Polymeric Nanocomposites for Automotive Applications

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1. Introduction

Current global expectations for fuel economy and low emissions for manufacturing and transportation are creating a demand for new low-cost, high-performance lightweight materials to replace metals. Nanocomposites are a novel class of polymeric materials exhibiting superior mechanical, thermal, and processing properties, suitable to replace metals in automotive and other applications.[1] This new technology is attracting the attention of the automotive manufacturing industry and its suppliers.[2–4]

The use of nanocomposites in vehicle parts and systems is expected to improve manufacturing speed, enhance environmental and thermal stability, promote recycling, and reduce weight. Applying this technology only to structurally non-critical parts such as front and rear fascia, cowl vent grills, valve/timing covers, and truck beds could yield several billion kilograms of weight saved per year. Nanocomposite plastic parts offer a 25% weight savings on average over highly filled plastics and as much as 80% over steel. Since approximately 90%[5] of the total energy used by an automobile during its life cycle is from fuel consumed, this reduction in weight offers the potential of significant energy savings for the automotive industry and vehicle users. Energy savings could be further expanded by applications into structural components, interiors, and body panels.

As important as the process advantages and weight and energy savings are the enhanced physical properties that nanocomposites offer. Nanocomposite-based parts provide stiffness, strength, and reliability comparable to or better than metals. They offer corrosion resistance, noise dampening, and enhanced modulus, thermal stability, and dimensional stability. However, it is still unknown if the cost/performance ratio of nanocomposites will be superior to the cost/performance ratio of materials currently used by the automotive industry.

2. Nanocomposites vs. Traditional Materials in Automotive Applications

The automotive industry is a materials intensive industry. A wide variety of metals, fillers, and plastics are used today to meet the requirements of specific applications. The ultimate drivers in materials selection are, of course, cost and performance. Materials are selected by identifying the best cost/performance ratio needed to meet the requirements of the application. This reality has driven the development of numerous approaches to enhance the properties of conventional materials.[6] Examples of these approaches include structural plastics, alternative metals and alloys, reinforcing fillers, and glass fiber composites. Each of these approaches has limitations. Structural plastics often require post-forming modifications of the surface and long cycle times and are more expensive. Light-
weight metals and their alloys are seeing increased use, primarily in non-cosmetic structures, for weight reduction. These metals, however, have the same processing limitations as steel and iron, and they usually add cost.

Reinforcing fillers such as talc, mica, and calcium carbonate, for example, introduce higher stiffness while also increasing weight and melt viscosity, and decreasing toughness, optical clarity, and surface quality. Glass-fiber reinforcement provides high stiffness with a corresponding increased difficulty of fabrication and cost. These traditional reinforcements and fillers must be used at high loading levels to increase modulus and improve dimensional stability, thus compromising weight, toughness, and surface quality.

In contrast to traditional fillers, nanofillers such as exfoliated clays are expected to be effective at a loading under 5% by weight, introducing only a minor increase in materials cost. They provide significant improvement in modulus, thermal stability, fire retardancy, dimensional stability, surface hardness, heat-distortion temperature, mar resistance, and barrier properties. Nano-scale reinforcement should enable part and system design of polymer composites that will be cost-competitive with other polymers, and eventually replace metals and glass, thus enabling the automotive industry to capture a leadership position in fuel-efficient, higher-quality, and durable vehicles.

Nanocomposites may be produced by incorporating nanometer-size clay particles in polymers such as polypropylene (PP), polyethylene (PE), polyesters, epoxies, etc. Several routes are currently proposed to make polymer–clay nanocomposites. The clay materials can be dispersed and exfoliated into polymers by conventional melt compounding or solution methods. Alternatively, nanocomposites can be made by the in-situ intercalation polymerization method, where the monomer is first intercalated in the clay, and subsequently polymerized in situ. This method was pioneered by Toyota Motor Company to create Nylon 6–clay hybrid (NCH), used to make a timing-belt cover, the first practical example of polymer–clay nanocomposites. Montmorillonite, a natural layered clay mineral, was modified with amino acids and converted to NCH by reactive intercalation with caprolactam. These polymer–clay, organic–inorganic molecular composites exhibit excellent mechanical properties compared with Nylon 6. The tensile modulus of NCH is twice that of Nylon 6 (2.1 vs. 1.1 GPa), and the CLTE is reduced in half (6.3 × 10⁻⁵ vs. 13 × 10⁻⁵) for a NCH containing only 1.6 vol.-% clay mineral. These properties result from the high dispersion of the clay in Nylon 6 and from the strong ionic interaction between the polymer and the anionic silicate layer.

3. Key Nanocomposite Properties for Automotive Applications

The use of polymeric nanocomposites in automotive applications depends on meeting stringent demands on cost and performance. Here we briefly outline some of the key automotive materials properties that need to be enhanced and controlled to make nanocomposites viable alternative materials for vehicle parts and systems.

3.1. Enhanced Modulus and Dimensional Stability

The properties of polymer composites have been studied and modeled extensively. The Kerner equation, for example, describes modulus in terms of volume fraction, aspect ratio, particle size, and maximum filler fraction. This model suggests that stiffness can be increased while maintaining as much toughness as possible by using smaller filler particles. This promotes adhesion of the filler to the matrix due to the increased surface-to-volume ratio. Conventional fillers, such as glass fibers, are typically 10 μm in diameter with aspect ratios of 20 to 60. This limits the modulus that can be achieved with glass fibers. Improvements in modulus can be achieved using surface-treated fillers to enhance the stress transfer between fiber and matrix. These improvements, however, are typically offset by decreases in toughness.

Composite models have been extended to the realm of nanocomposite systems. In nanocomposites the matrix and nanoparticles are interactive across interfaces of very large relative surface area. The high aspect ratios of nanoparticles, and the opportunity of higher dispersion over conventional fillers, make possible large increases in modulus and tensile strength, as well as large decreases in the coefficient of linear thermal expansion (CLTE), a key factor in dimensional stability and an essential factor to manufacture large vehicle parts.

Toyota Motor and Ube Industries have successfully developed a NCH polymeric nanocomposite. Montmorillonite, a natural layered clay mineral, was modified with amino acids and converted to NCH by reactive intercalation with caprolactam. These polymer–clay, organic–inorganic molecular composites exhibit excellent mechanical properties compared with Nylon 6. The tensile modulus of NCH is twice that of Nylon 6 (2.1 vs. 1.1 GPa), and the CLTE is reduced in half (6.3 × 10⁻⁵ vs. 13 × 10⁻⁵) for a NCH containing only 1.6 vol.-% clay mineral. These properties result from the high dispersion of the clay in Nylon 6 and from the strong ionic interaction between the polymer and the anionic silicate layer.
3.2. Higher Heat-Distortion Temperature

Depending on their application, automotive parts may have to withstand interior or engine compartment temperatures or elevated temperatures involved in paint application. Fillers such as talc, calcium carbonate, or the nanofillers proposed here increase the heat-distortion temperature of materials such as PP. These fillers create tie points between crystallites, bridging the amorphous phase and causing it to soften above its glass-transition temperature. Nanofillers, however, are not expected to impart many of the property losses of conventional fillers because smaller particles produce less stress concentration.[6]

The heat-distortion temperature of NCH nanocomposite was enhanced dramatically with respect to Nylon 6 by addition of 5 % clay (65 to 110 °C) as compared to 30 % mineral-filled Nylon 6 (65 to 120 °C).[10] However, the unusual enhancement for the NCH is probably due to the unique nature of the in-situ reactivity intercalated product and may not be as dramatic in other polymeric matrices.

3.3. Improved Scratch and Mar Resistance

Maintenance of surface quality is important in many automotive applications. Scratch and mar resistance is enhanced when modulus is increased.[11] Introduction of nanofillers, as described earlier, is expected to increase modulus and therefore increase scratch resistance. The addition of fillers, however, can also lower resistance to scratch and mar because of delamination and/or void formation from displaced filler particles. Nano-sized particles, unlike conventional fillers, are less susceptible to void formation. Smaller particles provide less stress concentration, which reduces the potential for damage. In addition, when nano-sized particles are displaced, the resulting voids are smaller, thus scattering less light. This decreases the amount of whitening created by particles which are displaced.

3.4. Toughness and Rheological Properties

Typically, the addition of a reinforcing filler to a polymer results in increased modulus, but reduced toughness and poorer rheological properties (which affect processing). Recent advances at Dow in constrained geometry polyolefin polymerization catalysis (Insite (trademark of The Dow Chemical Company) technology) have afforded polyolefin elastomers possessing unique physical and mechanical properties because of their narrow comonomer and molecular weight distributions.[12] This unique molecular structure results in many improved rheological properties, such as enhanced shear thinning, melt elasticity, and improved polymer melt processability. These attributes also allow for enhanced dispersion of these novel elastomers in PP as seen in the transmission electron micrographs shown in Figures 2 and 3.

Strengthening of the polymer–filler interface is critical to properly managing stress transfer during deformation. Most approaches to this problem involve the use of other polymers or low-molecular-weight additives which have some affinity for both the filler and the matrix polymer. A more rational methodology would involve the use of in-situ compatibilization, whereby either the nanofiller or the matrix polymer would be chemically designed so as to actually react with the other and form covalent bonds with it during the compounding process. This approach has a number of obvious costs and process advantages associated with it compared to other approaches, which may involve various pretreatment/compatibilization steps prior to actual compounding.
The rheological behavior of nano-reinforced polymers is also crucial to its success in the real world.\cite{13} Nanocomposite materials must be processable on existing injection-molding equipment with minimal deviation from current practices. In theory, if the dispersion/compatibility issue discussed above is managed properly, the impact on rheology due to the presence of the filler will be minimal. However, other molecular architecture approaches to the design of the matrix polymer can be applied if needed.

In summary, predictive models and qualitative arguments suggest that the proposed nanocomposite materials will exhibit properties which are significantly better than those of the automotive industry’s current state-of-the-art materials.

4. Polyolefin Nanocomposites

The replacement of metals and high-performance engineering thermoplastics by lower cost polyolefin-based composites or nanocomposites is an active field of industrial and academic research.\cite{1–8,10} The molecular structure and morphology of polyolefins can be designed in-situ by manipulation of catalysts and reactor operation parameters to deliver products and properties “on demand”. In addition, a broad scope of physico-chemical post-reactor and processing technologies can be applied to tailor the ultimate performance of composites and blends, such that desirable mechanical, thermal, rheological, and surface properties demanded by the market are delivered.\cite{13}

PP has great potential for composites and nanocomposites because it can be processed by conventional technologies, such as extrusion and injection molding, to make parts for automotive applications. The properties of PP reinforced by micro- and nanofillers give rise to composites with high rigidity and toughness.\cite{14}

Recently, PP-clay hybrid composites were prepared at Toyota Central R&D via melt intercalation of montmorillonite organo-clays with PP modified with either maleic anhydride (MA–PP) or hydroxyl groups (HO–PP).\cite{15,16} An example of similar PP-clay hybrid composites is shown in Fig. 4. A nanocomposite made from F-mica clay at a 10 wt.-% level modified with C16 amine in conjunction with 20 wt.-% MA–PP (4.2 % MA grafts) resulted in a well-exfoliated morphology with a Young’s modulus of 3460 MPa as compared with 1460 MPa for bulk PP. There was a corresponding increase in yield stress from 33 to 44 MPa.\cite{17} However, only C12, C16, and C18 amine modifiers in combination with MA–PP promoted exfoliation with PP in F-mica clays. The development of robust predictive methods for exfoliation based on fundamental understanding is an active area of research in materials modeling.\cite{18}

General Motors R&D and Montell USA have developed thermoplastic olefin (TPO) clay nanocomposites with reduced weight and good dimensional stability for exterior automotive applications.\cite{19} PE nanocomposites were formed effectively also byethylene homo- and copolymerization in the presence of organo-clays, catalyzed with methylalumoxane (MAO)-activated zirconocene, nickel, and palladium catalysts.\cite{20} Another strategy that may be used to obtain polyolefin-based nanocomposites is based on the in-situ intercalative polymerization of the monomer. In this technique, the monomer together with a polymerization initiator or catalyst is intercalated within the interlayer spacing of the layered silicates followed by polymerization, producing the polymer chains between the silicate layers. Bergman et al.\cite{21} demonstrated the in-situ intercalative polymerization of ethylene and propylene using a Brookhart-type catalyst intercalated in an organo-modified fluoro-hectorite, producing exfoliated nanocomposites with quite low polymerization activity.

Alexandre et al.\cite{22} describe the in-situ intercalative polymerization of ethylene in non-modified layered silicates (hectorite and montmorillonite) through the polymerization-filling technique (PFT). This technique consists in anchoring the polymerization catalytic complex at the surface, in the interlayer of the given filler and polymerizing ethylene from this surface. MAO/metallocene system is used in this study with the catalyst fixation ensured by the anchoring of MAO on the non-modified layered silicate. Nanocomposites based on PE matrices and non-modified layered silicates (hectorite, montmorillonite) could be prepared by the polymerization-filling technique using metallocene/MAO catalytic complex, as demonstrated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. In absence of molecular hydrogen as a transfer agent, the PE matrix of very-high to ultra-high molecular weight mainly controls mechanical properties of the composites. The addition of molecular hydrogen expectedly decreases the molecular mass of PE and yields
composites with improved tensile properties, characterized by a marked increase in Young’s modulus and improved strain behavior.

Nanocomposites made via melt compounding or by the various in-situ methods using polyolefin polymerization catalysts supported on micro- and nanofillers are a potentially promising route to new materials for automotive applications. Much work is needed to convert these initial results into the manufacture of parts for automotive applications.

5. Conclusions

Nanocomposites are a new class of polymeric filled composites with unique mechanical, physical, and processing properties. They may potentially be manufactured at low cost and may offer other advantages on density and processing with respect to metals and polymeric composites currently used in the fabrication of parts for automotive applications. Recent results on production of polyolefin nanocomposites by melt processing of organo-clays with modified polymers or by various in-situ polymerization methods suggest that these materials can be produced with current technologies. The current challenge is to develop nanocomposites at competitive cost and with superior performance to replace metals and/or existing polymeric filled composites.