# Magnesium-PMMA Composites Formed by Mechanical Alloying

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## Abstract

The mechanical alloying process is used to form poly methyl methacrylate (PMMA)-5 vol.% magnesium (Mg) composites by high-energy ball milling the blends for up to 10 hours. The milling products and their compacted composites are characterized and compared with milled pure PMMA. Mechanical alloying can cause degradation of the amorphous thermoplastic polymer in the powder mixture but also allows for increasingly fine dispersion of Mg in the PMMA matrix with milling. X-ray diffraction (XRD) and image analysis of optical micrographs show that the magnesium remains crystalline, and its particle size reduces with milling time from an average of 200 microns to under 10 microns after 10 hours milling. Additionally, peak broadening from XRD analysis shows decreasing crystallite size within the particles. The hardness of the composite increases with milling time by up to 7%, whereas the hardness of the milled pure PMMA decreases with milling time by about 5%.

Keywords: mechanical alloying, metal-polymer composite, particle size

## 1. Introduction

The combination of metals and polymers to form a composite material can be used to expand the range of achievable properties over that of each class of materials individually.[1] In particular, the addition of metallic particles to a polymeric matrix can increase density and electrical and thermal conductivity.[2] Significant research has been performed into the effects of dispersing metal particles into polymeric matrices using high-temperature processes.[1-3] However, less research has been done into forming metal-polymer composites by the low-temperature solid-state process of mechanical alloying, which has been shown to produce unique properties different from high-temperature processes.[4]

In mechanical alloying, two powders are placed in a vial with several hardened metal or ceramic charge balls. The vial is then milled by vigorous agitations, causing high-energy collisions between the balls in which powder particles are trapped between the balls, leading to deformation, fracture, and fusion of the powder particles. The important parameters in this process are milling time, specific energy input, and milling temperature. The specific energy input correlates to the mass of the charge balls compared to the mass of the powders in the vial, a parameter referred to as charge ratio.[5] Milling temperature can be controlled or allowed to increase due to the heat from the high-energy milling. Particle size decreases as milling continues, leading to closer interaction between the two powdered phases and, in many cases the formation of unique metastable structures.[4-5]

Mechanical alloying was originally developed by Benjamin *et al.* to produce oxide dispersion strengthened superalloys and has been studied extensively in metals to control microstructure, induce amorphization[7-9] and extend solubility limits.[6] Mechanical alloying has also been found to be a useful technique for forming polymer blends in the solid state.[5] In light of the potential property advantages that can be achieved with metal-polymer composites, it seems a logical next step to investigate mechanical alloying with metal and polymer powders.

Work done by Ishida and Tamaru studied the use of mechanical alloying to create metal-polymer composites with polytetrafluoroethylene (PTFE) powder for a polymer and copper or nickel for a metal. In both systems (PTFE/Cu and PTFE/Ni), the researchers found significant decreases in particle size with milling time.[4] Particle size was observed by Ishida and Tamaru to reach a steady state particle size by about 10 hours milling time.[4] However, other experiences with mechanical alloying of metals indicate that refinement of crystallite size can be achieved by continued milling once the steady state particle size has been reached.[10] This research will expand on the prior work described above with a new materials system and more emphasis on the resulting mechanical properties.

## 2. Procedure

### 2.1 Sample Preparation

The materials used in this research were a thermoplastic powder of poly methyl methacrylate (PMMA, >99% purity) produced by Precision Surfaces International (PSI-213-5) and a magnesium powder (99.8% purity, 50-100 mesh) produced by Atlantic Equipment Engineers. Mechanical alloying with a tungsten carbide vial and ball set was used to process the powders. A 19:1 volume ratio was held constant for the mixture of PMMA and Mg powders (5 V% Mg), which were prepared in an Ar-atmosphere glove box to avoid oxidation. The specific energy input was also held constant with a charge ratio of 3:1 (three charge balls with mass of 32.28 g, powder mass of 10.76 g). Five samples were prepared and milled for five milling times: 0, 1, 2, 5, 10 hours. Two control samples of pure PMMA with no Mg were also prepared, one not milled at all and the other milled for 10 hours, but with small samples removed at 1, 2, and 5 hours.

To assess the effect of milling time on mechanical properties (Vickers hardness) and microstructure, approximately five grams of each of the mixtures and the unmilled control were pressed into hardened specimens at 150˚C and 4 ksi (27.6 MPa) for 10 minutes. These specimens were then polished with alumina to the 0.05 µm particle size.

### 2.2 Thermal Analysis

The five mixture powder samples and the unmilled PMMA control powder were thermally analyzed using a Neztsch STA 449 C Jupiter simultaneous thermal analyzer to perform differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) concurrently. Each sample was heated from room temperature up to 350˚C at 20˚C/min in air to examine the alteration of the mixture with milling time. Sample masses were between 6 and 10 mg and the results were normalized by mass.

### 2.3 Microscopy

Optical microscopy was performed on the polished specimens at magnifications up to 100X to assess the variation in microstructure with milling time, particularly the interaction between the Mg and PMMA particles.

### 2.4 Hardness Testing

Vickers hardness tests (LECO LV 700 AT) were performed with 1 kgf for 10 seconds at ten locations on each of the hardened specimens for the five mixtures and the unmilled control. Averages of the ten readings on each were compared to analyze changes in mechanical properties with milling time.

### 2.5 Structure

The crystal structures of the four milled mixture powders and three milled compacts were analyzed by powder X-ray diffraction (XRD) using a PANalytical X’pert Pro PW3040 instrument. The peaks were analyzed to assess the decrease in Mg crystallite size with increasing milling time. Full-width half-maximum values were calculated by the X’Pert High Score Plus software at five prominent diffraction peaks as a function of milling time to quantify peak broadening and associated crystallite size reduction and d-spacing was used to analyze peak shifting.

### 2.6 Particle Size Analysis

A particle size analysis was performed on the micrographs at 5X and 10X magnifications using ImageJ 1.41 software. To perform this analysis, the micrograph images were converted first to 8-bit grayscale and then to binary by adjusting the threshold brightness to identify Mg particles from the PMMA matrix. The binary image was then refined to fill in holes and eliminate single-pixel indications. Finally, the software performed a particle size distribution analysis on the refined binary image to determine the average size (pixel area) and number of Mg particles in the micrograph. These pixel areas were converted to physical areas based on the magnification of the image and the average particle size for all the micrographs taken at the 5X and 10X magnifications were calculated. This limited sampling of the surface is not expected to give a definitive value for particle size as a function of milling time, but should provide an indication of the general trend, subject to variability.

## 3. Results and Discussion

### 3.1 Thermal Analysis

DSC and TGA curves for all five of the powder mixtures at milling times of 0, 1, 2, 5, and 10 hours are shown below in Figures 1 and 2, respectively, along with a 100% PMMA sample. All six DSC curves in Figure 1 show an endothermic event occurring from about 250-300˚C. This endothermic event decreases in intensity with increasing milling time and also occurs at a higher critical temperature as milling time increases. If one notes that the melting point of Mg is greater than 600$^{o}$C, it is safe to conclude that this endothermic event is the melting of the PMMA, which has been recorded in the literature to occur at 220-250$^{o}$C. It is, therefore, interesting to observe that the melting of the PMMA occurs with less intensity and at a higher critical temperature as milling time increases, probably due to smaller molecular weight as a result of bond-breaking during milling along with more intimate and homogeneous mixing with Mg. One should also note that by 10 hours milling time, the endothermic melting is no longer observed in the DSC curve, suggesting that the PMMA structure has been significantly changed due to the milling.

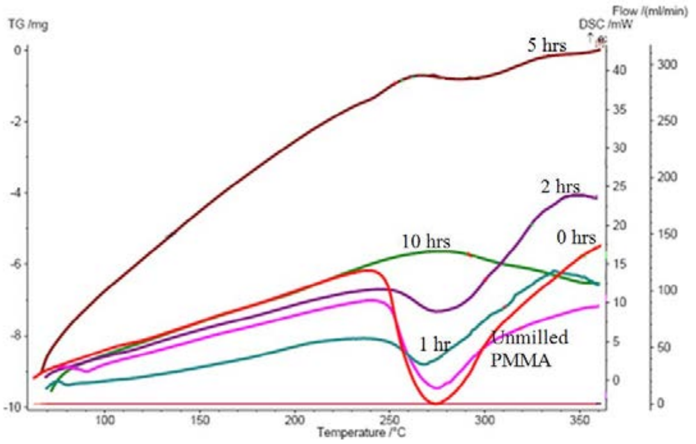

Figure 1: DSC curves for milling times of 0, 1, 2, 5, and 10 hours and unmilled pure PMMA

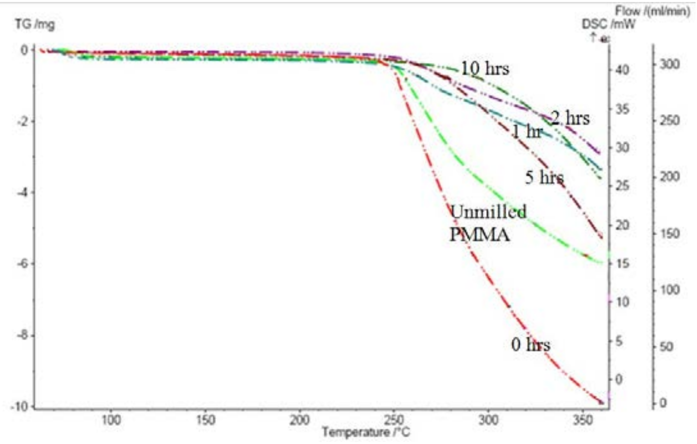

Figure 2: TGA curves for milling times of 0, 1, 2, 5, and 10 hours and unmilled pure PMMA

Consistent with the DSC curves, the TGA curves in Figure 2 show the greatest mass loss for the unmilled sample and decreasing mass loss with milling time. This would indicate that as milling time increases, less PMMA is melting and then volatizing to cause the loss in mass. The mass loss in the TGA also coincides with the endothermic event (PMMA melting and volatizing) seen in the DSC curves and shows the same increase in critical temperature with milling time that was observed by DSC. Overall, the thermal analysis by DSC and TGA indicates a change in the structure of the PMMA due to milling, most likely smaller molecular weights due to bond breaking during milling as seen by other researchers.[5] More intimate and homogeneous mixing with Mg with milling time could also contribute to the shift in critical temperature observed in the thermal analysis.

### *3.2 Microscopy*

Micrographs of pressed specimens of the powder mixture are shown at 5x magnification in Figure 3. In Figures 3a and 3b, the decrease in magnesium (dark due to oxidation) particle size with milling time can be clearly seen. The PMMA is seen in these figures as the lighter region and is translucent when observed directly, allowing view of internal Mg particles. When the specimens are pressed with heat, the PMMA crosses its glass transition and flows easily to form a polymeric matrix around the Mg particles, allowing for easy analysis of the change in Mg particle size. A distinct heterogeneity is present in the 1 and 2 hour samples, with little to no fine mixing between the Mg and PMMA, but simply Mg particles suspended in a PMMA matrix.

In Figures 3c and 3d, the 5 and 10-hour milled samples can be seen, showing much more homogeneity than the shorter mill times. It is apparent that a significant transition occurs between milling times of 2 and 5 hours. Up to 2 hours milling, Mg particle size is decreasing with milling time, but the specimens are distinctly heterogeneous, with little or no fine mixing between the two phases. However, by 5 hours milling significant homogenization and fine mixing has occurred with a decreasing percentage of distinct Mg particles (now lighter regions due to less oxidation ) present and an increasing percentage of matrix (darker due to dispersion of Mg), which consists of a mixture of PMMA and Mg. The key transition from 2 to 5 hours milling is in the degree of fine mixing of the two phases within the matrix; up to 2 hours milling, this matrix is composed almost exclusively of PMMA, but by 5 hours the matrix has begun to disperse and mix with Mg homogeneously.

In Figure 4, the four milled mixture samples can be seen at higher magnification, clearly demonstrating the change occurring within the matrix from pure PMMA to a fine homogeneous mixture involving Mg and PMMA. Figures 4a and 4b show a translucent matrix (now darker due to optical microscope effects) of pure PMMA with particles of Mg (grayish or black depending on oxidation at surface or being trapped internally) suspended, while Figures 4c and 4d illustrate an opaque matrix (multicolored region) of finely mixed PMMA and Mg still containing Mg particles (now primarily grayish), but in decreasing size and quantity. In Figures 4c and 4d, there appears to be a varied, almost bimodal distribution of particle sizes with the largest particles up to around 50 µm, ranging down to less than 10 µm.

### *3.3 Hardness Testing*

Vickers hardness testing was performed on the pressed specimens to observe the effect of milling time on the mechanical properties of the material. Although hardness is just one surface measure of a material's mechanical properties, hardness measurements tend to reflect general trends of mechanical strengthening in a material.[11] The change in hardness with milling time is shown in Figure 5 for both pure PMMA and the 5 V% Mg mixture. The results of hardness testing showed an increase in hardness with milling time for the mixture and a decrease in hardness with milling for the pure PMMA. After 10 hours of milling, the mixture is significantly harder than the pure PMMA.

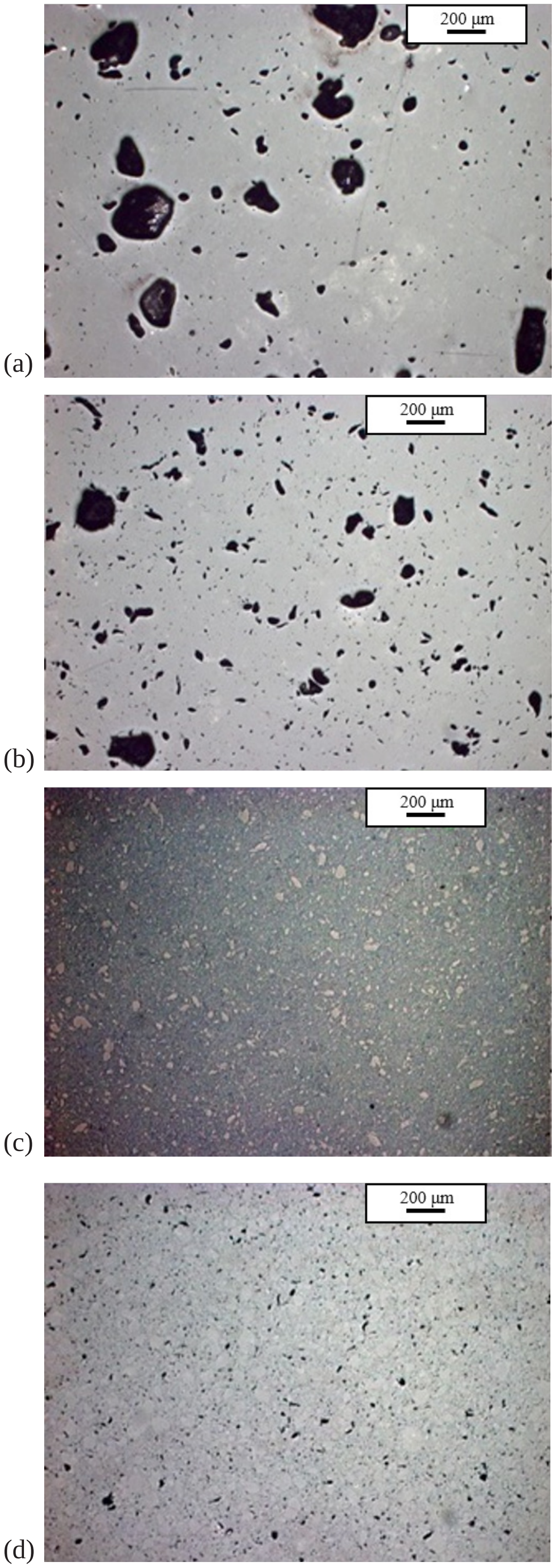

Figure 3: Micrographs at 5x magnification showing specimens milled for (a) 1 hour, (b) 2 hours, (c) 5 hours, and (d) 10 hours

However, the greatest average Vickers hardness recorded was for the unmilled pure PMMA, indicating that mixing with Mg and milling failed to improve hardness.

These results are consistent with experimental observations documented by other researchers mechanically alloying polymers[5] and can be explained by the degradation of the polymer during milling due to bond breaking and the corresponding chain molecular weight decrease. A reduction in hardness with increasing milling time is clearly observed in the pure PMMA data and is most likely caused by PMMA degrading during milling. Little change is seen from 5 to 10 hours as it appears that a steady state chain molecular weight is reached by 5 hours milling, with little change occurring due to additional milling. Likewise, the trend of increasing hardness in the PMMA/Mg mixture could be explained by the fine homogeneous mixing of the two phases leading to a strengthening of the matrix. The milling process yields Mg dispersed very finely within the PMMA matrix, offering strengthening over the milled pure PMMA.

### *3.4 Structure*

The structure of the powders as a function of milling time was analyzed by XRD to see the effect of milling. The full XRD spectrum can be seen for the powder form in Figure 6. A similar XRD curve was observed for the compact form not shown. Observation of the largest Mg peaks from the powder and compact forms demonstrates the decrease in Mg peak intensity with milling time. This decrease in peak intensity is caused by the decrease in crystalline particle size and crystallite size within the particles with milling time. Decreasing crystallite and particle size with milling seen in the XRD peaks correlate well with increasing hardness with milling. These decreases in particle and crystallite size can also be observed through peak broadening in the XRD spectrum by analysis of the change in a particular peak's full-width at half-maximum (FWHM). Particle size analysis by observation of optical micrographs provides another assessment of change in crystalline particle size, although not crystallite size.

Observation of peak broadening with increasing milling time shows that significant crystallite size reduction does not occur until 5 hours milling time as the 1 and 2 hours milled curves are quite similar, but considerable intensity decreases are seen at 5 and 10 hours milling. There is also an indication that a grain texture may be forming, due to the differing drops in peak intensity with milling time in the largest peaks. This differing peak behavior with milling indicates that preferential grain alignment is occurring among the crystallites within the Mg particles.

To analyze potential grain texture, crystallite size inferred from XRD peaks was plotted against milling time utilizing the Scherrer formula to calculate "effective crystallite sizes" from XRD peak broadening in the compact and powder form of the mixture.[7] In this analysis, with random grain orientation the various diffraction peaks should give the same

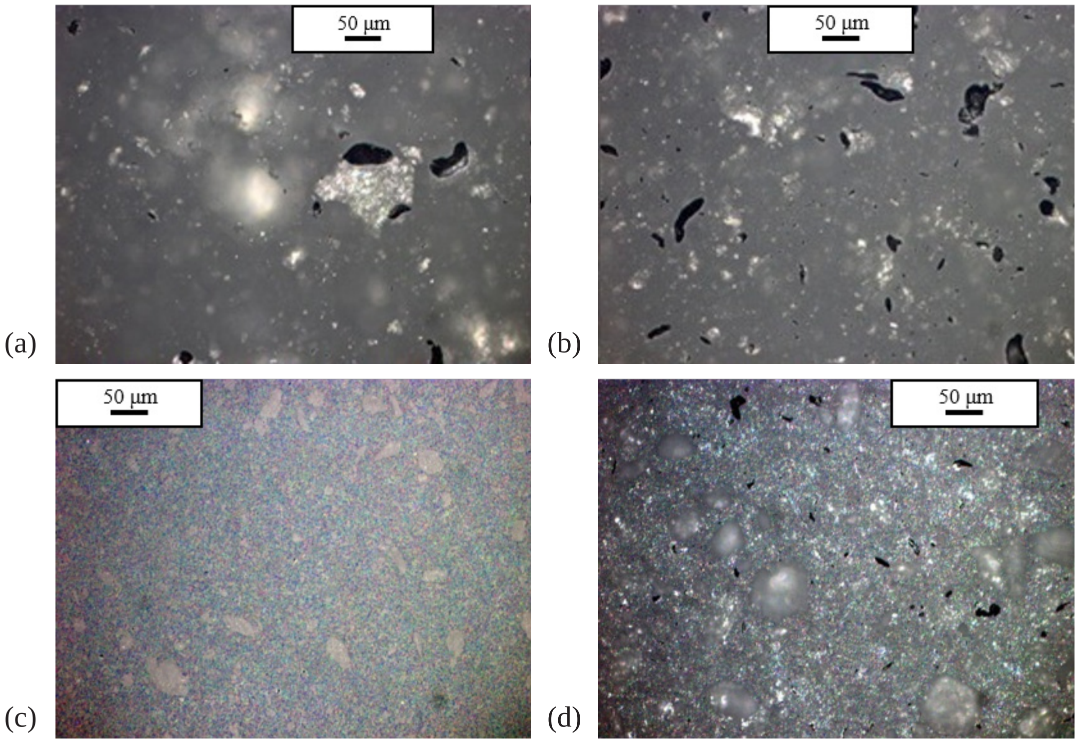

Figure 4: Higher magnification micrographs; (a) 1-hour milling at 20x, (b) 2-hour milling at 20x , (c) 5-hour milling at 20x, (d) 10-hour milling at 20x

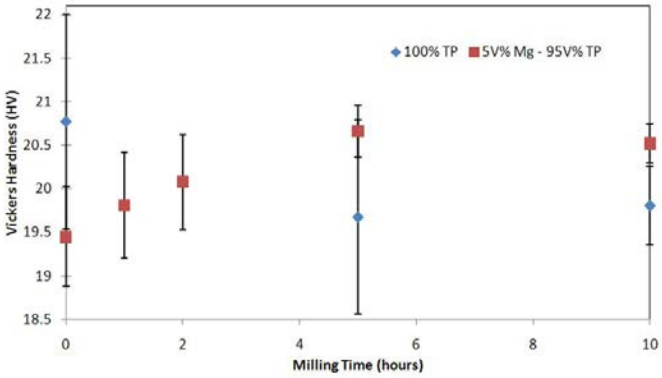

Figure 5: Comparison of Vickers hardness for pure PMMA and mixture as a function of milling time with error bars of one standard deviation

effective crystallite size because they are reflecting from the same lattice. If the sizes are not the same, this indicates the development of grain texture to cause preferential alignment of the grains. This analysis for both the powder and compact forms show little numerical indication of grain texture.

These largest Mg peaks also show some evidence of peak shifting with increasing milling time, with the peak angle variation potentially indicating a changing lattice parameter. To assess this, d-spacing was calculated for the largest XRD peak on the spectrum centered at about 2Θ = 34.3˚. These results seem to show a slight increase in the d-spacing with milling time, indicating the lattice planes are becoming slightly more spread apart, which could be caused by the minor diffusion of interstitial carbon into the Mg crystalline matrix with milling. However, while these trends are

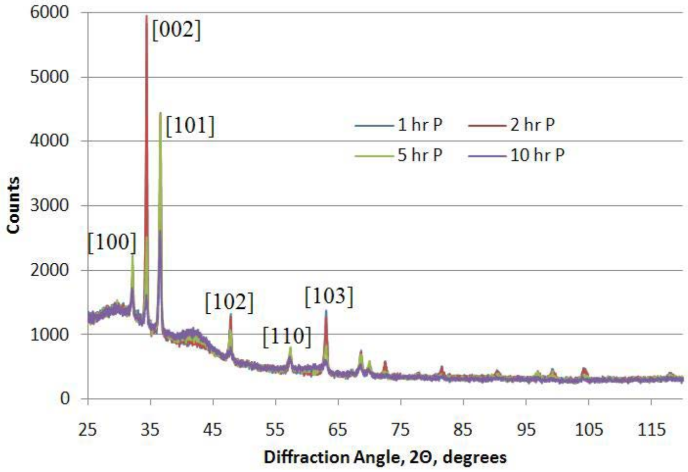

Figure 6: XRD graph for PMMA/Mg powder mixture for 4 milling times with full spectrum.

common in both the powder and compact form, it is difficult to draw any strong conclusions of the cause due to the small variation in d-spacing.

### *3.5 Particle Size Analysis*

To optically assess the change in Mg particle size with milling time, a particle size analysis was performed using micrographs at 5X and 10X magnification along with ImageJ software as described in the procedure section. This particle size analysis showed an expected sharp decline in visible particle size with milling time. Similar to the other analyses, the majority of the change in particle size occurred up until 5 hours milling, with very little change beyond that point. Figure 7 shows a graph of average particle size against

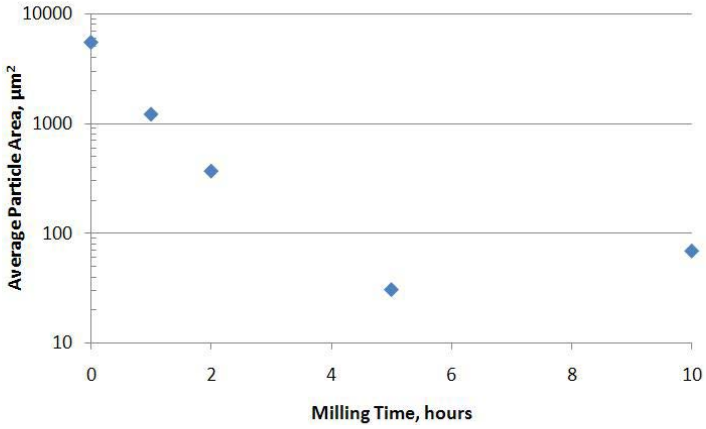

Figure 7: Particle size analysis results from micrographs at 0, 1, 2, 5, and 10-hour milling times

milling time illustrating the sharp reduction in particle size from 0 to 5 and 10 hours milling. The particle size analysis is generally consistent with other analyses performed, showing that the greatest effect of milling is seen up to 5 hours, with little change from 5 to 10 hours milling.

## 4. Summary

Low-temperature, solid-state mechanical alloying was used to produce metal-polymer composites of Mg and PMMA resulting in unique structures and altered mechanical properties. X-ray diffraction and microscopy point clearly to a reduction in Mg particle and crystallite size and increasing homogenization of the Mg within PMMA matrix with milling time. Hardness of the mixture increases with milling time, due to fine mixing and homogenizing of the matrix with milling, improving on the decreasing hardness trend exhibited by pure PMMA when milled.

This research provides a baseline for further work involving metal-polymer composites and mechanical alloying. The technique of mechanical alloying is ideal for producing metal-polymer composites, but is in need of more study and fine-tuning of the composition and milling time to maximize the resulting material’s properties.

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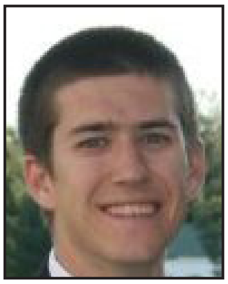
## About the Author



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