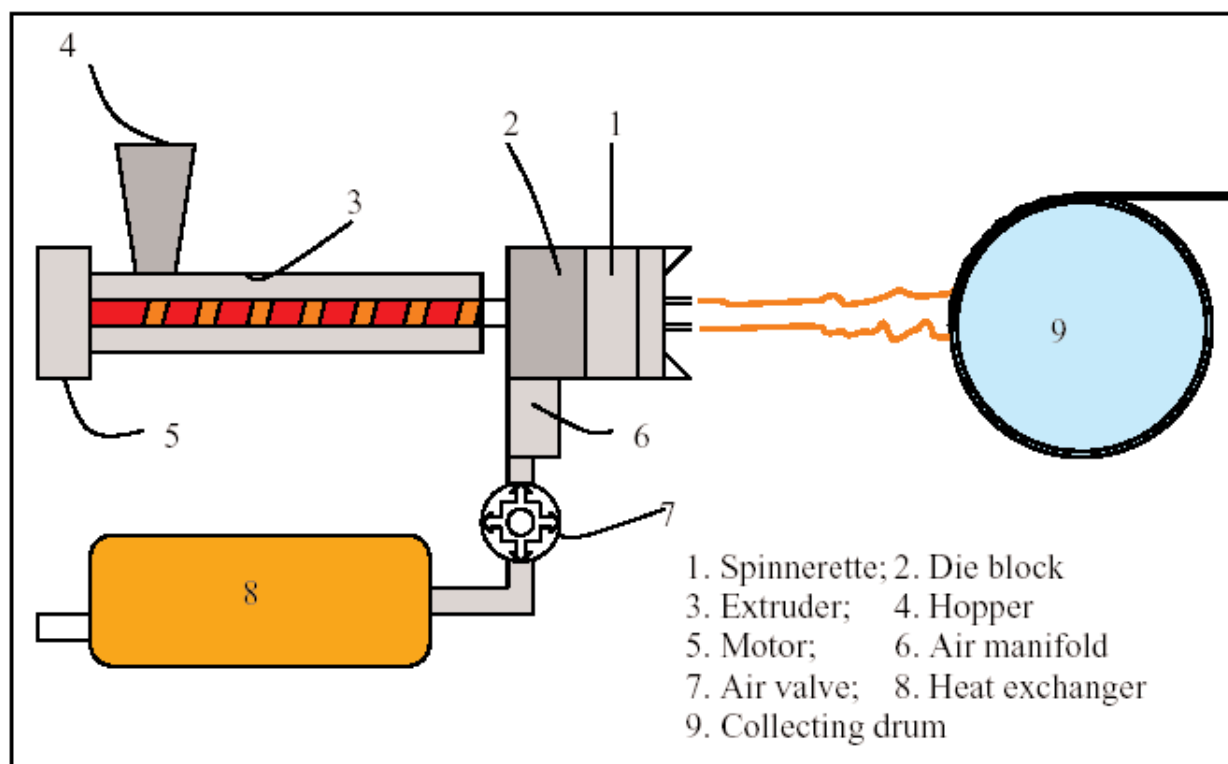


Figure 1
A SCHEMATIC DRAWING OF A MB PILOT LINE

by Ticona, NJ. The polymer has a nominal melt flow rate (MFR) 40g/10 min at 230°C and a melting temperature 165°C. Its specific gravity is in the range of 1.4-1.8g/cm³.

A 35 MFR polypropylene (PP) resin, supplied by ExxonMobil Chemical Company, is also employed for purging the MB system after the experiments.

Equipment

This study is conducted utilizing a 5-inch MB pilot system installed in the main facility of Biax Fiberfilm Corporation, Greenville, WI. This pilot line is equipped with a 1-inch extruder, a heat exchanger, a 5-inch spinning head assembly, and a drum collector. A schematic drawing of the MB pilot line is presented in *Figure 1*. The 5-inch spinnerette is a two-row-concentric-nozzle-type [9], with a total of 126 spinning holes. The nozzle inside diameter is 0.5 mm. *Figure 2* shows the schematic structure of the spinnerette. The distance between the spinning nozzle tip to the surface of the top plate (DTT), is an important factor for successful melt blowing of any suitable polymer. By utilizing spacers, the DTT can be adjusted accordingly.

Processing and sample preparation

In addition to DTT, the polymer throughput, airflow rate, melt/metal/air temperatures, and melt/air pressures are also important process parameters, which need to be carefully controlled for a MB process. The experimental settings of these variables are listed in *Table 1*. There are 3 thermocouples, a pressure transducer and a pressure gauge installed in the

spinning head for monitoring and controlling the air, melt, and die metal temperatures, the melt pressure, and the air pressure, respectively. The polymer throughput is directly controlled by the extruder screw speed and the airflow rate is adjusted by a conventional valve. At the end of the trials, the system is purged with a 35 MFR polypropylene.

At each processing condition, the fiber samples were collected at different locations along the MB spin-line with a device as described in references 6 and 7. The fiber sizes were determined by using an optical microscope, a CCD video camera, and an image analyzing software (NIH1.62, Scion Corporation). After proper calibration, 150 fiber diameters were recorded and the average is reported for each designated positions along the spin-line. The fiber diameter distribution profile was constructed by plotting the frequency of fiber diameter against the corresponding categorical group of the fiber size.

Results and discussions

1. The Resin

The key resin parameters include molecular weight, molecular weight distribution, additives, and the structure of the polymer, which are inherent properties affecting the process and the end product properties. Commercially, the molecular weight is indicated by melt flow rate (MFR), a term defined as the gram of polymer melt passing through a standard capillary within 10 minutes under a constant pressure at a standard temperature. For polymers of the same type, the higher the

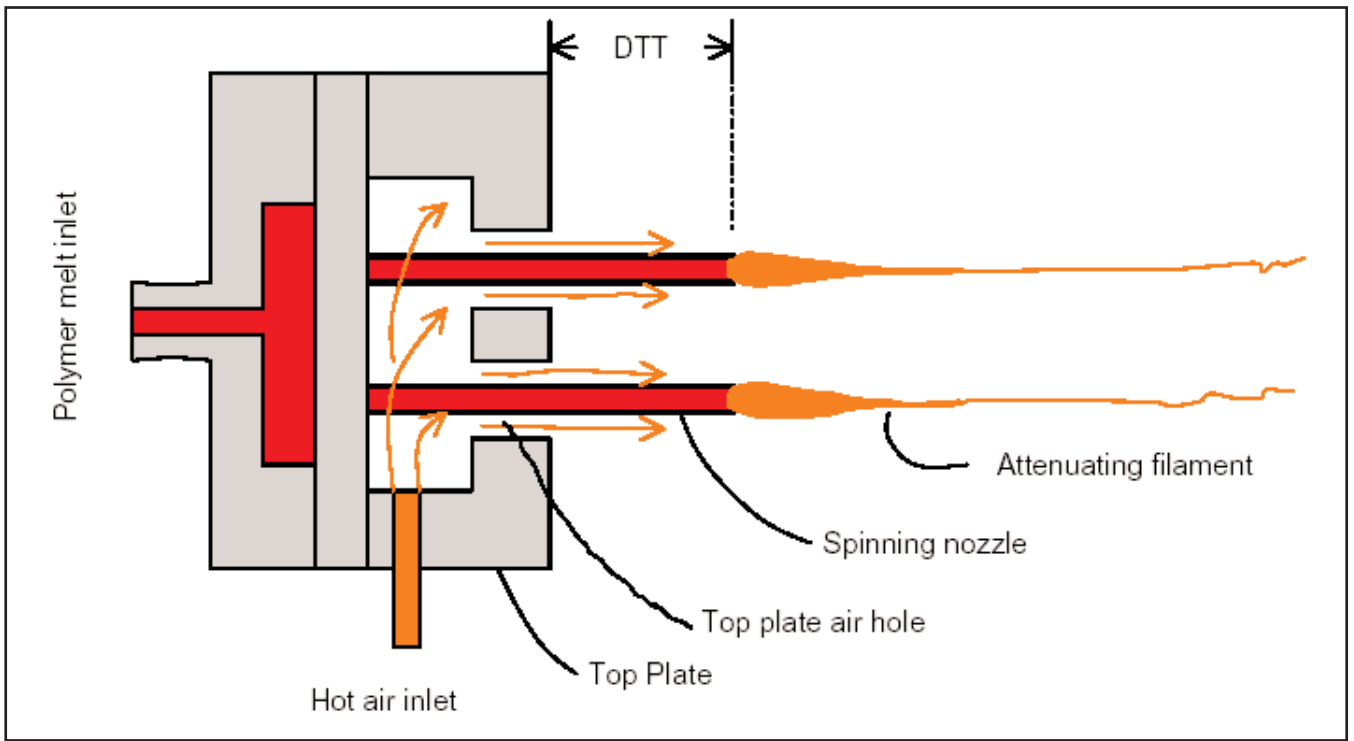


Figure 2
SCHEMATIC STRUCTURE OF THE SPINNERETTE

MFR, the lower the average molecular weight. Molecular weight distribution (polydispersity) is defined as the ratio of the weight average molecular weight divided by the number average molecular weight. Polydispersity is normally controlled by polymerization method and the use of different catalysts. A higher polydispersity for a resin is always associated with higher elongational viscosity of the polymer melt. Since production of finer fiber is one of the most important goals of the melt blown technology, polymer resins with higher melt flow rate and narrower polydispersity are preferred for

advanced fiber attenuation.

Although POM (FG40U01 CF2001) is a melt blown grade copolymer, it has a very low melt flow rate of 40g/10 min at 230°C according to ASTM D1238, which indicates that the resin has a high average molecular weight. The apparent melt viscosity measured at 450°F ranged from 75 Pa·s to 120 Pa·s at a moderate shear rate (2000 s⁻¹ to 200 s⁻¹), which is much higher than that of a MB grade PP (3 ~ 10 Pa·s) under its processing condition. Therefore, it is not surprising to find high melt pressure during the experiments, as presented in *Table 1*.

Table 1
PROCESSING CONDITIONS OF MELT BLOWING POM COPOLYMER

		Trial 1	Trial 2	Trial 3	Trial 4
<u>Extruder</u>	Zone 1	300°F	332°F	322°F	322°F
	Zone 2	400°F	405°F	405°F	405°F
	Zone 3	420°F	440°F	440°F	440°F
	Transfer line	430°F	444°F	444°F	450°F
<u>Spinnerette</u>	Melt pressure	1500 PSI	1378 PSI	1360 PSI	1268 PSI
	Melt temperature	426°F	437°F	433°F	442°F
	Air Pressure	10 PSI	11 PSI	11 PSI	11 PSI
	Air temperature	440°F	450°F	450°F	470°F
	DTT ¹	3.05 mm	1.52 mm	1.10 mm	0.13 mm

¹ Distance between the spinning nozzle tip to the surface of the top plate

2. General Observations

Under the conditions of Trial 1, the filaments solidified quickly near the exits of the spinnerette. The fibers exhibit relatively large diameter and brittleness, indicating very limited fiber attenuation. With a mechanical drawing device, the filaments can be drawn into very nice fibers. These fibers are stiff, strong and straight.

Trials 2 and 3 were conducted under a higher temperature profile and a reduced DTT. The filament attenuation is improved and fibers are much finer compared with those made in trial 1. However, the fibers are individual filaments without any bonding. There are no webs formed although the collecting distance varied from 5 to 18 inches.

With a different die setting and a higher air temperature, Trial 4 produced finer fibered MB webs, which presents a uniform web structures.

3. Fiber diameter

The fiber attenuation profiles are presented in Figure 3. For Trials 2, 3 and 4; POM fiber diameter reduces dramatically within the first 5 cm from the spinnerette, similar as those of melt blowing PP. The fiber diameter continues to decrease in the second 5 cm with a much lower attenuation rate. Beyond 10 cm from the spinnerette, the fiber size reduction is minimal under the experimental conditions. A preliminary examination reveals that the fiber diameter distribution is relatively narrow.

The effect of spinnerette setting on the fiber diameter profile is significant, as shown in Figure 3. At DTT of 3.05mm, the fiber size is measured 230 μm at and beyond 1.3 cm from the

spinnerette. This observation indicates that the fibers were solidified quickly after extruded through the spinning nozzles. With the decrease in TDD, one can find that the fibers attenuate much faster in the area close to the spinnerette.

By considering each individual air jets, one can estimate the air jet temperature profile by the following empirical formulation [8],

$$\frac{T_a - T_\infty}{T_{j,0} - T_a} = 1.79 \left(\frac{W}{z} \right)^{0.465}, \text{ if } z \geq 3.5W$$

$$T_a = T_{j,0}, \text{ if } z \leq 3.5W$$

Where:

T_a : the local air jet temperature

T_∞ : the ambient temperature,

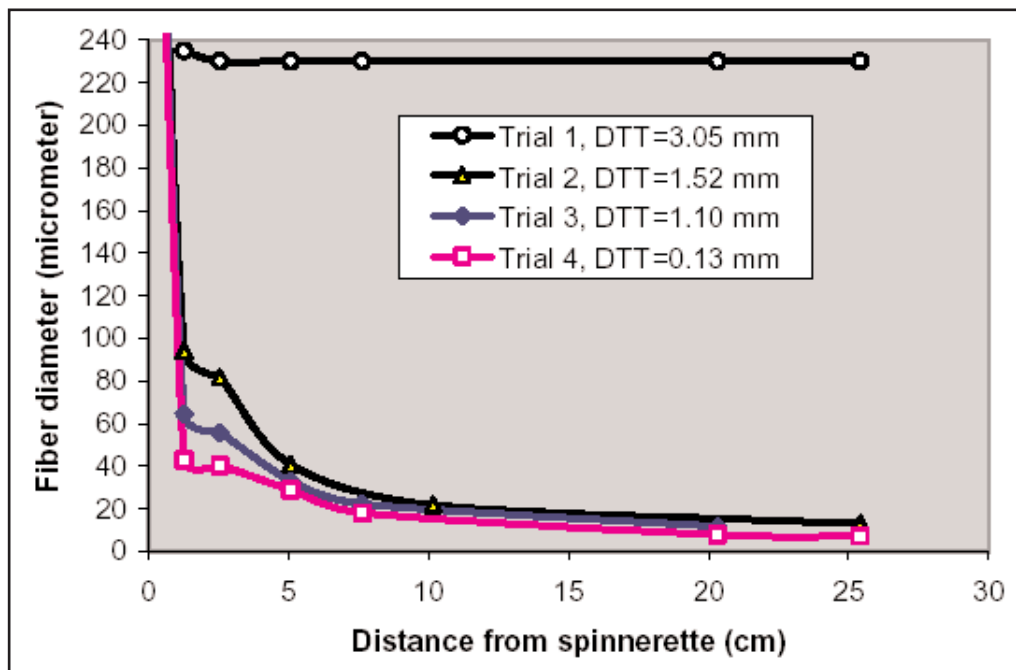
$T_{j,0}$: air temperature at the exit

W : the diameter of air jet, and

Z : distance from the air exit

For this study, the ambient temperature is 70°F, and the air jet diameter is 0.4572 mm. From these equations, the air jet temperature profiles can be calculated as shown in Figure 4. The air jet temperature remains constant for a very short time and then decreases dramatically due to rapid expansion and the involvement of the ambient air. In the case of Trial 1, the DTT equals 3.05 mm, the air temperature at the spinning nozzle tip is 344°F (173.3°C), which is only 10-15°F higher than POM's melting temperature and 211°F (99.4°C) at a distance of 12.7 mm from the spinnerette top plate. It is not difficult to understand that the filaments' elongational viscosity at the nozzle tip is large enough to resist the air dragging force. In the case of Trial 2, the DTT is 1.52 mm; the air temperature at the spinning nozzle tip is 450°F, which reaches 330°F at a distance of 3.5 mm from the spinnerette top plate. Similarly, for trial 4, the DTT is 0.13 mm; the air temperature at the spinning nozzle tip is 470°F, which reaches 330°F at a distance of 4.0mm from the spinnerette top plate. As the DTT decreases and the air temperature increases, the filaments have longer time to be exposed to high temperature air jet. In other

Figure 3
POM MB FIBER DIAMETER PROFILES AT DIFFERENT CONDITIONS



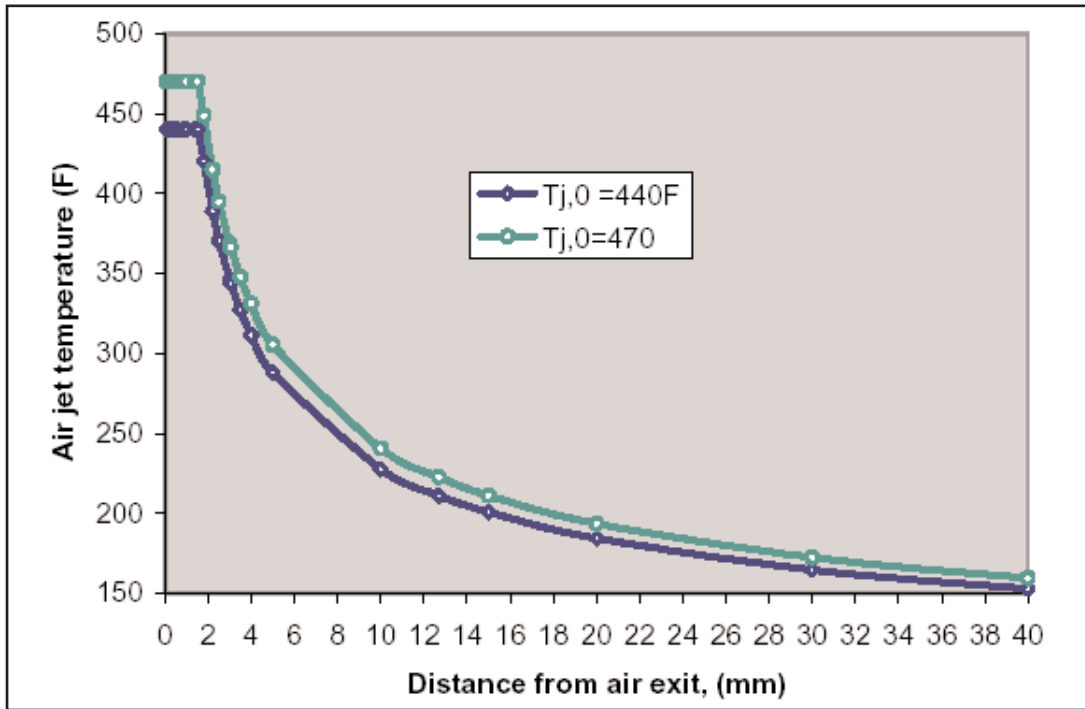
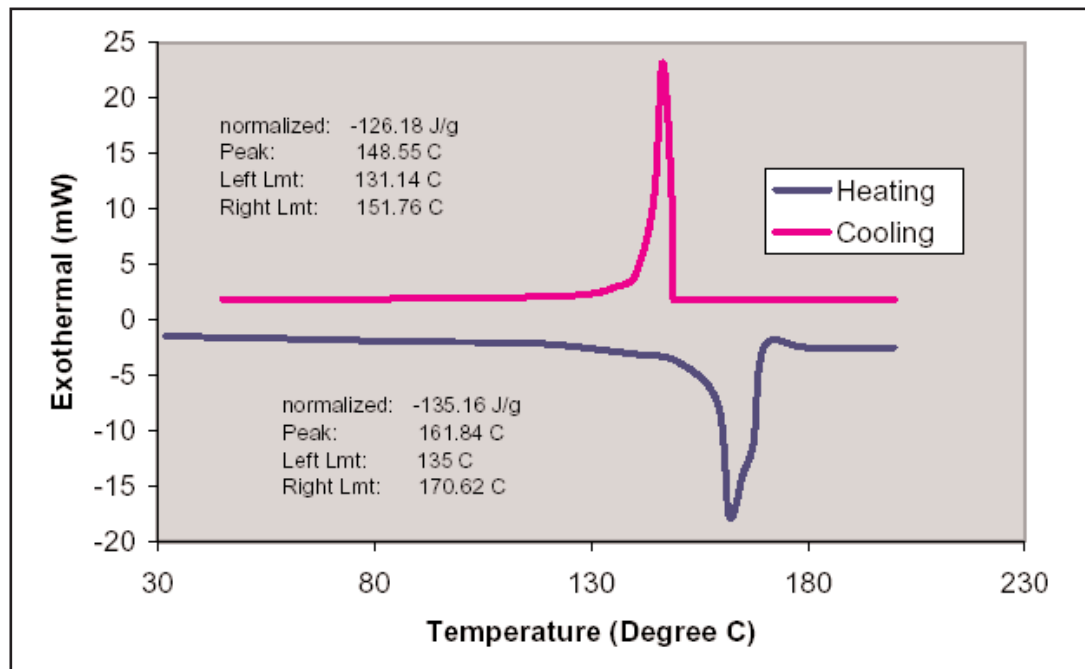


Figure 4
CALCULATED AIR JET TEMPERATURE PROFILES

words, the filaments should be kept under higher temperature for a longer distance, which is critical for major fiber attenuation. As shown in *Figure 3*, Trial 4 exhibits more attenuation compared with Trials 1, 2, and 3. Therefore, the spinnerette setting is one of the most important operation parameters.

inert in many cases, so no reaction will occur when it comes in contact with most of the common polymers. On the other hand, there are not many choices for melt blowing POM. The one used in this study is currently the highest in melt flow rate that is available for melt blowing process. The MB operation window is much smaller than that available with PP.

Figure 5
DSC CURVES OF POM MB MICROFIBERS



4. A Comparison with PP

Compared to PP, POM is more challenging for making fine fibered webs due to its unique properties. Melt blown grade PP resins have a broad spectrum of availability ranging from a few hundred MFR up to 2000 MFR. Even 35 MFR PP can be used for melt blowing. PP is more forgiving in terms of its operation window. Thermal degradation will happen significantly only when the processing temperature approaches 600°F with a prolonged resident time. PP is chemically

During processing, the POM melt should not be in contact with polyvinyl chloride or oxidizing agents at any time. Great care shall be taken when attempting to reduce the melt pressure by increasing temperatures. Excellent ventilation during the operation is highly recommended since decomposing POM may generate formaldehyde.

POM MB fibers exhibit high crystallinity due to the excellent structural regularity. The thermal analysis (scanning differential calorimetry (DSC))

results (Figure 5) reveal that POM MB fibers have a heat of fusion value of 135.16 J/g, which reflects an 41.42% crystallinity (Heat of fusion for 100% crystalline POM is 326.3 J/g [2]). The DSC cooling curve showed that the POM crystallization started at about 150°C (302°F) and stopped at about 130°C (266°F). Considering the average fiber velocity, the crystallization happens in a fraction of a second. The drag force of primary air causes the polymer molecular orientation along the fiber axis, which promotes the formation of the crystalline structures. The cooling effect from both primary hot air expansion and secondary ambient air also contribute the relatively high crystallization.

When compared with PP, POM MB fibers are more silk-like with significantly fewer fused fiber bundles. POM MB web is not as readily made as that of PP. Special efforts, including spinnerette settings, air temperatures, air volume, and DCD, need to be made for producing a MB web. The fiber-to-fiber bonding is not strong due to the fibers' crystalline nature, which results in unique web structures.

Summary

This preliminary study shows that melt blowing POM is, at present, considerably more challenging when compared with melt blowing PP. However, it was shown that POM can be attenuated to microfibers and producing well-bonded webs requires special efforts to fine tune the process conditions. The products produced exhibit excellent air permeability, good resilience, and low friction properties. A modified MB system is being assembled to deal specifically with highly crystalline polymers such as POM. To ensure a friendly melt blowing process with a large operation window, the development of POM with higher melt flow rate will be appreciated by process engineers, which may also provide a challenging development task for polymer scientists. Further study using this system will be conducted in the near future with a focus on the process/property relationship and application development. The author would like this report to initiate the interest of industry leaders in potential market applications for POM MB.

Acknowledgement

The author is grateful for Ticona and ExxonMobil for providing polymer resins for this study. He also thanks Drs. Yizhong Wang, Haoming Rong, and Arvind Karandikar for their help and suggestions. The assistance from his colleagues at Biax Fiberfilm Corporation is greatly appreciated.

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