

# Production of Air-Stable Aluminum Nanoparticles Using 1,2-Epoxy-9-Decene/ Methyl Methacrylate Monomers and Poly (Methyl Methacrylate) as Capping Agents

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## ABSTRACT

We report here the synthesis of air-stable aluminum nanoparticles (Al NPs) using copolymerization of 1,2-epoxy-9-decene and methyl methacrylate (MMA). We also report on the stabilization of Al NPs with poly (methyl methacrylate) (PMMA, MW = 120,000). Here, the PMMA adsorbs to the incipient Al NPs to create a hydrophobic barrier that stabilizes the NPs from oxidation by atmospheric O<sub>2</sub> and H<sub>2</sub>O.

**Keywords:** Aluminum, nanoparticles, polymerization, PMMA

## 1 INTRODUCTION

Reactive metallic nanoparticles have many energetic applications in fuels and hydrogen production/ storage. Aluminum is a popular metal for these applications due to its high energy density, low cost, and ready availability. While Al NPs are potentially useful, their high reactivity makes them unstable under normal atmospheric conditions. As a result, their synthesis and stabilization are important and challenging issues [1,2,3].

Recently, we developed a convenient and effective route for stabilization of Al NPs that uses the nascent metal core as a polymerization initiator for various organic compounds. In our previous work, we have used this method to polymerize a variety of epoxides to create polyether-coated Al NPs. We have also used copolymers with epoxides and alkenes, and simple polymers based on polyenes [1,2,3]. These products have demonstrated air stability of weeks to months with little to no degradation in the active Al content. Interestingly, when we

attempted direct capping of nascent Al NPs using polyethylene glycol (PEG), we observed rapid and complete oxidation of the nanoparticle cores even under air-free conditions [2].

Since our previously synthesized Al NP's were not dispersible in nonpolar solvents such as toluene, our goal was to find polymer capping agents that stabilize the Al NPs and that are dispersible in toluene and other nonpolar solvents. In this work, we present results on the capping and stabilization of Al NPs with a copolymer of 1,2-epoxy-9-decene and methyl methacrylate (MMA) as well as results on the direct capping of the Al NPs with poly (methyl methacrylate) (PMMA). This system is also stable, in contrast to the PEG/Al NP system.

## 2 EXPERIMENTAL

**2.1 Reagents and Materials:** *N,N*-Dimethylethylamine alane (H<sub>3</sub>Al'NEtMe<sub>2</sub>, 0.5M in toluene), titanium (IV) isopropoxide (99.999% trace metals basis), 1,2-epoxy-9-decene (96%), methyl methacrylate (MMA) (≥98.5%), poly (methyl methacrylate) (PMMA, M<sub>w</sub>= 120,000), and toluene (anhydrous, 99.8%) were all supplied by Sigma-Aldrich. Both alane and titanium (IV) isopropoxide were stored under argon. Toluene was distilled over sodium metal under an argon atmosphere while MMA was distilled over molecular sieves. A 5.0×10<sup>-5</sup> M PMMA solution was prepared by dissolving 1.8g in 300 ml freshly distilled toluene. Several freeze-pump-thaw cycles were performed for all of the capping agents to remove O<sub>2</sub>.

**2.2 Synthesis:** A modification of the synthetic protocol proposed by Haber and Buhro was used to prepare the Al NPs [4]. All reactions were

carried out on a Schlenk line under argon atmosphere. Alane (6.5 ml) and freshly distilled toluene (15 ml) were added to a clean, dry round-bottom flask and purged 3 times with argon. The resulting clear solution was heated to 85°C with stirring. At this temperature, 0.8 mL titanium isopropoxide (0.0338 M in toluene) was added followed by the immediate addition of either 1,2-epoxy-9-decene/MMA or PMMA, leading to a color change from clear to brown. The resulting mixture was refluxed at 85°C for 1 hr and then cooled to 25°C. All solvent was then removed, and the resulting gray solid was heated *in vacuo* at 85°C overnight. For the copolymer system of 1,2-epoxy-9-decene and MMA, the MMA solution was added 60 s after the addition of 1, 2-epoxy-9-decene. A 10: 1 to Al: cap molar ratio was used along with a 1:1 1,2-epoxy-9-decene: MMA molar ratio. For the Al NPs capped solely with PMMA, 5 ml of a 0.00005 M PMMA solution were used.

**2.3 Analysis:** All powder X-ray diffraction (PXRD) experiments were performed on a Rigaku Ultima IV diffractometer equipped a scintillation counter detector and a Cu source operated at 40kV, 44mA, and 1.76 kW. The presence of face-centered cubic (fcc) Al was confirmed by comparison with the appropriate pattern from the ICDD Crystallographic Database. The presence of elemental aluminum was determined using a TA Instruments model Q2000 differential scanning calorimeter (DSC) and a TA Instruments model Q500 thermogravimetric analyzer (TGA). Samples were analyzed from 25°C to 725°C using a 10°C/min temperature profile. Fourier transform infrared spectroscopy (FTIR) measurements were made using a Shimadzu model FTIR-8400S spectrometer equipped with an attenuated total reflectance (ATR) crystal. The electron micrographs were captured using a FEI Inspect F50 scanning electron microscope (SEM) equipped with a STEM detector. Samples were cast on Formvar grids provided by Ted Pella.

### 3 RESULTS AND DISCUSSION

We previously reported the passivation of Al NPs capped with 1,2-epoxy-9-decene<sup>4</sup>. In this system, the electron-rich Al NP core initiates a ring-opening polymerization of the epoxide. We see the terminal alkene functionality undergoes thermally-induced cross-linking after heating to create a very air-stable hydrophobic polymer cap. For the 1,2-epoxy-9-decene/ MMA

copolymerization, we see similar behavior. Figure 1 shows a schematic of how 1,2-epoxy-9-decene interacts with the Al NPs and how the terminal alkene on 1,2-epoxy-9-decene reacts with the alkene of MMA. This copolymerization leads to the formation of a polymer matrix around the Al NPs to prevent reaction with water or oxygen.

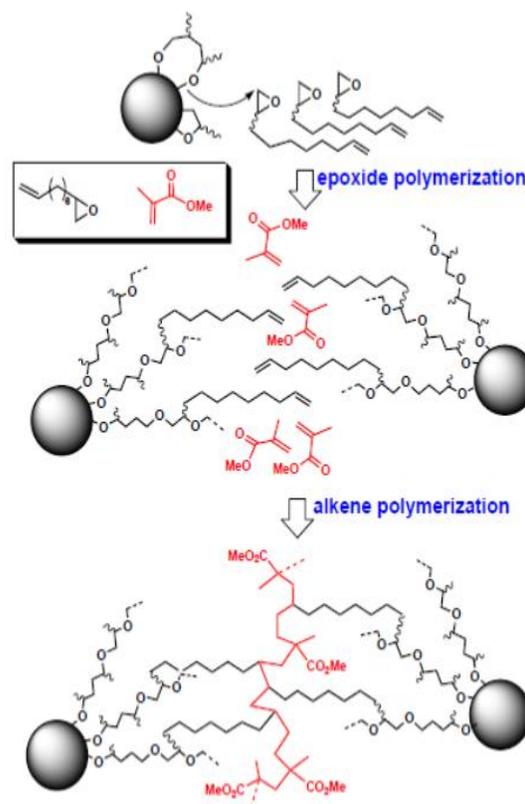


Figure 1: Schematic showing how 1,2-epoxy-9-decene reacts with Al by ring opening polymerization and how terminal alkenes polymerize to form a polymer matrix.

An infrared spectrum is presented in Figure 2, which shows that the terminal alkene of 1,2-epoxy-9-decene polymerizes with MMA to form an interconnected polymer matrix as confirmed by the absence of an alkene C=C stretching frequency at 1600 cm<sup>-1</sup>. There is an ester C=O stretch around 1750 cm<sup>-1</sup> as well as an ether C-O stretch at ~1100 cm<sup>-1</sup>, thus lending support to the notion of polyether formation as a result of epoxide ring opening.

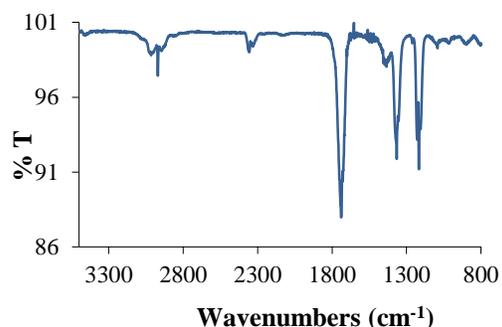


Figure 2: FTIR spectrum of Al NPs capped with a copolymer produced from 1,2-epoxy-9-decene and MMA.

Figure 3 shows the FTIR spectrum of pure PMMA and the FTIR spectrum of PMMA-capped Al NPs. Major differences are noted between the two spectra. Both spectra have ester C=O stretches around 1750  $\text{cm}^{-1}$ ; however, the pure PMMA spectrum has an ether C-O stretch around 1130  $\text{cm}^{-1}$  while the PMMA-capped Al NP spectrum has an ether C-O stretch around 1210  $\text{cm}^{-1}$ . This shift in the ether C-O stretches suggests that there is some interaction between the Al NP core and the PMMA cap.

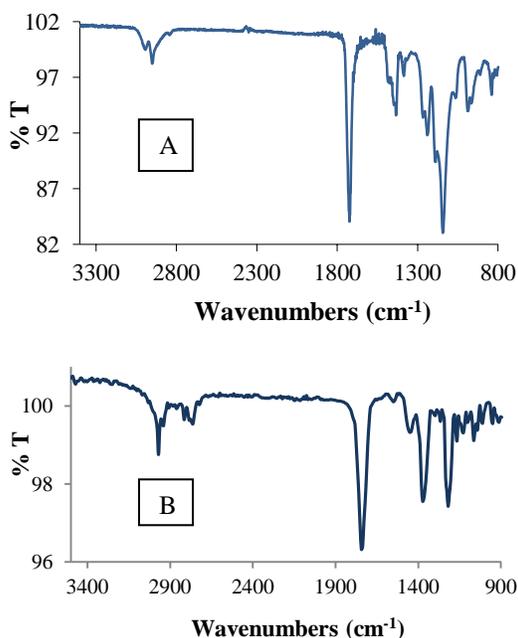


Figure 3: FTIR spectra of A) pure PMMA, and B) Al NPs capped with PMMA.

Figure 4 shows a STEM image of Al NPs capped with PMMA. The image shows that

the Al NPs are embedded in a polymer matrix, as is suggested in the Figure 1 schematic.

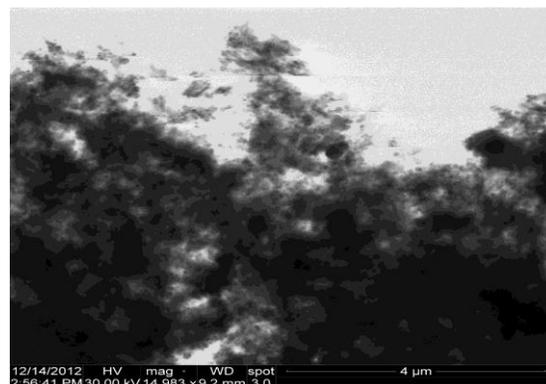


Figure 4: STEM of Al NP capped with PMMA.

The peaks seen in the PXRD pattern shown in Figure 5 correspond to those reported for face-centered cubic (fcc) Al. In addition, the PXRD of Al NPs capped with 1,2-epoxy-9-decene/MMA shows that, after 28 days air exposure, elemental Al is still present. Also, the PXRD of Al NP capped with PMMA shows that crystalline Al is present after 2 months of air exposure.

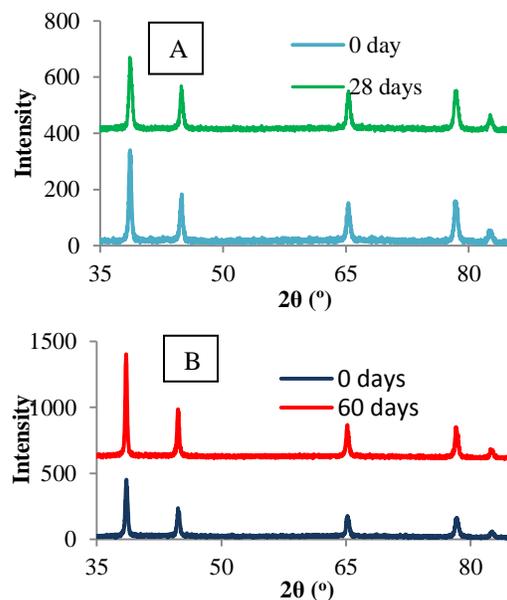


Figure 5: A) PXRD of Al NP capped with 1,2-epoxy-9-decene/ MMA with 0 day and 28 days air exposure, and B) Al NP capped with PMMA with 0 days and 60 days air exposure.

In conjunction with the presence of metallic Al seen in the diffraction pattern following the designated aging period, we can determine the degree of oxidation based on variations in the Scherrer widths over time (Table 1). The Al core sizes for both Al NPs capped with the 1,2-epoxy-9-decene/MMA copolymer and the Al NPs capped with PMMA are smaller overall than those previously reported for epoxide-coated Al NPs [1,2,3]. The core size decreases by 2 nm after 28 days air exposure for Al NPs capped with 1,2-epoxy-9-decene/ MMA. A similar decrease in particle size is seen for Al NPs capped with PMMA after 60 days air exposure. These particle size decreases are indicative of oxide layer growth that is occurring at a much slower rate than that which was reported for Al NPs capped with epoxyalkanes [1].

Capping agents	Al Core Size (PXRD)	Solubility in Toluene
Epoxydecene/MMA*	18.0 nm	dispersible
After 28 days	16.0 nm	
PMMA	13.3 nm	dispersible
After 60 days	10.8 nm	

Table 1: Size and solubility of the Al NPs composites

\*10:1 Al:capping agent molar ratio

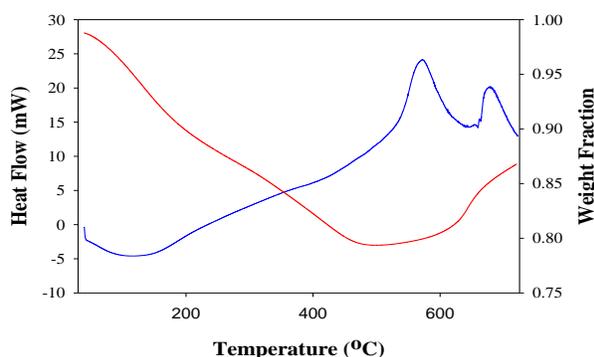


Figure 5: DSC-TGA of Al NPs capped with 1,2-epoxy-9-decene/ MMA copolymer.

Thermal analysis of the Al NP copolymer system is presented in Figure 5.

Combustion of the polymer cap gives a very broad exothermic peak between 200 and 400 °C while combustion of Al gives the narrower exothermic peaks at 570 °C. The accompanying mass loss and gain for each of these events, respectively, is seen in the TGA scan. The mass gain around 630 °C is due to formation of heavier Al<sub>2</sub>O<sub>3</sub>.

## 4 CONCLUSION

PMMA-coated Al NPs with Al core diameters of 18 nm and 13 nm, respectively, were synthesized. We also used PMMA in contrast to PEG as a capping agent. The resulting Al NP polymer composite is air-stable for more than one month as seen in the PXRD powder patterns. The FTIR spectra confirm the presence of polymer on the Al NP surface while PXRD, DSC, and TGA confirm the presence of elemental Al in the Al NPs. For both the copolymer system and the PMMA system, the resulting nanomaterials were dispersible in toluene.

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## REFERENCES

- [1] Chung, S. W.; Gulians, E. A.; Bunker, C. E.; Hammerstroem, D. W.; Deng, Y., Burgers, M. A.; Jelliss, P. A.; Buckner, S. W, *Langmuir*, 25(16), 8883-8887, 2009.
- [2] Hammerstroem, D. W.; Burgers, M. A.; Chung, S. W.; Gulians, E. A.; Bunker, C. E.; Wentz, K. M.; Hayes, S. E.; Buckner, S. W.; Jelliss, P. A., *Inor. Chem.*, 50, 5054-5059, 2011.
- [3] Thomas, B. J.; Wentz, K.; Gulians, E. A.; Bunker, C. E.; Hayes, S. E.; Jelliss, P. A.; Buckner, S. W., *Preprint. Symp. American Chemical Society: Div. Fuel Chemistry*, 57, 667-668, 2012.
- [4] Haber, J. A.; Buhro, W. E., *J. Am. Chem. Soc.*, 120 (42), 10847-10855, 1998.