Nanoclay-enabled nanocomposites continue to rapidly grow in novel applications including food and beverage packaging, biomedical tools, fire retardants, automobile/aerospace parts industry, etc. Previous studies have found adverse toxicological effects due to the exposures to raw nanoclay materials, including pulmonary health effects (e.g., respiratory tract irritation), hamamelolysis, cytotoxicity effects (e.g., decreased cellular proliferation), mitochondrial and membrane damage, reactive oxygen species generation, and genetic effects. Manufacturing, use, machining, and disposal of nanocomposites used in those applications could lead to the potential release of aerosolized particulates including intact nanocomposite, nanocomposite with surface nanoclays protrusions, or free released nanoclays particles from the polymer matrix. Occupational exposures to airborne nanocomposites are expected to increase in the near future, but are poorly understood.

The objective of this study was to simulate industrial sanding of nanoclay-embedded polypropylene composites and to characterize particles generated to estimate occupational exposure levels.

Methods and Materials

Nanoclay-enabled polypropylene nanocomposite synthesis: Polypropylene (PP, Amoco BP 1346) was selected as a model virgin thermoplastic material. Two types of nanoclay, Cloisite® 25A and Cloisite® 30A (Southern Clay Products, Gonzalez, TX) at 1% and 4% of concentration by weight, were embedded into the PP via melt mixing and compression molding using a 370-ton press in a built-in house. Virgin PP (0% nanoclay) served as a comparative control of non-ENM-enabled thermoplastic composite (Fig 1).

Characterization of mechanical properties: Mechanical properties including Young’s modulus, tensile strength, toughness, and elongation at break were determined using an Instron E1000 under a 2 kN load cell. Toughness was then calculated by integrating the area under stress-strain curve. Crystallinity and degree of nanoclay dispersion of each composite was determined with a PANalytical X’Pert Pro and a Bruker D8 Discover XRDs. Visualization of dispersed nanoclay within the PP matrix was also performed via TEM analysis.

Controlled Machining of Nanocomposites: Sanding particles of nanocomposites and virgin materials were generated using an automated controlled exposure system. (Fig 2, Table 2). Two types of sandpaper (2KN and SIC) and two grit sizes (P100 and P180) were studied. CPC, SEM, AFM, APF, MOUD iodimetric, and ICM samplers were deployed to analyze particle release real-time and for post-machining analyses. Temperature was also monitored during sanding.

Electron Microscopy Analysis: Computer-controlled scanning electron microscopy (CCSEM) analysis coupled with EDS was conducted on collected inhalable size fraction filters by R.J. Lee Group to determine number, mass, size, and chemistry characterization of generated dusts. FESEM images and EDS images of the individual particles ≤ 1 μm were captured during the CCSEM alignment using IsisSEM software (about the potential release of nanocomposites). Criteria were developed to sort composite and sandpaper particles based on our working example comparing particle morphology and elemental composition. ONC protrusions were identified and quantified by evaluating > 200 particles per sample.

Conclusions

- Airborne particle release during machining of ONC-enabled polypropylene nanocomposite depended on coating type, percent ONC load, ONC dispersion within the matrix, and sandpaper grit size. These factors impacted nanocomposite tensile strength, toughness, and elongation at break.

- Nanocomposites with 1% ONC loading resulted in 69,000 particles/cm² during machining, regardless of coating type followed by 4% Cloisite® which showed improved dispersion compared to 4% Cloisite®. Both 1% nanocomposites showed decreased mass loading towards increased confidence in the ultralight particle release compared to 4% and virgin composites. Tensile strength of each nanocomposite was highly correlated with airborne particle concentration.

- Collected airborne dust particle (≥ 1 μm) was a complex mixture comprised of nanocomposite particles and sandpaper particles, dominated by elemental composition. Nanocomposite particles dominated the mass release for most nanocomposites while calcium-rich and carbon-rich non-composite particles dominated percent number release.

- 22.55% of nanocomposite particles had ONC protrusions out of the PP matrix with the remainder of composite possessing detectable levels of ONC embedded in the matrix. Limited analysis of ultralight particle suggested that free release of ultralight aluminate particles (i.e. nanoclay) was rare.