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INTRODUCING NAS®, THE TRANSPARENT POLYMER FOR FOOD CONTACT APPLICATIONS

by

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Introduction

The global household appliances market is estimated to grow at a compound annual growth rate (CAGR) of around 6% during 2018 – 2022. Each year new devices are launched to add home comfort and make our daily life easier. Whether in large appliances such as refrigerators and washing machines or small appliances such as coffee machines, kitchen equipment and reusable food storage items, polymers enhanced the functionality and revolutionized the design of the household devices.

Identifying the right plastic resin of choice according to their specific needs and in line with the regulatory requirements is a key task within the household product manufacturers. For household appliances and accessories intended to come (directly or indirectly) in contact with food, the material selection narrows down to polymer grades that enable the finished article to comply with the requirements and migration limits set in food contact regulations. These limits are included with the aim to protect the consumer to the exposure of substances based on a toxicological risk assessment.

Increasing regulatory trends make food contact legislation evolve in terms of analytical techniques, rules for testing food contact materials and tighter specific migration limits (SMLs) and restrictions for monomers, additives and starting substances.

Considering the latest regulation updates, NAS® polymer has become a very interesting alternative fulfilling the latest regulations (e.g. FDA and (EU) 10/2011). Since its introduction into the market NAS®, INEOS Styrolution’s styrene-methyl methacrylate (SMMA) has always been distinguished by its impressive optical clarity.

Accordingly, this copolymer offers a perfect fit for household applications where enhanced transparency and gloss is required in conjunction with short-term repeated use food contact. As a matter of fact and committed to the steady growth of the NAS demand, INEOS Styrolution recently invested in a new production line in Ludwigshafen, Germany. With this in place, the NAS® polymer can now be sourced either from the US (Decatur plant) or from our new European production plant in Germany.
Figure 1: “Venice” glassware collection: Brighter, lighter and clearer due to INEOS Styrolution’s NAS®

(Courtesy of Fratelli Guzzini)

What is NAS®?

NAS® is an amorphous random copolymer of styrene and methyl methacrylate (see figure 2) that is clear, stiff, and fails in a brittle manner.

The NAS® copolymer, also called styrene acrylic copolymer, bears a synergy of properties of its individual components. The styrene component confers an easy processing, low density and low moisture absorption while the MMA (acrylic) component contributes for a good surface hardness and the outstanding “sparkling” clarity. Together, this results in a good balance of the best of both worlds and a clear alternative for applications requiring glass like appearance, good chemical resistance (e.g. against alcohols) and easy processing.
This is of advantage for innovative designs, no matter if the article is thick or thin walled or a combination of both as exemplified in the below tumbler and shot glass examples.

**Figure 3:** NAS® Tumbler (Courtesy of Fratelli Guzzini) and shot glass combining thick and thin wall thickness elements

**Water-clear appearance**

In copolymers such as SAN, the acrylonitrile component results in a yellowish base colour, which is disguised with the use of blue tinting agents. The absence of acrylonitrile in NAS® allows for a lighter color tone that resemble the water-clear look. Figure 4 provides some measurements of the pellet b component color tone for SAN (blue tinted and natural) and NAS®.

NAS® opens space for creativity (higher design freedom) for the introduction of new eye-catching articles.
**Customized color tones**

In some cases, OEMs wish to have a tailor-made color tone. Light and constant color tones such as blueish tinted colors or smoke topaz translucent colors are achievable with NAS® resins. Figure 5 shows an example of a customized color for a milk container developed by a premium branded coffee machine manufacturer.

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**Figure 4**: Pellet b component color tone comparison

Reading of the pellets, D65/10°, Hunterlab (working standard: calibrated white tile)

NAS® shows a neutral water-clear color tone compared to competitive materials.
Customized translucent light colors are possible with NAS®

**Figure 5**: Melitta® water milk container made out of NAS® for the new Melitta® CI Touch®

(Courtesy of Melitta)
Optical properties, “Sparkling Clarity”

The optical properties of a material determine how it will interact with light. Some of the key optical properties of transparent product families are the material’s refractive index, the haze and the light transmission properties:

- **Light transmission values**, which are a key indicator of transparency and measures the intensity of light passing through a test specimen after taking into account reflection losses at the two surfaces.
- **Refractive Index**, which is a measure of how much light is bent (or refracted) as it passes through a substance. The higher the refractive index, the greater the angle that the ray of light will bend at the surface interface when passing from one medium into another.
- **Haze**, which represents a measurement for the light that is scattered more than 2.5° from the direction of the incident light beam.

These values are for instance considered for the design of optical lenses. Table 1 shows some typical optical properties among different transparent product families and Figure 6 displays some typical light transmission values at different wavelengths.

<table>
<thead>
<tr>
<th>Material (typical values)</th>
<th>Method</th>
<th>Units</th>
<th>PMMA</th>
<th>NAS</th>
<th>SAN</th>
<th>PC</th>
<th>GPPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light transmission at 550 nm</td>
<td>ASTM D 1003</td>
<td>%</td>
<td>92</td>
<td>91</td>
<td>88</td>
<td>89</td>
<td>89</td>
</tr>
<tr>
<td>Haze</td>
<td>ASTM D 1003</td>
<td>%</td>
<td>&lt; 0,5</td>
<td>&lt;0,5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Refractive Index (nD), Sodium D Line, 589 nm/ 23°C</td>
<td>ISO 489</td>
<td>-</td>
<td>1,491</td>
<td>1,564</td>
<td>1,569</td>
<td>1,587</td>
<td>1,591</td>
</tr>
</tbody>
</table>

*Table 1: Typical optical properties among different transparent product families*
It can be observed that PMMA acrylic polymers possess a fairly low refractive index and demonstrate an excellent high level of light transmittance (i.e. 92% in the visible light region) and low haze values. NAS® resins benefit also from their acrylic content and offer an excellent combination of high light transmission (consistent with the low refractive index) and low haze featuring the sparkling clarity attribute. Figure 7 shows an example of an application benefiting from this attribute.

Figure 6: Light transmittance of different amorphous thermoplastics

Figure 7: Sparkling clarity bottle cooler
Mechanical and Physical Properties

Brittle polymers absorb a relatively small amount of energy prior to fracture and breakage occurs still within their elastic limit. Ductile polymers continue to deform beyond its elastic limit undergoing a plastic (non-reversible) deformation. Because of the brittle behavior of NAS® polymers, greater care must be taken during the design phase and the consideration of draft angles to ensure an easy and proper ejection from the mould.

Other polymer families showing high stiffness and brittle behavior are polymethylmethacrylate (PMMA), polystyrene (GPPS) and styrene acrylonitrile copolymer (SAN), as shown in Figure 8. Compared to a ductile material such as Polycarbonate (PC), brittle polymers offer an outstanding high stiffness (resistance to deformation when applying load to them) as indicated by its high modulus of elasticity.

Figure 8: Impact strength and modulus of elasticity comparison among different transparent product families

Why to use NAS® over other competitive product families

The following short information serves as a quick guide to highlight the advantages of using NAS® polymer compared to specific transparent product families.

**NAS® over GPPS**

NAS® shows better scratch resistance than conventional PS and is suitable for applications that demand higher optical quality (e.g. high transparency and water clear colour tone) and chemical resistance. On this latter point, a further important differentiation of NAS® compared to GPPS moulded parts is the superior residential dishwasher resistance performance.

**NAS® over PMMA**

NAS® has lower density, improved flow, better chemical resistance against alcohols and less molded-in stress than acrylic polymer (PMMA).

**NAS® over SAN**
According to the food contact regulation (EU) 10/2011 the specific migration limit for acrylonitrile monomer is non-detectable (ND). NAS® is based on a different monomer package than SAN and has proven to be an effective material alternative for certain food contact applications when it comes to demonstrate compliance with demanding migration limits.

When specifically comparing further aspects between the property profile of SAN and NAS® (refer to spider chart in Figure 9) the key advantages of NAS® over SAN relate to the “sparkling” clarity and water clear appearance as well it’s easy processing (high flow grades). The main trade-off points against SAN are the chemical and thermal (“heat”) resistance.

Note: Performance for any property is proportional to the distance on axis from center.

**Figure 9**: Spider chart comparing NAS® against SAN
NAS® over PC and Copolyesters

The advantages of NAS® are its easier processing combined with its optional and easier drying due to material hydrophobicity, superior stiffness and scratch resistance and its lower density.

Compared to other product families such as polycarbonates, copolyesters and acrylics (see figure 10), NAS® features savings of around 10% weight due to its lower density. This transfers to important cost savings for the manufactures.

![Density comparison graph](image)

Figure 10: Density comparison

Stable Production Process

NAS® is manufactured by free radical polymerization in a continuous process using a specialized “GPPS” process. This specialized polymerization process allows a high degree of flexibility in terms of the ratio of the monomers incorporated into the copolymer (i.e. n: styrene and m: methyl methacrylate ratio as described in chemical formula of Figure 2). By changing the styrene to comonomer (methyl methacrylate) ratio, different grades can be engineered. Typically, the predominant component is styrene (>60%) to benefit from an easy processability and the methyl methacrylate is used to fine-tune the copolymer with the sparkling clarity. The transparency and appearance of the pellets speaks for itself (as shown in Figure 11).
Without going into much detail, the mentioned production flexibility has to do with the reactivity of the SMMA comonomer system. Compared to other comonomer systems such as SAN, the SMMA copolymerization is fairly close to the ideal copolymerization (a copolymerization in which the growing chain end reacts and displays the same preference for adding one or the other of the two monomers during propagation).

Under such condition, the composition of the copolymer is very close to be the same as the one reflected by the monomer feed over the entire composition range. In contrast, SAN copolymers suffer from composition drifts when the monomer feed varies significantly from the azeotropic mixture, the point where monomer and copolymer have the same composition (38 mol% or 24 wt% AN). As a result, variations in the AN content of the copolymer are more difficult to achieve over the entire range compared to SMMA copolymers. To illustrate this, Figure 12 shows the composition diagram for SMMA copolymer (red line, very close to the identity dotted line) and SAN copolymers (green line).

Consistent part appearance is important. The NAS® production technology enables reliable colorant loadings and very stable lot-to-lot color consistency. Chart 13 shows for example the pellet colour measurements among different production runs (b axis).
**Processing advantages, Post processing operations**

NAS® is a low moisture absorbing copolymer and in many instances processes readily without pre-drying. There are combinations of conditions that require the product to be dried, such as high humidity and heavy section molding. In order to produce moldings with a suitable surface and good properties, the moisture content of the granules should not exceed a certain permissible moisture level. As shown in Table 2 and compared to other competitive transparent products, NAS shows a lower water uptake allowing **optional and easier drying** due to material hydrophobicity. This is not the case for hygroscopic resins and polycondensates such as polycarbonate where the presence of moisture can lead to hydrolytic degradation and special attention needs to be paid to ensure an effective drying.

*Figure 13*: Pellet Color $b^*$ measurements
Reading of the pellets, D65/10°, Hunterlab

NAS® features an excellent color consistency from lot to lot.
Moisture absorption, equilibrium at 23 °C/ 50 % relative humidity

Molding compositions do not normally have to be predried before injection molding but predrying is advisable prior to processing to balance seasonal fluctuations in ambient conditions.

Table 2: Drying conditions and moisture content considerations

Given its amorphous nature and glass transition temperature (Tg), NAS® enables an energy-efficient production due to the lower processing temperatures that are required. Figure 14 shows the melt and mould temperatures recommended for the processing of polycarbonates, copolyesters and NAS®. Compared to polycarbonate the melt temperature can be reduced by a delta of about 60°C using a styrene-methyl methacrylate copolymer.

**Figure 14:** Example of typical melt and mold processing temperatures

In some cases and according to the design and part requirements additional assembly/welding steps are considered. NAS® can be welded using several methods such as hot plate, ultrasonic or laser welding. Since machine parameters, material properties and the type of joining surface can have a profound effect on the quality and appearance of the welded seam, preliminary tests are essential in every individual case. NAS® moldings can also be connected to parts made from related thermoplastics like Zylar, which is INEOS Styrolution’s Methyl Methacrylate Butadiene Styrene (MBS) transparent and impact modified copolymer.
Applications

Designers look to create household appliances that keep up with ever-changing technological progress and consumer demands. NAS® grades offer food contact compliance and are known for their water clear color, easy processability and pleasant touch and feel attributes. This opens up a wide range of possibilities within household and electronic industries. Some applications examples within household items are bottle coolers, coffee machine water tanks, water purifiers, dry food containers, fridge drawer and storage organizers, drinkware, tableware and designer -look salad bowls. For electronics, applications such as back lighted LED-light guides and indoor lamp housings are worthwhile to mention.
Attachment: Additional application pictures

Polyoptics Light Guide

Refrigerator drawers
Water filter
Water filter in use

Transparent jars and glasses
Transparent jar

Bowl (Fratelli Guzzini)
Glass

Water container in coffee machines