ADVANTAGES OF NEW METALLOCENE-BASED MELTBLOWN RESINS

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INTRODUCTION

Metallocene catalysts for propylene polymers were developed in the late 1980s and early 1990s. Propylene polymers made with these novel catalysts were first commercialized by EMCC in 1995. These new metallocene-based materials have found commercial success in applications such as spunbond nonwovens, high-strength fibers, and medical devices. Narrow molecular weight distribution (MWD), consistent rheology, high clarity, and cleanliness are among the valued attributes.

Now metallocene technology has been extended to high melt flow rate (MFR) resins for meltblowing applications. The topic of today’s presentation will be the advantages of metallocene propylene polymers in meltblown applications.

MATERIAL PROPERTIES

Whereas traditional Ziegler-Natta (Z-N) catalysts produce broad MWDs and require controlled rheology (CR) treatment to raise the MFR and narrow the MWD, metallocene catalysts produce high MFR, narrow MWD products directly in the reactor. The narrow MWD and exceptional cleanliness of metallocene products make them well-suited for spunmelt processes such as spunbond, traditional fiber spinning, and meltblowing.

Our newest product, called Achieve™ 6936G1, is a 1500 MFR metallocene propylene polymer designed specifically for demanding meltblown (MB) applications. This material is produced as a free-flowing powder. As a result of its inherent narrow MWD and the absence of oligomers typically produced by a CR process, this material has exceptionally low extractables, as will be shown later. Since no peroxide is used in the manufacture of these metallocene resins, they are able to meet the requirements of FDA regulation 21 CFR 177.1520(c) 1.1b.

The shear viscosity of high MFR materials is difficult to measure because of the low rheological forces generated during testing. A special technique using a small diameter capillary with high length/diameter (L/D) was used to measure the shear viscosity of the new material. A comparison to conventional peroxide-coated granules (PCGs) of comparable MFR shows the mPP has similar apparent shear viscosity over a range of temperatures covering typical meltblowing (MB) processing temperatures.

MELTBLOWN PROCESSING

Increasing line speeds, lighter basis weights, and higher performance expectations have placed greater demands on meltblown resins in recent years. The meltblown process requires low viscosity polymer and very consistent melt rheology at the die tip. The low viscosity allows the molten polymer filament to be easily drawn to fine fibers in the high velocity MB air stream. Consistent rheology
at the die tip is required for best operability. Small-scale variations in the
elongational rheology at the nose tip of the die can result in fiber breaks. Fiber
breaks can lead to “fly” and/or “shot” and lower the quality of the MB fabric. Also,
if the rheology drifts over long periods of time, the process conditions may have
to be readjusted occasionally to produce the best fabrics.

The absence of peroxide eliminates one source of variability in resin viscosity at
the die tip. The rheology of the resin no longer depends on the concentration and
uniformity of peroxide. Also, since there is no longer a chemical reaction during
the extrusion process, the metallocene polymers are less sensitive to melt
temperature and residence time variations.

Melt temperature has a significant effect on the viscosity of the resin and is a key
variable in optimizing the meltblown process. If the melt temperature is too low,
the fibers will not draw down easily and higher air rates will be required to
produce fine fibers. The fabrics produced at such conditions will not be as
uniform as those produced at higher temperatures and will tend to feel stiff or
course. As melt temperature is increased, the fabrics will become more uniform
and the maximum air rate that can be achieved without “fly” will be reduced. If the
temperature is too high, however, the fibers will not cool down quickly enough to
prevent excessive shot formation. Shot can “burn” through thin MB fabrics
causing a severe reduction in liquid barrier properties. For hygiene type fabrics,
the optimum temperature is usually the maximum temperature that can be run
without generating excessive shot. At optimum process conditions, the best
balance will be struck between fabric uniformity, low shot, and softness. The
best process conditions for hygiene type fabrics can be determined by measuring
hydrohead and air permeability values as process conditions are varied.

The liquid barrier properties of meltblown fabrics generally improve as air rates
are increased at a given temperature. The air rates in this study were set by
increasing the air until “fly” was produced and then reducing the air rate until the
fly disappeared. The air rates were optimized in this manner for each throughput
rate, process temperature and die-to-collector distance (DCD) used. The air
temperature was set close to the die temperature in this study. Fabrics were
produced over a range of die/air temperatures to find the best conditions for each
material.

Although DCD at normal operating conditions has little effect on fiber size, it is a
critical factor in determining fabric uniformity and shot formation. Higher DCD
results in less uniform, more lofty fabrics and reduced shot formation. Lower
DCDs produce more uniform fabrics, but may result in increased levels of shot.
DCD should be optimized for each type of material, MFR, throughput, process
temperature, basis weight and belt speed.
FABRIC PROPERTIES

An array of designed experiments was conducted to explore the meltblown product properties, improvements in process efficiency, and potential for increased productivity. Initial trials were conducted on the 0.5 m MB pilot line at TANDEC. These were followed by trials on a commercial 4.2 wide Reicofil® 3 SMMS production line.

A comprehensive evaluation of Achieve™ 6936G1 was conducted on the 0.5 m MB pilot line at TANDEC. The effects of process conditions such as melt temperature, air flow rate, DCD, and throughput rate were explored. MB fabrics having a basis weight of 25 g/m² (gsm) were made from the new metallocene material and compared to those from a conventional 1500 MFR PCG grade.

The results show hydroheads improve for both materials as the air and die temperatures are increased. The fabrics produced are soft, uniform and have very little or no detectable shot at die/air temperatures set at the lower temperatures. Shot levels became noticeable at the highest temperature and further increases would likely have led to unacceptable levels of shot and lower hydroheads. One advantage of Achieve 6936G1 is that it produces an improvement in hydrohead compared to the conventional PCG product.

The effect of air rate on fabric properties was determined for each material at two different process temperatures. For each test, air rates were increased in steps until “fly” was observed. As air rate is increased, hydroheads generally improve for both materials. Another advantage of Achieve 6936G1 is that it requires less process air to reach a given hydrohead than the PCG comparison resin.

To evaluate Achieve 6936G1 at commercial conditions, time was leased on a 4.2 m Reicofil® 3 SMMS production line. Various constructions were evaluated including MB, lightweight SMS, and heavy basis weight SMMS. ExxonMobil’s PP3155 was used for all spunbond layers. The laminates were targeted at hygiene and medical type applications.

Once again, the MB fabrics from Achieve™ 6936G1 have higher hydroheads compared to fabrics made with the PCG comparison grade, confirming the pilot line results. The hydroheads are shown in Figure 1. Air permeability measurements, as illustrated in Figure 2, show the Achieve fabrics have more resistance to air flow. Lower air permeability values usually mean higher hydroheads, except when shot (and associated pinholes) cause premature leakage of the test liquid.

The heavy basis weight (50-60 gsm) SMMS fabrics produced results similar to those of the MB fabrics. The SMMS fabrics made with Achieve 6936G1 had higher hydroheads and lower air permeability than those made with the PCG grade.
Another important quality of the MB barrier layer is its resistance to penetration by sprayed liquids. This is especially important in medical applications such as surgical gowns. The Achieve 6936G1 fabric has outstanding spray impact resistance as compared to the conventional fabric. In an average of five tests performed on SMMS fabrics by a contract lab, the fabric with Achieve MB allowed less than 0.5 gram of water to pass through, compared to over 3 grams for the fabric containing conventional MB.

![Figure 1: Comparison of MB Fabric Barrier Properties](image1)

Today’s medical fabrics are often treated with additives to improve resistance to penetration by alcohol-based fluids. While these additives can dramatically improve the alcohol repellency, they also can be somewhat detrimental to the hydroheads. SMMS fabrics were treated by a third party lab and hydroheads were compared before and after treatment. The fabrics with a MB layer made from an Achieve polymer provide high hydrohead even after treatment with the alcohol repellent.

![Figure 2: Comparison of MB Fabric Air Permeability](image2)

In order to better understand the source of the excellent barrier properties in MB fabrics made with Achieve polymer, capillary porometry experiments were conducted on several MB and SMMS fabrics. The fabrics made with Achieve polymer were found to have fewer large pores, a smaller average pore size, and
a more narrow pore size distribution. The smaller average pore size is what gives the Achieve fabrics their higher hydroheads and lower air permeabilities. A comparison of the pore size distribution between fabrics made with Achieve™ polymer and those made with the PCG meltblown grade can be seen in Figure 3.

![Figure 3: Comparison of Pore Size Distribution in MB Fabrics](image)

As discussed earlier, the narrow MWD and absence of peroxide treatment are expected to give the metallocene fabric low extractables. To better simulate real end-use type conditions, extractables were measured on MB fabrics rather than on the thin films specified in FDA tests. Because of the high surface area of the fine fibers, this test is more stringent. Both hexane and xylene Soxhlet extractions were performed on fabrics made from the Achieve 6936G1 metallocene polymer and the conventional PCG grade of similar MFR. The fabric made with Achieve polymer gave substantially lower extractables than the conventional fabric in both tests. The lower extractables are important in end-use applications and during MB processing. The lower amount of very low molecular weight material is expected to reduce die build-up and may increase the interval of time between die changes and equipment clean-up.

The excellent properties of fabrics made with Achieve 6936G1 make them well-suited for applications in hygiene products, medical fabrics, and filtration media. The finer pore size provides better filtration capability for filter media and improved barrier properties for medical applications. In hygiene applications, the higher hydroheads can improve the performance of the product or the manufacturer may be able to take advantage of the better barrier properties by reducing basis weight or increasing line speed. The low extractables make meltblown fabric produced from Achieve propylene polymers especially well-suited for producing liquid filtration media and pre-moistened wipes.

CONCLUSIONS

A new high MFR propylene polymer based on metallocene technology has been developed and designed for meltblowing applications. The new polymer, named Achieve™ 6936G1, delivers enhanced fabric properties including higher barrier
properties and very low extractables. The manufacturer may be able to take advantage of the higher barrier properties to reduce basis weight or increase line speed. Because this material is so clean, the nonwoven manufacturer may be able to extend the intervals between die changes and process clean-ups. The absence of peroxide in this product leads to reduced viscosity variations and more consistent extrusion performance. Reduced process air rates are possible with this material, which can reduce energy costs. Due to these advantages, this innovative new meltblown material is expected to gain rapid acceptance in the nonwovens industry.