Characterization of a Paint-PMMA Polymer Blend

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Abstract

The disposal of waste latex-based paint poses significant financial and environmental problems in the United States. A potential solution is to recycle latex paint by removing the water from the paint, and melt-processing it with poly(methyl methacrylate) (PMMA) to create an immiscible polymer blend. Prior research shows that a 20-80 weight percent (wt %) composition ratio of latex paint to PMMA provides similar mechanical behavior in tension as PMMA. For this study, a novel melt-processing method that mixes components and fabricates parts in a single step was used to prepare 20-80 wt % Paint-PMMA blends. The flexural, impact, thermal, and structural properties were characterized and compared with neat PMMA. Results indicate that Paint-PMMA is a viable, less expensive alternative to PMMA while also mitigating the disposal of waste latex paint.

1. Introduction

Collecting and managing waste paint is a significant problem facing the United States. With an estimated 17 to 35 million gallons of paint unused each year, waste paint constitutes the single largest volume of material collected by local government household hazardous waste collection programs.¹ Of this estimated figure, approximately 50% of this unused paint is latex-based paint.¹

The disposal of latex paint poses financial and environmental problems. Of all household hazardous wastes, paint is the most expensive material that local governments must manage and discard.² The cost for a municipality to properly collect and dispose of waste paint is at least $8 per gallon.¹ If all paint, including latex and oil paint, were properly managed by all municipalities, it would cost an estimated total of $275 million per year.¹ Proper latex paint disposal is not only a costly affair for local governments, but also a painstaking process for consumers. Liquid latex paint cannot be put into garbage trucks because of the risk of equipment contamination and must be placed outside to dry prior to disposal.³ While the paint is drying, it is necessary to keep all children, pets, and wildlife away from it.¹ The drying process requires time and effort, and local governments attribute instances of improper disposal to the difficulty of the drying process.²
The issue of latex paint also lies in its harmful effects on the environment. While the U.S. has been shifting away from using notoriously environmentally harmful oil-based paints and toward latex paint, latex paint is still an environmental concern. The most pressing environmental concern associated with latex paint is its improper disposal into bodies of water. Aquatic life is exposed to latex paint through the spilling and dumping of the paint into storm drains. According to the California Department of Fish and Game, “latex paints, having both toxic constituents as well as high concentrations of pigments with increased turbidity can be extremely deleterious to fish and aquatic life and must not be allowed to enter waters of the State or be placed at a location where it can enter such waters.”

Since the burden of disposing of latex paint has proven to be very inefficient and a significant deterrent for consumers, recycling latex paint could avoid many of these harmful effects. The purpose of this research project is to test if dried latex paints can be mechanically mixed with the thermoplastic polymer poly(methyl methacrylate) (PMMA) in order to form a functional immiscible polymer blend that shares similar properties with PMMA. Ideally, this could eventually bypass the challenges associated with waste latex paint management.

2. Background

Polymers are macromolecules comprised of a carbon backbone and represented by a unique repeat unit. These repeating units, which are groups of atoms centered around one or more carbon atoms, are chemically linked together through covalent bonding to form long polymer chains with high molecular weights. Depending on the structure, polymers can be classified as either thermoplastic or thermoset. Thermoplastic polymers, such as PMMA and latex, have covalent bonding along the main chains and secondary bonding between chains. Thermoplastic polymers are recyclable because they are able to be melted, cooled into a desired shape, melted again, and re-shaped over many cycles. Thermoset polymers, on the other hand, form crosslinks between polymer chains and degrade when reheated. Accordingly, thermoset polymers can only be formed once and are therefore not recyclable.

The thermoplastic nature of both PMMA and latex allows for them to be melt-processed into an immiscible polymer blend. An immiscible polymer blend is a combination of two or more polymers that are physically, rather than chemically, mixed together and remain as distinct phases. Therefore, the two polymers form a mechanical bond between one another. This contrasts with miscible polymer blends, in which two polymers are mixed together to form a chemically homogeneous blend with only one phase present. A miscible polymer blend generally has properties intermediate between the two original polymers. The advantage of an immiscible polymer blend is that under ideal conditions of mixture composition and processing methods, its mechanical properties can actually supersede those of the original polymers. Achieving superior mechanical properties requires dispersive and distributive mixing and good interfacial adhesion between the components so that applied stresses may be efficiently transferred between the two phases.
There are several important mechanical and thermal properties that must be compared when evaluating polymers due to the varied behavior they exhibit under different conditions of temperature and load. For instance, when considering the mechanical properties of a material, the maximum load it can withstand at room temperature must be determined. The external force, or load, acting on a material is known as stress. When a stress is applied to a material, the material sustains deformation, known as strain. Stress and strain are often coupled together to form stress-strain curves. Stress-strain curves are used to determine the amount of strain a material undergoes when a certain magnitude of stress is applied to it and to determine the point at which the material can no longer sustain a load, fracturing as a result.

The modulus of elasticity, or Young’s Modulus (E), demonstrates the relation between stress and strain by measuring a material’s resistance to elastic deformation. A material’s modulus can be determined by calculating the slope of its stress-strain curve in the elastic region. Thus, the stiffer the material, the higher the modulus. The equation to measure modulus of elasticity is: $E = \frac{\text{stress}}{\text{strain}}$.

All polymers experience a certain amount of elastic deformation before reaching a yield point. Elastic deformation refers to the temporary deformation that a material experiences that will not permanently alter the shape of a material, while plastic deformation refers to the permanent and non-recoverable change in the form of a material. The yield point on the stress-strain curve is the point at which elastic deformation ends and plastic deformation begins. Because plastic deformation is irreversible, the start of plastic deformation represents the onset of material failure. Ductility is the measure of the degree of plastic deformation that a material can sustain before it fractures. Polymers can be characterized as brittle if the polymer cannot undergo a significant amount of plastic deformation without fracturing or ductile if it can undergo a significant amount of plastic deformation without fracturing.

Polymers can be further characterized as amorphous, semi-crystalline, or crystalline based on the structure and interactions between their polymer chains. Amorphous polymers, such as PMMA and latex paint, have a highly randomized molecular structure. As a result, they often exhibit viscoelastic behavior at intermediate temperatures. As temperature decreases, amorphous polymers enter a glassy phase where the modulus of their stress-strain curve approaches zero. As temperature increases, the material becomes soft enough for the chains to freely flow. At this temperature, modulus is negligible.

The significance of this behavior is that PMMA experiences instantaneous elastic strain in response to stress, but recovers this deformation in a time-dependent, viscous manner. Although the phase transition from glassy solid to viscous liquid is not immediately distinguishable, the temperature that divides the two states is referred to as the glass transition temperature (denoted as $T_g$).

Crystalline polymers have a much greater degree of order than amorphous polymers. In the solid state, the molecules line up in a repeating array across the entire structure. Thus, there is a clear distinction between the solid and liquid states of crystalline polymers, as the molecules completely break away from their crystal structures in the liquid state and the polymer chains lose their
ordered array. The melting point is the name given to the temperature at which the phase change occurs. Semi-crystalline polymers share properties of both amorphous and crystalline polymers. Some portions of the polymer are amorphous, while others are crystalline in scattered areas. This means that semi-crystalline polymers have both a glass transition temperature and a melting point.8

2.1 Latex Paint
Latex paint is the most popular type of paint, representing over 85% of paint sales in the United States.10 Compared to its counterpart, oil-based paint, latex paint accounts for 89% of all interior paints and 71% of all exterior coatings.1 Latex paint consists of four main components in the following proportion: 50% water, 25% acrylic binder, 15% TiO\textsubscript{2} pigment, and 10% extenders and additives.1 The acrylic component is thermoplastic.

The waste latex paint employed in this polymer blend was obtained in solid form from a corporate source. Since this paint is taken from the waste stream, there is always the possibility that contaminants are present in the paint.

2.2 PMMA
Poly (methyl methacrylate), more commonly known as Plexiglas®, is a glassy thermoplastic polymer of methyl methacrylate [Figure 1].21 PMMA has a high flexural modulus, high mechanical strength, low elongation at break, and high shatter resistance.11 Because of its low water absorption, products made from PMMA have good dimensional stability.11 PMMA is often used as a substitute for glass because of its clear optical properties and can be used for products ranging from swimming pool enclosures to optical fibers for telecommunication and endoscopy.12

PMMA was selected for this paint-polymer composite because it shares many similar chemical properties with latex paint, is relatively cheap, and is easy to process.4,11 The PMMA used in this project was PMMA, Atluglas V045100.

2.3 Paint-PMMA Mixture
In this project, latex paint was mixed with PMMA in a 20-80 wt % ratio. This composition ratio was selected based on evaluation of previous research done on this topic, in which it was concluded that latex paint could be blended with common polymers, such as high-density polyethylene (HDPE) and PMMA, without compromising the mechanical properties of the unfilled polymers.3 Accordingly, latex paint could potentially be blended with polymers, and these blends may be used in the same unfilled polymer applications in an effort to recycle the unwanted latex paint. By blending this waste latex paint with PMMA, the financial and environmental burdens associated with waste latex paint management could potentially be avoided as long as the properties of this immiscible polymer blend, or plastic composite, are similar to the properties of PMMA and found to be appropriate for a given application. In a previous study that tested the properties of various paint-polymer blends, the 20-80 ratio of Paint-PMMA showed properties that in one case even exceeded those of unfilled PMMA. Since composites often have high stiffness, strength, and toughness, further testing was desired to corroborate the results of the previous study.13
3. Method

3.1 Sample Preparation

A Ryobi BS902 Band Saw was used to cut large blocks of dried latex paint into smaller pieces, better suited for grinding. Using a modified Nelmor Granulator, the dried latex paint was ground into flakes. The PMMA was dried in a Lindberg Blue Mechanical Oven at 85 °C for 24 hours and the ground latex paint was dried in an Across International Vacuum Drying Oven at room temperature for 24 hours to remove absorbed water molecules from the material. The dried materials were mixed together in small 100 gram batches — 20 grams latex paint and 80 grams PMMA — to establish the proper composition ratio in preparation for injection molding. Comparatively small amounts of carbon black were also added to the mixture to achieve a uniform specimen coloring throughout the melt-blending process.

3.2 Processing

Injection molding is used to mass-produce plastic products with varying shapes and designs. It is the most common method for processing thermoplastics such as PMMA. For this research, 20-80 wt % Paint-PMMA was injection molded to form an immiscible polymer blend using a Negri Bossi V55-200 injection molding machine operated at 216 °C and 320 RPM [Figure 2]. The mold yielded flexural and impact specimens with dimensions set by the American Society for Testing and Materials (ASTM) for use in testing. The specimens used in flexural testing were molded according to ASTM D790 standards with a width of 13 ± 0.5 mm and a thickness of 3.2 ± 0.4 mm [Figure 3]. The impact bars were molded at length 63.5 ± 2.0 mm, width 12.70 ± 0.20 mm, thickness 3.0 to 12.7 mm, as dictated by ASTM D256-10 [Figure 4].

The injection molding process was then repeated to mold the PMMA with the injection molding machine operating at 216 °C and 320 RPM. Both materials were allowed to rest for 40 hours before testing commenced as dictated by ASTM standards.

3.3 Flexural Testing

For mechanical property testing, flexural testing is performed on a material to determine flexural modulus of elasticity, flexural strength, and a material’s stress-strain curve. The flexural modulus of elasticity describes the material’s resistance to elastic deformation and aids in characterizing material failure. Flexural strength is the stress value at a material’s fracture. It is important to note that because flexural strength is the greatest value of stress that a material can withstand, it is also the effective strength of a material. In this analysis, the stress at yield point is taken as the effective strength of the tested materials because stress did not increase significantly thereafter. Aside from recording the flexural stress, it is equally important to note the strain at this point. The strain at yield describes the amount of deformation a material can undergo prior to experiencing plastic deformation.

A three-point flexural bend test was completed according to ASTM standard D790 using an MTS QTest controller [Figure 5]. For both materials, flexural tests were run at a calculated span of 52.288 mm and rate of crosshead motion of 1.4 mm/min. The same span and rate of crosshead motion was used for both materials as the specimen dimensions fit within the standard
deviations for these specifications, which is important for uniformity in analysis and comparison. Every tested specimen was centered on the lower supports with the direction of flow pointing the same way and then preloaded to 4 N. In accordance with ASTM standards, at least five specimens were tested for each sample.15

3.4 Impact Testing
Impact testing is used to determine a material’s ability to resist stress being loaded at a rapid rate.8 Using an Instron Dynatup POE 2000, an Izod Impact test was done on both the PMMA and Paint-PMMA according to ASTM standard D256-10.17 During impact testing, the pendulum swings and hits the material at a pre-made notch. The energy absorbed by the material at impact is recorded and used to determine the Izod impact resistance of the specimen.17

Prior to testing, the impact specimens were manually notched according to ASTM standards at a 45° ± 1° angle with a depth under notch of 10.16 ± 0.05 mm. Before impact testing occurred, a velocity test for the pendulum was run to ensure that its velocity was within ASTM standards. The pendulum’s velocity was determined to be 3.46 m/s, meeting ASTM standards.17 An impact energy of 2.7 J was inputted before running the impact test. After inputting impact energy and the specimen’s particular dimensions, which includes thickness, width, and depth under notch, the pendulum swings and breaks the specimen in the vice at the pre-notched region and records the impact resistance. For each sample, at least ten specimens were tested in compliance with ASTM standards.17

3.5 FTIR Analysis
Fourier Transform Infrared Spectroscopy (FTIR) uses infrared light to detect the types of bonds present within molecular structures. A range of frequencies of infrared light are emitted into the material being tested and data is collected based on the percent transmittance of the light at each particular wavelength. The absorbance at a certain infrared wavelength corresponds to specific types of bonding. Since no two unique bonds will have the same infrared spectrum, the spectra produced can be used to determine the bonds present in the material.18 An FTIR test was performed on 3 specimens each of PMMA, latex paint, and the Paint-PMMA mixture in order to characterize the makeup of the 20-80 wt % Paint-PMMA blend as compared to the unfilled polymer and original paint samples.

3.6 DSC Analysis
Differential Scanning Calorimetry (DSC) measures the thermal transitions of polymers. During DSC, an empty aluminum pan is used as a reference. Meanwhile, the material being tested is placed into another pan known as the sample pan.4 To determine the heat capacity of the sample a temperature sweep is done. The sample pan and the reference pan are maintained at the same temperature, so that the material with the higher heat capacity absorbs more heat. The difference in heat absorption is proportional to the difference of the two materials’ heat capacities. As a result, the glass transition temperature and melting point of a polymeric sample can be found, as well as the degree of crystallinity. Glass transition temperature refers to the temperature at which polymer chains gain
additional mobility due to bond rotations, and with increased heating are eventually able to flow past one another.\textsuperscript{4} The glass transition temperature is characteristic of amorphous polymers and the amorphous region of semi-crystalline polymers. Melting point is the temperature at which crystalline and semi-crystalline polymers lose their ordered structure and become liquid-like.\textsuperscript{4}

In this research, DSC was employed to characterize the thermal properties of PMMA and the paint component. This testing was done using a TA Instruments Q1000 Differential Scanning Calorimeter under an atmosphere of dry nitrogen. The heat absorption of PMMA was compared to an aluminum reference pan. Three Heat-Cool-Heat runs of DSC were completed with a temperature range of -25 °C to 220 °C at a heating rate of 10 °C per minute. The three samples were prepared to 10.0 mg ± 1.0 mg.

Modulated DSC (MDSC) differs from regular DSC in that it measures both the heat capacity and the heat flow of a material in a single temperature ramp by “superimposing a modulated heating rate on top of a linear heating rate.” MDSC “offers increased sensitivity for detection of weak transitions.”\textsuperscript{19} In this analysis, MDSC was used to measure the thermal transitions of 20-80 wt % Paint-PMMA in order to observe a more visible change in the composite’s glass transition temperature than could be observed with regular DSC. The 20-80 wt % Paint-PMMA sample underwent a temperature ramp of -25 °C to 220 °C at 3 °C per minute with a 2 °C modulation temperature amplitude every 40 seconds using the modulated mode of the TA Instruments Q1000 Differential Scanning Calorimeter (MDSC). A sample of 10.2 mg of the Paint-PMMA composite was used for this test.

4. Results

4.1 Flexural Properties

Five specimens were tested for the PMMA and seven specimens were tested for the Paint-PMMA as dictated by the ASTM standards.\textsuperscript{15} The stress-strain curves for both the PMMA and the 20-80 wt % Paint-PMMA blend were generated from the collected stress and strain data points [Figure 6, Figure 7]. A representative specimen from each sample was selected for comparison and is presented on a separate graph [Figure 8].

Upon testing, both the PMMA and 20-80 wt % Paint-PMMA were found to have an average modulus of 3.1 GPa [Figure 9]. Since the modulus of elasticity is a very important property of polymers, it is very promising to find that blending the latex paint with the PMMA was not detrimental to its modulus. The PMMA was able to withstand an average stress at yield of 100 MPa, while the 20-80 wt % Paint-PMMA blend had an average stress at yield of 79 MPa [Figure 10]. The percent strain at yield was similar for PMMA and Paint-PMMA blends at 4.95 % and 4.72 %, respectively, [Figure 11].

During testing, two Paint-PMMA specimens fractured while no specimens fractured for the PMMA. Upon further examination, noticeable inclusions of material other than paint or PMMA were found within the composite on the fracture surface [Figure 12A]. Contaminants like these act as stress concentrations, because the stress surrounding the inclusion is higher than the applied load and results in premature fracture. [Figure 12B]. Thus, the flexural
strength of the Paint-PMMA blend might be artificially low and may increase with a cleaner source of waste paint.

4.2 Impact Properties
The impact test is used to determine the impact resistance of a material by calculating the sample’s energy absorbance at impact. Impact resistance is calculated by dividing the total energy absorbed at impact by the specimen thickness. Throughout the tests, specimens underwent a uniform impact energy due to the pendulum strike of 2.7 J at an impact velocity of 3.46 m/s. All specimens exhibited complete breaks. The impact resistance was similar for the PMMA sample at 59 J/m and the 20-80 wt % Paint-PMMA sample at 55 J/m [Figure 13]. The standard deviation of the PMMA sample is larger at 6 J/m compared to that of 20-80 wt % Paint-PMMA sample at 2 J/m. Importantly, the impact resistance of the 20-80 wt % Paint-PMMA sample fell within the standard deviation of the impact resistance for PMMA.

4.3 Structural Properties
The FTIR spectra of PMMA corresponded very closely to the PMMA reference spectra [Figure 14, Figure 15]. The peak in the 2750-3050 cm\(^{-1}\) range indicates a CH stretching vibration and the following peak around the wavenumber 1730 cm\(^{-1}\) indicate CO double bond stretching vibration. Other peaks in the wavenumber ranges of 1395-1450 cm\(^{-1}\) and 1040-1260 cm\(^{-1}\) represent CH\(_3\)/CH\(_2\) deformation vibrations and COC single bond stretching vibrations, respectively. The rightmost peak at 800-1000 cm\(^{-1}\) indicates a COC single bond deformation vibration.

The FTIR spectra for the latex paint was not completely uniform over the three trials conducted [Figure 16]. This indicates that the paint had a varying composition between the samples, which is to be expected with mixed, waste paint that may not be of the same type. The variation occurs most saliently in the wavenumber range from 600-1400 cm\(^{-1}\). The FTIR spectra of PMMA and latex paint indicate that they have similar chemistry.

The 20-80 wt % Paint-PMMA had very uniform spectra that likely resulted from consistent composition, thorough mixing, and proper dispersion among the 20-80 wt % Paint-PMMA specimens [Figure 17]. The three most prominent peaks from the FTIR spectra of the PMMA remain present in the 20-80 wt % Paint-PMMA spectra, and the Paint-PMMA spectra appear to include peaks from both the PMMA and paint spectra [Figure 18]. The significance of this is that many of the bonds present in the original materials are still present in the polymer blend, as is characteristic of an immiscible polymer blend. One characteristic that very clearly signals the presence of the latex paint in the 20-80 wt % Paint-PMMA is the peak at the lower end of the wavenumber scale, around 600-750 cm\(^{-1}\), because it is manifest in both the paint and Paint-PMMA spectra.

4.4 Thermal Properties
In analyzing the DSC results, the glass transition temperature of the PMMA was found to be 105.5 °C [Figure 19]. The MDSC graph of the 20-80 wt % Paint-PMMA displays two glass transition temperatures of 24.5 °C and 96.8 °C for the latex portion of the blend and for the PMMA portion of the blend respectively [Figure 20]. The results of the MDSC initial heat run for the 20-80 wt % Paint-PMMA mixture demonstrate
that the $T_g$ of PMMA is lowered by about 9 °C when blended with paint. The DSC tests also confirm that the Paint-PMMA composite has two distinct phases—a PMMA phase and a latex phase—as is characteristic in immiscible polymer blends. There was no melting temperature observed for either PMMA or the Paint-PMMA composite, which means that neither material has a crystalline structure. This result is consistent with the amorphous form of PMMA.

4.5 Possible Sources of Error

Upon observing the flexural fracture surfaces of two 20-80 wt % Paint-PMMA specimens, white contaminants were visible [Figure 12]. Contaminants in waste-sourced materials are a common problem and act as stress concentrations within the polymer blend, which causes pre-mature fracture during mechanical property testing. To address this problem, one can improve the collection process to better clean the waste materials and also use recycled materials to fabricate parts with large cross-sections, in which the effect of the contaminants is minimized.

5. Conclusion

Waste latex paint was collected, dried, and injection molded with PMMA to prepare an immiscible polymer blend of 20 wt % paint and 80 wt % PMMA. The flexural, impact, thermal, and structural properties were characterized for the 20-80 wt % Paint-PMMA blend and for neat PMMA. The Paint-PMMA blend demonstrated a modulus of elasticity equal to that of PMMA and similar impact resistance. These two characteristics indicate that the 20-80 wt % Paint-PMMA plastic composite would be suitable to replace PMMA in certain applications because these mechanical properties are not sacrificed with the blending of paint and PMMA. It may therefore be feasible to use a Paint-PMMA composite as a medium to recycle unused latex paint and to subsequently use the composite in specific applications as a substitute for PMMA. However, the marginally lower yield strength of the 20-80 wt % Paint-PMMA composite reflects that the material will begin to plastically deform under less stress than PMMA itself and is therefore not appropriate to replace PMMA in all applications. Further investigation should be completed to determine the response of Paint-PMMA blends to stresses applied over a long period of time as compared to the response of PMMA. Therefore, latex paint blended with PMMA has potential to serve as a material that can ameliorate some of the burden of disposing unused paint by creating an immiscible polymer blend with comparable mechanical properties to PMMA.

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7. References


8. Figures

Figure 1. Repeating unit of PMMA

Figure 2. In injection molding, the material is fed through the hopper, pressurized and heated in the plasticizing/feed screw, fed through the nozzle into the mold, and ejected upon cooling.
Figure 3. 20-80 Paint-PMMA and PMMA flexural specimens as molded according to ASTM D638-08 tensile bar dimensions\textsuperscript{16}

Figure 4. 20-80 Paint-PMMA and PMMA impact specimens according to ASTM D256 dimensions\textsuperscript{11}

Figure 5. A three-point flexural bend test being performed on a 20-80 Paint-PMMA flexural specimen
Figure 6. Stress-Strain curves for PMMA

Figure 7. Stress-Strain curves for 20-80 Paint-PMMA
Figure 8. Stress-Strain curves for a representative specimen from both the PMMA and 20-80 Paint-PMMA specimens
Figure 9. Flexural Modulus for PMMA and 20-80 Paint-PMMA

Figure 10. Stress at Yield (MPa) for PMMA and 20-80 Paint-PMMA
Figure 11. Percent Strain at Yield for PMMA and 20-80 Paint-PMMA
Figure 12. Both images show the fracture of a 20-80 Paint-PMMA flexural specimen.

A) The fracture surface shows contamination indicated by the white inclusions.

B) An uneven fracture surface
Figure 13. Impact Resistance (J/m) for PMMA and 20-80 Paint-PMMA
Figure 14. Reference FTIR Spectra for PMMA
Figure 15. FTIR Spectra for 3 specimens of PMMA

Figure 16. FTIR Spectra for 3 Paint samples
Figure 17. FTIR Spectra for 3 specimens of 20-80 Paint-PMMA

Figure 18. FTIR Spectra overlay with a representative specimen of from PMMA, Paint, 20-80 Paint-PMMA
Figure 19. DSC of PMMA

Figure 20. MDSC of 20-80 Paint-PMMA