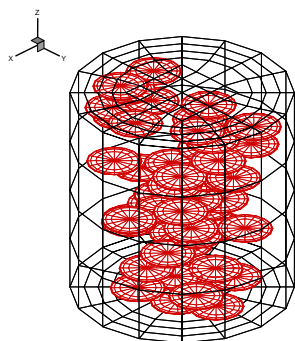


Technology Review

Enhancing Gas Barrier Properties of Polymer Nanocomposites

Background: The migration of gases through materials has been a critical factor in the ability of food packagers to increase the shelf life of products. The migration of CO₂ out of soda bottles can reduce shelf life by allowing the soda to



Idealized Oriented Layered Nanoparticles

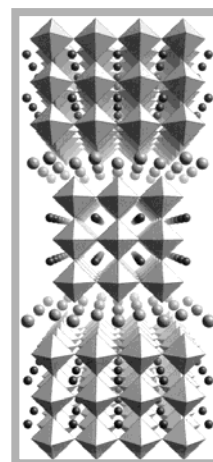
become “flat.” Oxygen migrating into beer bottles reacts with the beer to make it “stale.” The migration of oxygen through auto and truck tires causes the steel belt to rust, reducing the tire’s life. This is particularly important in large industrial truck tires that may be retreaded many times before the “carcass” is discarded. Polymeric materials are attractive candidates for each of these and many other applications. The central issue that confronts the manufacturer is the minimization of gas migration. In other words, one desires to maximize the gas barrier properties of the material.



Purpose: Research on the introduction of clay and clay-like nanoparticles, both natural and synthetic, into polymers is centered on the maximization of these barrier properties.

Specific Research Problems: There are four problems that arise when trying to maximize the barrier properties of polymer/“clay” nanocomposites. **Exfoliation:** The aspect ratio of the particles must be such that they are very thin in cross section, but present a large surface area in its flat dimensions, with the objective of maximizing gas permeability while minimizing the effect of the particles on material clarity, color, weight, etc. This means that the clay particles that grow as aggregates or “books” of sheets, must be broken up or exfoliated into individual sheets that have a thickness of on the order of one nanometer with lengths and widths on the order of 500 nanometers. **Compatibility:** Second, the particles must be compatible with the polymeric substrate. Since natural clays are alumino-silicates, they must be prepared or “functionalized” so that they will be compatible with the polymer. This process related to natural clay products can be quite complex given the wide chemical variability of different samples, even from the same mine. **Orientation:** Third, once the particles are dispersed in the polymer, they must be oriented so that the flat surface of the clay is parallel to the surface of the packaging material to maximize the barrier effects.

Reaggregation: And finally, during processing, these particles must be kept from reaggregating or “clumping up,” thus destroying the benefits of the approach. For industrial applications, the process point, the method, and the form of clay introduction into the polymer nanocomposite production process must be compatible with the kinds of chemical reactions that take place during this process.



Layered Perovskites

Research Activities: Current research is carried on in four areas:

1. **Nanoparticle synthesis (Dr. zur Loye):** Synthesis and exfoliation of synthetic layered materials that offer a range of potential advantages over the natural clays that have traditionally been used in polymer nanocomposites.

2. **Nanoclay exfoliation, functionalization, and modification (Dr. Scrivens):** This research is centered on the preparation of stable suspensions of well characterized and exfoliated samples of natural montmorillonite clays in various solvents. These suspensions are then converted to perfectly exfoliated clays in a variety of polymer matrices for use as reference standards.
3. **Compounding Nanoclays with polymer melts (Dr Papathanisiou):** The process of introducing the nanoparticles into the polymeric medium has associated with it a host of chemical and mechanical activities that may aid or may hinder the development of well exfoliated and well oriented nanoparticles that will maximize the gas barrier properties of the nanocomposite. Polymer reaction mixing and twin screw extrusion are used to create the nanocomposites while monitoring such variables as torque, temperature, viscosity, etc. The physical and mechanical properties of these products are evaluated to determine if target properties such a clarity and stiffness are being achieved.
4. **Nanocomposite characterization (Dr. Ploehn):** Throughout the process of producing and evaluating a variety of polymeric nanocomposite products under different controlled conditions, the nanostructure of these products is continually assessed using the most advanced tools of nanoscale evaluation. Scanning Electron Microscopy and Atomic Force Microscopy allow for the visual assessment of particle exfoliation and alignment that will be essential in understanding the reasons for the physical properties observed.



18mm co-rotating TSE (Leistritz)

Recent Significant Achievements: New approaches to the functionalization of montmorillonite clays have been developed that offer the hope of being able to control how and when these particles aggregate and disaggregate in the particular medium of interest. New ways by which these particles are prepared, transported, and introduced into polymer of interest are being developed. Our ability to synthesize a wide range of synthetic layered materials with specific functionality built into them has been steadily improving, and our ability to characterize the results of these experiments at the nanoscale with electron and atomic force microscopy is at the forefront of polymer nanocomposite technology.

Specifically the first steps in developing a viable PET monolayer high-barrier material have been achieved. A well-exfoliated montmorillonite clay has been incorporated into a PET matrix, bottles have been blown, and gas permeability measurements have been made.

Current Intellectual Property: The University of South Carolina is the owner of a portfolio of intellectual property donated by Eastman Chemical regarding the use of clay nanoparticles in polymers for the purpose of influencing the gas permeability of packaging materials. While some licenses are now in effect concerning certain specific applications, a wide range of additional opportunities for the application of such materials still exist. Both zur Loye and Scrivens have made recent invention disclosures regarding the synthesis of specialized layered materials and the functionalization of natural clays.



Haake PolyDrive batch mixer with on-line torque measurement

Industrial Relationships: As a result of the donation

of patented technology, USC has an ongoing relationship with Eastman/Voridian as well as with Nanocor/Mitsubishi Gas Chemical with whom the University has a current license agreement.

Future Research Goals: The use of natural material such as montmorillonite clays poses a host of technical issues that must be overcome in order to have complete control over the barrier properties of layered particle polymer nanocomposites. The functionalization of these particles and the development of new synthetic layered materials will be essential developments in the creation of packaging and other materials that exhibit a wide range of properties that can be designed into them. This goal of complete control of nanoparticle functionality and therefore geometric arrangement in the polymer constitutes the long-term research goals of the research efforts. The team has also developed research plans that include the investigation of more esoteric aspects of nanocomposite formation that will both include and transcend the current vision of barrier property enhancement.

Broad Implications and Applications: If control over the geometric arrangement of layered nanoparticles can be achieved, the implications are formidable. Materials can be designed with any level of gas permeability desired. Such material can be used not only in packaging but also in sensors and other specific usages in which barrier properties are critical. Such control will take us far in developing designer materials that exhibit any desired properties that can be “tuned” into a material for the specific purpose required.