MAGNUM™ ABS: The Benchmark ABS for Extrusion

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1. ABSTRACT

Acrylonitrile-butadiene-styrene (ABS) resins are widely used for applications such as appliances, toys, office equipment, sanitary wares, and more. Extrusion of ABS covers around 13% of the total ABS market in Europe, namely through sheets, edge bands, and profiles. ABS extruded into sheets and formed into final parts, finds its way into furniture, automotive, buses, trucks, recreational and utility vehicles, sanitary applications, advertisement boards, luggage and doors. For optimum product performance and cost efficiency, the ABS resins require specific attributes. These are an excellent lot to lot consistency, a white and thermal stable base color, an adequate UV stability, a low amount of unmelts and a high product purity. Because sheets and edge bands are demanded in a wide range of colors, self-coloring has become a key cost driver through necessities such as color matching, UV absorbers, and optical brighteners. Limited run sizes and regrinding also lead to increased scrap and constant color adjusting. Because the surface quality of thermoformed parts is so critical, presentation of unmelts and high levels of volatile organic compounds in the resins affect aesthetics. This study discusses the attributes of ABS specifically for extrusion and thermoforming, and compares the benefits of MAGNUM™ ABS versus several emulsion ABS. It is intended to provide information to manufacturers of extrusion applications to select the most suitable ABS materials for optimum production performance and cost efficiency.
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2. INTRODUCTION

Trinseo is a global materials solutions provider and a manufacturer of plastics, latex binders, and synthetic rubber. In particular, for the plastic MAGNUM™ ABS, Trinseo has production locations in Europe (Terneuzen, the Netherlands) and the US (Midland, Michigan). A new production unit for MAGNUM™ ABS in Zhangjiagang, China, was started up in the third quarter of 2017. Like the sites in Terneuzen and Midland, this unit is based on Trinseo’s proprietary mass polymerization process technology which yields ABS of a superior quality to competitive ABS resins produced in China today. MAGNUM™ ABS delivers great resin attributes for extrusion, and its downstream processes of thermoforming and lamination. It is an ideal fit for automotive interiors, buses, trucks, recreational and utility vehicles, appliances, furniture, sanitary applications, and building and construction applications, where aesthetics are important. For end-use applications in which looks matter, MAGNUM™ ABS can be an advantageous choice for customers in Asia who need to meet demanding customer aesthetics while keeping fabrication costs down. This paper will focus on describing the benefits of MAGNUM™ ABS for extrusion applications.

3. THE ABS MARKET IN EUROPE

Extrusion of ABS covers around 13% of the total ABS market in Europe. There are three subcategories in the ABS extrusion market: sheet, edge bands, and profiles. Sheet is the largest application, followed by edge bands, which is also a large-volume application, whereas profiles are of a smaller volume and more fragmented.

The ABS extrusion market has a wide diversity of applications. ABS extruded into sheet finds its way into furniture (high-gloss kitchens and bath wares), vehicles that are produced in relatively small series (e.g. exterior and interior parts for agricultural, utility and recreational vehicles, and license-free cars), buses (interiors), trucks (interiors and exteriors), automotive (interiors and, to a limited extent, exteriors), sanitary wares, advertisement boards, luggage, and doors. The majority of the sheets that go into these applications are coextruded with polymethylmethacrylate (PMMA). Edge bands and profiles are often mono-layer extruded.

In Europe, Trinseo has a market leading position in extrusion with MAGNUM™ ABS, due to the inherent attributes of MAGNUM™ ABS that are advantageous for extrusion.

4. ABS SHEET EXTRUSION

4.1 Primary and Secondary Plastics Processes

There is some complexity in the channel-to-market of ABS sheet extrusion. The sheet extruder does not supply directly to the brand owner, but to a thermoformer. The transformation from granules to end products goes through two different plastics processes, which have their own necessary ABS resin attributes: the primary process is sheet extrusion and the secondary process is thermoforming. The majority of all extruded sheet is thermoformed. The thermoformed parts go to the brand owner who does the final assembly into the end product, and sells the end product either directly to the end user or through a retailer.

A similar channel-to-market exists for edge bands and films for furniture. Extrusion of the edge bands and films is also the primary process. The extruders supply the edge bands and films to furniture manufacturers, who apply secondary processes of bending, lamination and gluing of the edge bands and films onto wooden boards,
which are sold to retail shops as full furniture cupboards, or to distributors as furniture panels for “do it yourself” items, before they end up at the consumer.

### 4.2 ABS Resin Attributes

The primary (extrusion) and secondary (thermoforming, bending, lamination and gluing) processes require specific attributes from the ABS resins. Sheets and edge bands are offered in a very wide range of colors, making easy and efficient self-coloring important attributes of the ABS. A low base color and a good lot-to-lot consistency will improve coloring efficiency and will avoid color dosing corrections, enhancing productivity and reducing scrap. Side trim and other clean post-industrial scrap like off grade sheets are re-grinded and re-used during extrusion. Therefore, good thermal stability with retention of color and properties is important. All ABS resins yellow under solar exposure, but some types yellow less, requiring less UV absorber to maintain part color perception and potentially reducing costs. Surface quality of thermoformed parts is critical, and the number of surface defects should be minimal. Consequently, the number of unmelts (so-called ‘gels’ in the ABS) should be minimal as well. Purer ABS with low levels of volatile organic compounds (VOCs) will result in purer and cleaner surfaces after extrusion, with improved adhesion properties for lamination and gluing processes. Purer ABS products with fewer VOCs will also cause less odor nuisance for the operators, as well as for the consumers.

### 5. MAGNUM™ ABS vs. EMULSION ABS

There are two main methods for commercial production of ABS: solution polymerization and emulsion polymerization. The first is also called mass polymerization. The industry typically labels these as mass ABS (mABS) and emulsion ABS (eABS). MAGNUM™ ABS is produced using the mass polymerization process. Although most of the ABS worldwide is produced through the emulsion process, the mass process has a number of advantages that are described in this chapter.

In the emulsion process (1), first, rubber latex is produced by means of emulsifiers, followed by the polymerization of styrene and acrylonitrile in the presence of the rubber latex. Part of the polymerized styrene-acrylonitrile is grafted onto the rubber. This grafted rubber concentrate (GRC) is then either mixed with additional emulsion-prepared styrene-co-acrylonitrile (SAN) copolymer and then coagulated, or first isolated and then compounded with SAN. The emulsion process is a batch type of process, offering greater production flexibility.

In the mass process (1), rubber is dissolved in a mixture of the monomers styrene and acrylonitrile and a solvent. This solution is pumped into the first reactor in a series of reactors that are interconnected. The polymerization starts in this first reactor by increasing the temperature in the presence of an initiator, and continues further downstream until completion in the last reactor. The final step is the removal of residual monomer and solvent. The mass process is a continuous type of process, and has somewhat less production flexibility.

The advantages of the mass process are the absence of impurities like emulsifiers, leading to a cleaner and purer ABS product, and by virtue of being a continuous process, also leading to better lot-to-lot consistency, as well as improved rubber efficiency, making MAGNUM™ ABS less sensitive to rubber degradation processes.

The rubber phase morphology of MAGNUM™ ABS is different to that of eABS. Figure 1 shows a transmission electronic microscopy picture of cross sections of granules of MAGNUM™ ABS and eABS. The light gray phase in the pictures is the SAN phase. The
dark gray phases are is the rubber particles. MAGNUM™ ABS has larger and occluded rubber particles, whereas the eABS has smaller particles with hardly any occlusions. Therefore, the MAGNUM™ ABS rubber particle morphology is characterized by a high rubber efficiency.

Trinseo offers four standard ABS grades from the new Zhangjiagang plant. The impact/flow chart (Figure 2) gives an overview. The charpy impact was measured according to ISO 179-1/1eA and the melt flow rate according to ISO 1133 at 220°C and 10 kg. There are two low-flow grades designed especially for extrusion (MAGNUM™ A290 and A440), one medium-flow grade suitable for both extrusion and injection molding (MAGNUM™ A371) and one high-flow grade designed for injection molding (MAGNUM™ A136). MAGNUM™ A290 is the high-impact grade, whereas the three other grades are so-called medium-impact grades.

In this chapter, one compares MAGNUM™ A290 high-impact ABS (further referred to as “MAGNUM™”), with a high-impact emulsion ABS produced in Asia (referred to as “eABS”). In some cases, a comparison with other emulsion ABS is conducted, referred to as eABS1, eABS2, etc.

Readers should note that all comparative data represent a snapshot in time as random single lots of the various ABS resins. All comparative data was measured in Trinseo labs in Terneuzen, the Netherlands.

![Figure 1: Rubber particle morphology of MAGNUM™ A290 vs. a high-impact eABS](image-url)
5.1 Improved Lot-to-lot Consistency
Due to the nature of mass polymerization, the run sizes of MAGNUM™ ABS can exceed 1000 MT, ensuring a very high lot-to-lot consistency within such a campaign. In emulsion polymerization processes, run sizes are generally smaller. With MAGNUM™ ABS, customers usually receive multiple shipments from the same production campaign, which avoids the need to make adjustments in color masterbatch dosing or extrusion process settings, and potentially reducing the amount of extrusion scrap.

5.2 Whiter Base Color
The base color of MAGNUM™ granules is much whiter than eABS granules, which look somewhat yellow (Figure 3). Consequently, coloring (especially of whiter colors) may be easier and cheaper with MAGNUM™. Figure 4 shows how adding 4% of white masterbatch (WMB), containing 50% of titanium dioxide (TiO2) to MAGNUM™ leads to a 2.5 units lower b* value, compared with eABS. A lower b* value means a less yellow appearance. To reach the same b* value with the eABS, the amount of WMB has to be increased to 12%. The color data was measured on a Data Color Spectraflash SF600 PLUC-CT in reflection mode and illuminant/observer of D65/10°.

One may use an optical brightener (OB) to reduce yellowness. Optical brighteners emit blue light when exposed to ultraviolet (UV) light and may compensate for such yellowness. However, these OBs lose their blue-emitting effects over time. The rate of decrease is dependent of the amount and time of exposure to UV light. Figure 5 demonstrates that the eABS with 4% WMB and OB remains significantly more yellow than MAGNUM™ without OB. The relative b* value difference of eABS with OB vs. MAGNUM™ with OB does not improve.

Table 1 shows the cost differences for coloring with a WMB, based on a price of 2.9 US$/kg for TiO2. eABS is 116 US$/MT more expensive to color. In addition, the increase in WMB (to achieve the same b*) reduced the practical impact performance by 15%, here measured as an instrumented dart impact according to ISO 6603-2. In addition, the part density increased by about 9%, which goes against trend of light weighting in cars and recreational and utility vehicles.

High dosing levels of TiO2 may cause surface defects in sheets and thermoformed parts. High pigment loadings increase the risk of pigment agglomerates due to
dispersion issues. Figure 6 shows an electronic microscopy picture of a cross section of an ABS sheet, where the agglomerate is visible just under the sheet surface, creating a surface defect. Element analysis shows the agglomerate mainly consists of TiO2. The element chromium (Cr) is related to the special surface treatment of the sample, which is necessary for the electron microscopy.

In extrusion, it is common to process regrind. Regrind is collected from shredding the side trim of extruded sheets and shredding scrap sheets, edge bands or profiles from the startup and shutdown production runs. Each time ABS is reprocessed, a color shift may occur due to the repetitive thermal load on the plastic. Therefore, an adequate thermal stability of the ABS is required to limit these shifts in properties. In essence, regrind is composed of ABS plastic that has been extruded once, twice, and three times, etc. respectively in ever-smaller fractions. In multilayer sheets, the regrind can be embedded in a core layer and color shift may not be that critical. However, for mono-layer sheet applications, extra use of color masterbatch may be necessary to mask the effects of the regrind, which may lead to increased cost and reduced impact performance.

Figure 7 displays a picture of a reprocessing experiment. Both MAGNUM™ and eABS were reprocessed six times on a small twin-screw compounder. Glass vials sorted from left to right, with increasing numbers of regrind passes, show the color shift. The color of MAGNUM™ after six passes is visually lighter than the start color of the neat eABS. After six passes, the latter has shifted more in color, especially toward red, as shown by a substantial shift in the a* value (Figure 8). The a* value is expressed as a numerical value measured under reflective mode, and represents a color number along the green-to-red axis.
Figure 4: $b^*$ values of MAGNUM™ ABS vs. eABS with white masterbatch

Figure 5: $b^*$ values of MAGNUM™ ABS vs. eABS with white masterbatch and optical brightener

<table>
<thead>
<tr>
<th></th>
<th>Cost to color TiO₂ ~ 2.9 US$/kg</th>
<th>Falling Dart Impact Total Energy [J]</th>
<th>Density [kg/l]</th>
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<tbody>
<tr>
<td>4% WMB</td>
<td>58 US$/MT</td>
<td>26.7</td>
<td>1.124</td>
</tr>
<tr>
<td>12% WMB</td>
<td>174 US$/MT</td>
<td>22.7</td>
<td>1.230</td>
</tr>
<tr>
<td>Delta</td>
<td>+116 US$/MT</td>
<td>-15%</td>
<td>+9.4%</td>
</tr>
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Table 1: Cost and density savings when using MAGNUM™ ABS
Figure 6: Agglomerate of titanium dioxide in ABS sheet

Figure 7: Color shift to yellow when reprocessing ABS
Greater UV Stability

Natural ABS will yellow and lose ductility when exposed to ultraviolet (UV) light. UV protection by means of UV absorbers is necessary to maintain color and mechanical properties, as UV radiation attacks the ABS, affecting both the rubber particles and the SAN matrix. The transmission electron microscopy pictures in Figure 9 demonstrate the effect on the rubber particles. The dark gray isolated phases are the rubber particles, and the light gray phase in between is the SAN. After UV exposure, one can see that over a distance of about 20 microns below the surface, the rubber particles are not visible anymore. Due to the UV exposure, the rubber has been cross-linked and almost all double covalent bonds in the polybutadiene are lost. Consequently, they are not visible anymore with the used-electron microscope technique. This implies that this 20-micron layer of the ABS has become brittle. Deeper inside the ABS, the rubber particles are not affected. The depth of embrittlement is a function of the amount of UV exposure.

Figure 9 also shows an infrared spectrum of the ABS before and after UV exposure. One can see an extra peak at 1725 cm^{-1}, which is typical for a carbonyl functionality (C=O), and is due to photodegradation of SAN (2). The broad peak between 3200 and 3500 is N-H stretching vibration for amides, which are formed during photodegradation of SAN (2). Photo degradation of SAN causes the formation of yellow color bodies and chain scission, leading to reduction of the SAN’s molecular weight.

In the following paragraphs, results of accelerated UV exposure tests of MAGNUM™ and eABS are discussed. To simulate indoor conditions, so-called QUV-A tests are used, whereas QUV-B tests are used to simulate outdoor conditions. The QUV-A test uses lamps radiating with 340 nm wave length and a cycle of eight hours' UV exposure with a 60 °C black panel temperature, followed by four hours' condensation with a 50 °C black panel temperature. The energy exposure is 0.77 W/m2. The QUV-B test uses lamps radiating with 313 nm wave length and a cycle of four hours' UV exposure with a 60 °C black panel temperature, followed by four hours' condensation with a 50 °C black panel temperature. The energy exposure is 0.63 W/m2. The color data was measured on a Data Color Spectraflash SF600 PLUC-CT in reflection mode and illuminant/observer of D65/10°.
Figures 10 and 11 respectively show the evolution of the $b^*$ value and delta $E^*$ values, after exposure to a QUV-A-accelerated weathering test. Both MAGNUM™ and eABS were loaded with 4% WMB. After 300 hours, the $b^*$ value of eABS is about 80% higher than MAGNUM™. The delta $E^*$ value is a numerical value that expresses the total color change vs. the original color before submission to the test. One can conclude that the eABS color ages twice as fast as the MAGNUM™. Theoretically, this means that MAGNUM™ needs around half the amount of UV absorber compared with eABS for indoor exposure conditions, which would represent significant cost savings.

Figures 12 and 13 indicate the evolution of the $b^*$ value and delta $E^*$ value after submission to a QUV-B test. After 300 hours of exposure, the eABS has a 26% higher $b^*$ value than MAGNUM™. The delta $E^*$ values show that aging is faster for eABS vs. MAGNUM™. In this case, one can theoretically reduce the amount of UV absorber by about 30% when loading the UV absorber into the bulk of the ABS sheet. However, it is more cost-effective for outdoor applications to put a relatively high amount of UV absorber into a cap layer of PMMA or acrylonitrile-styrene-acrylate (ASA).

Note that specific accelerated weathering testing is recommended to determine the adequate amount and type(s) of UV absorbing, and/or light stabilizing additives, for the actual application.

Figure 9: Degradation of ABS due to UV light exposure
Figure 10: Accelerated QUV-A weathering test; $b^*$ evolution vs. exposure time

![QUV-A weathering graph with $b^*$ values vs. exposure time for MAGNUM + 4% WMB and eABS + 4% WMB]

Figure 11: Accelerated QUV-A weathering test; delta $E^*$ evolution vs. exposure time
(dashed line depicts faster discoloration of eABS)

![QUV-A weathering graph with delta $E^*$ values vs. exposure time for MAGNUM + 4% WMB and eABS + 4% WMB]
5.4 Low in Unmelts
Unmelts in ABS, also called gels, can cause aesthetic surface defects because gels do not melt during extrusion and may form a surface irregularity. Such irregularities are especially noticeable in cases where a high-gloss acrylic cap layer is coextruded.

In relatively thick sheets, these unmelts not usually visible after extrusion, unless they are located very close to the surface of the sheet (Figure 14). However, when thermoforming the sheets into a three-dimensional part, the wall thickness of the final part may become a lot thinner than the original sheet thickness. Consequently,
unmelts that were not visible after extrusion become visible as optical surface defects in the end product.

In an extruded film (Figure 14), the gels are more likely to be visible after extrusion as it is already thin, and they become even more visible after thermoforming. ABS films are used in very demanding applications regarding surface aesthetics, such as automotive interior trims and furniture. The extruded film is cut to size, formed, and back injection molded into decorative parts for automotive, or cut to size and glued onto wooden boards in the case of furniture.

Figure 15 shows how a gel positioned close to the surface of an extruded sheet causes an aesthetic surface defect. The picture on the left side is a top view of the sheet surface, while the image on the right is the cross section microscopy picture of the sheet through the gel. This shows the location gel just underneath the sheet surface, as well as the deformation of the surface.

The next series of graphs depict a comparison in the amount of gels in MAGNUM™ vs. several eABS grades, counted and categorized by means of a Trinseo internal method. Two different and relatively large gel size categories are looked at in particular, referred to as “medium” and “large” gels. These are the gel size categories that are more likely to be visible to the consumers in the end application. Smaller gel size categories are critical for the most demanding applications. For those, Trinseo offers special low and ultra-low gel grades in Europe. These grades will not be produced in the new Zhangjiagang plant, but can be imported from Europe.

Figures 16 and 17 indicate that there are significantly less medium- and large-size gels detected in MAGNUM™ compared with various commercial eABS grades available in China. Therefore, the risk for aesthetic surface defects in extruded and thermoformed parts is higher with these tested eABS grades than with MAGNUM™.
Figure 15: Unmelts in ABS sheets causing visible surface defects

Figure 16: Relative number of medium-size gels in MAGNUM™ ABS vs. various eABS

Figure 17: Relative number of large-size gels in MAGNUM™ ABS vs. various eABS
5.5 A Purer Product

The purity of ABS can be evaluated by means of differential scanning calorimetry (DSC) and by measuring the amount of volatile organic compounds (VOCs). Figures 18 and 19 show DSC plots of MAGNUM™ and eABS over a temperature range of 20 to 250 °C. MAGNUM™ has only one change at about 105 °C, representing the melting of the SAN matrix. Note that the changeover of the rubber phase happens at sub-zero temperatures. eABS has, in addition to the SAN change at about 108 °C, three changeovers at around 45, 70 and 128 °C. These additional changeovers can be referred to as impurities, as they are not SAN. These impurities may be emulsifiers, waxes or mold release agents. Mold release agents may be intentionally added, but they are not generally beneficial in an extrusion process. The presence of emulsifiers is inherently related to the emulsion ABS production process, whereas MAGNUM™ mass processes are free of such impurities. DSC is not a quantitative method, but one can generally state that the weight % of these impurities needs to be about 1% or more to become visible in DSC. Impurities can plate out on the die or on the roll stack, which have to be manually removed at regular intervals, causing production loss and adding cost.

Purity of ABS can also be expressed by the amount of VOCs. The higher the amount of VOCs, the less pure the ABS. These VOCs may cause an unpleasant smell during extrusion of the ABS, and the end consumer can also be exposed to unpleasant odors in cases of indoor applications such as automotive, truck and vehicle interior trims, and furniture. Figure 20 shows a comparison of measured VOC levels in various eABS vs. MAGNUM™. The VOC level is expressed as microgram total carbon emission per gram ABS, and was determined by means of headspace gas chromatography using a flame ionization detector. The measured levels of VOCs in eABS are substantially higher than in MAGNUM™.

Figure 18: Differential scanning calorimetry plot of MAGNUM™ ABS
6. CONCLUSION

In this study, a high-impact MAGNUM™ ABS was compared with a high-impact emulsion ABS, and other emulsion ABS grades. The results exposed the following advantages of MAGNUM™ ABS over typical emulsion ABS resins:

- MAGNUM™ ABS has substantially less yellow in its base color.
- MAGNUM™ ABS stays more color-neutral after reprocessing.
- Upon exposure to UV radiation, white-colored MAGNUM™ ABS retains greater color stability.
- The number of unmelts or gels in MAGNUM™ ABS is substantially lower.
- The amount of VOCs in MAGNUM™ ABS was considerably lower.
In practical terms, the whiter base color of MAGNUM™ ABS substantially reduces pigment cost—especially when seeking lighter, brighter shades. Due to better thermal stability, MAGNUM™ ABS reduces color corrections when reprocessing as regrind. When exposed to UV radiation, white-colored MAGNUM™ ABS reveals a slower rate of discoloration, which may reduce the cost of UV absorbers. The considerably lower amount of medium and large gels in MAGNUM™ ABS reduces the risk for aesthetic surface defects of high-gloss thermoformed parts. MAGNUM™ ABS is also a purer product, with significantly less VOCs. Through choosing MAGNUM™ ABS, extrusion customers can achieve production efficiencies and cost savings through whiter base color, better color stability, lower gels and purer product nature.

7. REFERENCES
1. Modern Styrenic Polymers, J. Scheirs and D. Priddy, Wiley
2. Mechanism of poly (styrene-co-acrylonitrile) photo oxidation, Mailhot & Gardette

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