Makevale

Polymethyl methacrylate:

PMMA polymer bead manufacture and applications

White Paper

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Poly(methyl methacrylate) (PMMA), better known as acrylic, is a transparent plastic with a range of properties that make it suitable for a wide range of uses.

Not all PMMA beads are created equal. PMMA is typically produced via suspension polymerisation from a monomer, methyl methacrylate (MMA), into PMMA beads, usually a fine white powder. The beads are then further processed and/or used to manufacture other products, for example a denture base prosthesis. PMMA beads can also be used to enhance the physical properties of a formulation, such as helping thicken superglue so it can be more accurately applied.

First created in sheet form in 1932, acrylics can be found in multiple applications. These include medical, orthopaedic and dental devices, glass transportation, embedment casting and adhesives. PMMA beads are used as rheology modifiers, in casting precision components and as packaging material. PMMA is often incorrectly cited as the primary raw material for acrylic nails. However, artificial nail powders are commonly made from Poly(ethyl methacrylate) (PEMA) blended with small quantities of PMMA or Poly(ethyl methacrylate-co-methyl methacrylate).

Many high-performance applications demand high quality acrylics that rely on equally high purity raw materials and reproducible production processes. To create PMMA beads that can be used in demanding applications requires expertise in selecting and procuring raw materials, detailed knowledge of how to control the polymerisation, alongside a deep understanding of the end-use. The latter is essential because each application requires PMMA beads with very specific properties. Designing-in these properties starts right at the beginning of the process with raw material selection.

There are several stages between the MMA monomer and the end-product.

The first stage is creating the PMMA beads via suspension polymerisation, a chain growth free-radical polymerisation technique. The PMMA beads can also be created using other production processes, including, solution polymerisation. However, suspension polymerisation is the greenest process and allows lab-level control over an industrially viable, high-volume process that yields perfectly spherical and clear polymer beads that can be size specified to between ten to 2000 microns (10-2000µm).

To create PMMA requires four active ingredients:

- MMA
- An initiator
- Water
- A suspending agent

Generating PMMA beads with the finely tuned physical qualities required for high-performance applications starts here. The choice of MMA, initiator and suspending agent all impact on the final bead characterisation. The inhibitor used to prevent spontaneous polymerisation of the MMA during storage is also a factor. Put simply, lower quality raw materials and processes can result in lower quality beads that will only be suitable for high volume bulk manufacture of low quality products suitable for industrial applications.

A free-radical polymerisation reaction occurs over three stages:

- Initiation
- Propagation, including chain transfer
- Termination.

Process control is also a vital element of the final PMMA bead qualities. The quantity and quality of the initiator will affect the final beads' chemical and physical properties.

By carefully adjusting the active ingredients and the processes, it is possible to control key bead properties such as:

- Particle size
- Morphology
- Surface characteristics
- Residual initiator
- Molecular weight

Precise control of these properties during bead production is essential. If the bead properties are outside of specifications, this will have detrimental implications downstream during the end-application / product manufacture.

Finally, even though the bead manufacture is typically a volume activity, pharmaceutical-grade production disciplines are essential to ensure quality. Carefully weighing out ingredients under controlled conditions, handling processes that mitigate the risks of cross contamination, mixing and environmental controls, must be observed. Otherwise, quality issues will arise downstream.

The PMMA beads once manufactured are used for:

1. **Physical applications: to improve performance during the end-application production process, such as rheology modifiers, and as an interleavant packing material.**
2. **Chemical applications: to manufacture end-applications / products, such as bone cement, dentures, architectural applications and embedment casting.**

PMMA applications require beads with specific characteristics. As a result, the original specification of the bead properties and the bead production process are tailored according to the application. This sounds obvious, but when end-users ask why their product is not performing, the root of the problem can often be traced back to the choices in raw materials and PMMA production process.

The table (overleaf) includes some common applications and products, the bead specifications and the desired outcome. These examples highlight the link between the end-product or process performance and the specification and production process of the PMMA beads.

As the table (overleaf) demonstrates, the bulk production of designer polymer beads using laboratory-standards and processes requires expertise and experience of managing the complex underlying chemistry and process controls. Get it right, and the end-product or process will perform according to specification. Get it wrong, and the result is poor performance or product failure and damage to brand.

Not all PMMA beads are created equal: how PMMA bead properties are tailored for specific applications

Application	PMMA Bead Specification	Impact & Outcome
Rheology/viscosity modifiers for cyanoacrylate adhesives. PMMA is added to cyanoacrylate as a thickening agent to give the adhesive a more viscous consistency so it can be applied accurately.	Bead size, surface chemistry (ion content)	Low residual ion content prevents premature polymerisation reaction in superglues. Particle sizes influence dissolution time and production time reliability.
Interleavant packaging material. PMMA is used a packaging material for float glass.	Bead size and shape, molecular weight	Spherical beads do not damage the packaged material (e.g. glass) Controlled particle size distribution (PSD) prevents uneven packaging material distribution when the orientation is changed during transport, as well as dead weight. Molecular weight control can avoid glass pitting.
Sculpted cosmetic nails. PMMA is mainly used in combination with PEMA in sculpting nail powders.	Bead size, surface chemistry, flow modifier, clarity/ colour (additive levels), molecular weight	The polymers particle size, molecular weight and flow modifier control how the brush-bead forms, self-levels and keeps shape on the nail. Additives, such as initiators, must be carefully controlled to have reliable drying times and to avoid discolouration.
Dentures. The PMMA powder and liquid monomer are mixed to form a dough. The dough is placed/poured into a mould and is cured to produce a denture.	Molecular weight, bead size, residual peroxide, choice of raw materials, processing materials, colourants/ pigments, compliance with medical device regulations	This is a medical class (IIa) product and as such, must be certified for use in the oral cavity. Raw material choices have to adhere to local and international regulations. Processing materials also have to comply. Handling and dough characteristics are determined by particle size, and molecular weight. The peroxide associated with the polymer bead determines the curing time and the degree of polymerisation which in turn affects residual monomer concentration and the mechanical properties of the prosthesis. Molecular weight impacts on the hardness and impact resistance. Larger bead size improves powder flow which influences the pigment dispersion. Type of pigment is also important, as is the homogeneity of the pigmentation
Architectural applications / embedment casting. The PMMA powder and liquid monomer are mixed to form a slurry. This is poured into a mould and is left until it has gelled. The article is then cured to produce a clear cast article.	Clarity/discoloration (additive levels), molecular weight	Additives, such as initiators, must be carefully controlled as residual reagents discolour the acrylic Higher molecular weights mean tougher, enhanced mechanical properties Particle size affects the polymer swelling time, which in turn is related to pour-time Molecular weight affects the hardness and shrinkage.

Get in touch

Makevale has more than 40 years of experience in developing high-performance polymers across multiple industries, working with clients to create the perfect formulas to meet their manufacturing challenges. For further information on our PMMA beads and acrylic powders and liquids, contact our team for free, no-obligation advice.

For further information about our products and services, and how we could work together to solve your challenges, please contact our expert team..

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