The PMMA Revolution

By Kirk Goodrum

Figure 1– PMMA roof membranes in bright white offer cool roof benefits with exceptional durability.

INTRODUCTION

Almost 175 years ago, the low-slope roofing membrane industry began with the use of a field-applied liquid component and a reinforcing fabric. Built-up roofs using coal tar or bitumen were the standard for well over a century; however, in the last 50 years, factory-produced membranes grew in popularity and also secured a place as a dominant method of roofing application. During recent years, fluid-applied materials—albeit without the use of a kettle—have been filling a need for difficult applications where prefabricated membranes are not the easiest solution.

Fluid-applied materials used as flashing solutions have led to the resurgence of the concept. Such membranes improved the continuity from the roofing membrane to the vertical termination. The development of high-performance materials to be used at these critical junctions is a major advancement for roofing manufacturers and applicators alike. Based on the reliable performance of the flashing materials, professionals are now beginning to use them for complete roof systems.

Modern fluid-applied membranes are one of the fastest growing sectors of the roofing market. Although they maintain the field-constructed concept of the past, that is where the similarities end. The liquid and reinforcement components that are utilized today are highly engineered. Whether it is the base polymers, the types of curing mechanisms, or the versatility in design, this is not your grandfather's roofing.

HISTORY OF PMMA

One of the predominate chemistries in Europe and North America is polymethyl methacrylate, commonly referred to as PMMA. PMMA is a widely used polymer known for its toughness and clarity. Applications for PMMA range from bone cement and dental fillings to countertops, road markings, and aquarium glass. The uses for PMMA are quite extensive, but a commonality lies in their intended exposure to harsh in-service conditions. Its ability to handle abrasion and its inherent resistance to degradation from ultraviolet (UV) radiation makes PMMA a solid choice for rugged applications such as roofing and waterproofing.

The use of PMMA in roofing and waterproofing has a surprisingly long history. Even though it is often categorized as new technology, it has been used in roofing for over 30 years in Europe and 15 years in the United States.

Although the roofing industry is slow to accept new technology, PMMA shows signs of achieving this recognition, evidenced by its growing presence in the market.

WHAT IS PMMA?

PMMA resins, in liquid form, are an intermediate step toward achieving a PMMA roof membrane. Although the liquid contains some PMMA, it is mostly comprised of methyl methacrylate (MMA) monomer blended with a complicated concoction of additives aimed at achieving a particular set of performance characteristics. PMMA resin requires a peroxide to initiate a reaction, which turns the MMA monomers into a high-performance PMMA membrane.

The process of curing PMMA is called free radical polymerization. A peroxide is used to react with the MMA monomer and create an unpaired electron. The monomers then begin to link together like a chain. Pure MMA would be too hard and brittle for roofing and waterproofing applications, so additives included in the formulation serve the purpose of increasing flexibility. The key to formulating flexible PMMA is to use additives that participate in the reaction and do not migrate from the cured film.

APPLICATION OF PMMA

The PMMA polymer chain has a unique feature that makes it ideal for fluid-applied field applications. The end of the polymer chain is always available for additional links. So, when catalyzed liquid is applied over a cured membrane, such as a lap or tie-in, the polymer chain can continue from the cured membrane into the membrane that is forming. The polymer chain creates a chemical bond between layers of material. A chemical bond is much stronger than a simple adhesion bond and adds a level of attachment that is unmatched outside of factory-controlled conditions. This bonding can be formed on day one or at year ten when an additional penetration through the system is needed.

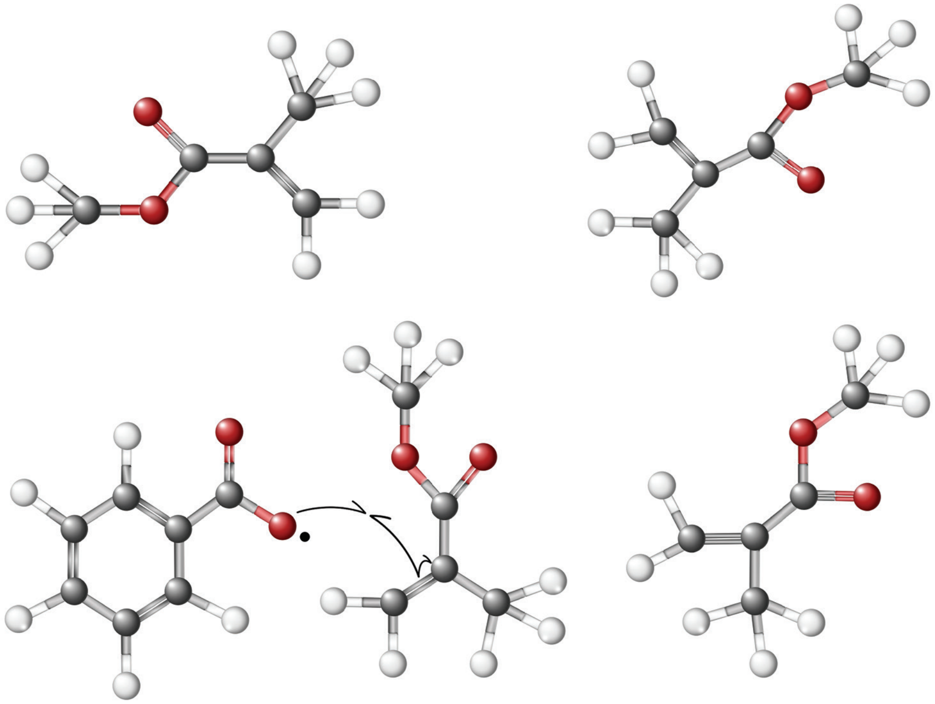

Figure 2 – Peroxide catalyst attacks the carbon double bond to initiate the formation of the polymer chain.

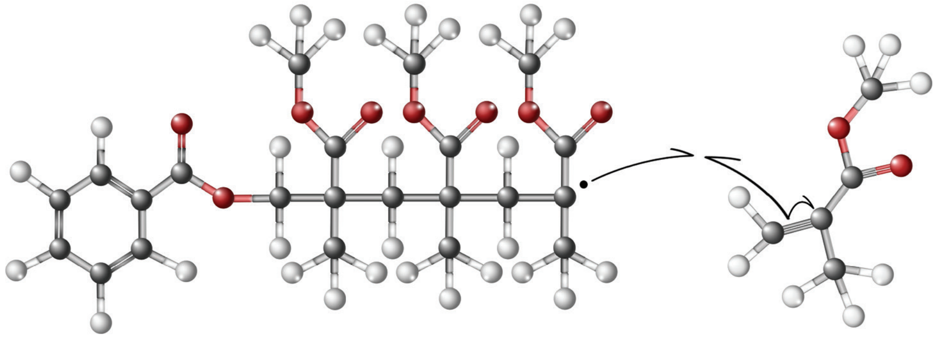

Figure 3 – Polymerization continues as the monomers react with the free radical on the end of the chain. The image represents polymerization in the simplest form and does not include additional components that may participate in the reaction.

Figure 4 – PMMA systems provided an efficient application solution for the crowded roof of this facility.

Figure 5 – Fully reinforced, seamless PMMA flashing applications effectively address both standard and challenging details.

Figure 6 – PMMA roof membrane systems are fully reinforced, layered applications consisting of one coat of primer (if required) and a waterproofing membrane comprised of two resin waterproofing coats and polyester fleece fabric.

Polymerization reactions can be inhibited by oxygen, meaning that oxygen will cause a problem in the formation of the chain. In practice, this is only an issue at the surface of the liquid after it has been applied. PMMA formulations contain an additive that forms a barrier on the surface of the liquid as it cures that protects it from oxygen. Air movement is helpful in forming the barrier layer. This is usually not an issue on most rooftops but can be problematic in corners or spaces where movement is limited. High temperature can also cause issues with the formation of the film and, as a result, leave a sticky or uncured surface layer. The liquid resin will quickly absorb the heat from the substrate during application. For this reason, it is critical to monitor substrate temperature, along with ambient temperature, during application of PMMA. Most manufacturers recommend PMMA not be applied above a maximum substrate temperature—typically around 120˚F (49˚C)—so that the barrier film can properly form.

Rapid loss of MMA is also an issue at elevated temperatures. In hot climates, it may be necessary to work at night or cooler parts of the day to avoid high substrate temperatures. At high temperatures, the MMA can boil, causing pinholes and frothing in the cured coating. Some manufacturers offer base sheets with reflective surfacing to lower substrate temperatures and allow application later in the day.

PMMA polymerization reaction can occur at temperatures below freezing. Most manufacturers will allow application down to 23˚F (-5˚C), which can be a distinct advantage in colder climates. Materials should be kept in conditioned storage to maintain the proper viscosity and aid in the dispersion of the peroxide. Proper dispersion of the initiator is important to the uniform curing of the membrane. Manufacturers recommend that the initiator be stirred into the material for at least two minutes to ensure full dispersion.

If you have ever been in a nail salon or had a tooth filled, you probably would recognize the unique aroma of PMMA. There are alternative versions of methacrylates that are marketed as “low odor.” The basis of design is the replacement of MMA with a different, larger methacrylate monomer. The lower-odor formulations generally have a smell similar to that of the MMA-based versions, but the larger monomer does not evaporate quite as quickly, which lowers vapor diffusion in an area. The low-odor versions have been on the market for a relatively short period of time. These “low-odor” products generally require significant formulation changes in order to achieve performance similar to traditional PMMA formulations in laboratory testing.

Durability, chemical resistance, and speed of application are three important attributes that lead professionals to use PMMA. Since PMMA is catalyzed, a membrane approximately 90 mils thick can be applied in a single step. A two-thirds/one-third application philosophy is generally a good concept for PMMA. This means that two-thirds of the resin is placed below the polyester reinforcing fabric, and one-third is placed on top. The amount of resin under the fleece is critical, because when the polyester reinforcement is placed into the liquid, the fabric will absorb a significant amount of the base coat. Insufficient material can leave voids under the fabric after absorption. The catalyzed resin can be applied with a roller or specialized application tools. PMMA is not typically sprayed.

Figure 7 – Trained crews can apply PMMA roof membrane systems very efficiently. This application efficiency, together with PMMA's fast cure times, allows advantageous scheduling options.

The polymerization of PMMA usually takes less than 45 minutes, depending on the temperature, and the membrane is rainproof in 15 minutes. For many roofers, the peace of mind that comes from knowing that the material is fully cured when they go home for the night is valuable.

In addition to roofing, PMMA can be used for balcony and parking deck surfacing and waterproofing. Its ability to withstand the rigors of pedestrian and vehicular traffic is well known in Europe and makes PMMA a premium choice for many business owners. Inherent toughness makes PMMA a viable option for commercial roofing.

CONCLUSION

The roofing industry deals with long life cycles, which inevitably affect the speed of technology evolution and acceptance. Combine that with the influence of wisdom and some hard-learned lessons, and the resistance to change is understandable.

PMMA has established itself over the last three decades as a leader in fluid-applied technology. UV resistance, durability, and fast cure make it a great choice for roofing and waterproofing applications. It seems that PMMA is no longer just a new technology that everyone is watching with a wait-and-see attitude, but an exciting advancement in roofing and waterproofing that could be the beginning of a fluid-applied revolution.

Kirk Goodrum

Kirk Goodrum is the research and technical development manager for Siplast. He earned his degree in physics from Henderson State University prior to joining Siplast in 1999. Goodrum is the subcommittee co-chair of ASTM D08.25, Liquid Applied Polymeric Materials Used for Roofing and Waterproofing Membranes, and past Technical Committee chair for SPRI. He also actively participates in organizations such as ASTM, ARMA, CRRC, RCMA, and CSA to develop standards and papers for use in the industry.

Roof Cleaning Destroys Historical Artifacts

Two years after a £2 million project was completed to repair and clean the 150-year-old glass roof of Oxford University's Natural History Museum, university authorities admit that removing a century and a half of dirt from the 8,500 glass tiles covering the structure has caused "rapid and irreversible" damage to many of the priceless objects inside the museum.

In 2013, museum curators closed the building for 14 months as the glass tiles were individually removed and resealed. The ultraviolet (UV) film that had covered the roof was removed in the process and not replaced, leaving exhibits that were not protected by individual cases exposed. Temperatures inside the building soared to 111°F (44°C), and low humidity resulted.

Photos submitted by the museum showed that the skins of stuffed animals have cracked and faded under the sun's rays, and staff warned that a set of scientifically important whale skeletons were at risk.

Historic England, backed by the university, is proposing to apply a new, gold-colored UV film to the roof, in spite of the fact that the building's historical appearance will be altered. It also plans to install a new air conditioning system to reduce temperatures.

— The Telegraph