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Chemical Additives: Applications and Analytical Methods

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Specialty chemicals, or chemical additives, are rapidly becoming a trillion dollar industry and are used in a wide range of industrial sectors, including energy, cosmetics, detergents, food, materials, textiles and pharmaceuticals. Chemical additives are added to materials or products to enhance their performance, stability and lifetime or to instill other beneficial properties to the material as a whole.

> **Regardless of what type of additive is being used, it is critical to fully characterize it, as well as any material it will interact with, before, during and after it is used for its specific function.**

There is a wide range of additive types, including surfactants, enzymes, nanoparticles (metal, inorganic and polymeric), fragrance molecules, dyes and more. Each specific additive provides a unique benefit or function to a material or process. In fact, sometimes chemical additives are referred to as functional chemicals or chemical agents. Some chemical additives or additive packages can consist of multiple components and/or provide multiple functions that can reduce the number of ingredients a compounding chemist or formulator needs to sample and test.

Surfactants are widely used as additives in detergents to increase the cleaning effectiveness of a detergent formulation. Simpler, cheaper detergents may contain one basic surfactant but premium, higher-end detergents often contain multiple, more complex surfactants that enable faster cleaning and a broader range of stain removal capabilities. Additionally, enzymes may also be added to help remove specific stains such as proteins or starches. Finally, surfactants are also widely used in oil-recovery initiatives. Enhanced or tertiary oil recovery involves treating oil wells with chemicals that actively remove additional quantities of oil that are not removed by inherent pressure or pumping. Surfactants and surface active agents are also important in controlling the settling rate of dispersed particles in a product. Dispersants, deflocculants, emulsifiers and surfactants help to keep particles, fillers, oil droplets or dirt suspended in a liquid or to form a colloid. In applications where particles need to be removed from a product or process, settling agents or flocculants are used. Softening, chelating or sequestering agents are useful for capturing dissolved metal ions in a liquid.

Nanoparticles are often used as reinforcing filler additives for applications related to strength, hardness and stability enhancement. A wide range of nanoparticles can be added to polymers or other scaffolds to increase the strength of the resulting product. Coupling agents are often required to provide an interface between the matrix and reinforcement that transfers stress. Additionally, nanoparticles may have an active function in self-healing materials. In this case, a scratch or indentation in a material causes a nanoparticle containing a catalyst and polymer precursor to break open, release the contents which then mix and polymerize, thus ‘healing’ the scratch in the material.

Fragrances are routinely added to formulations such as detergents, soaps and shampoos to enhance the customer experience. Colorants, pigments and dyes are similarly added to cement, lubricants, coatings, plastics, elastomers and other materials to modify the color of the finished product, again, to achieve a desired product look and customer experience. Pigments consist of fine particles that must be dispersed properly in the finished product. The fineness and surface characteristics can alter how well the pigment mixes into the product.

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Foam control agents are important in coating, adhesive, sealant and elastomer (CASE) applications. Defoaming agents are often added to paints and coatings because dispersed bubbles can produce defects in a dried or cured coating. Lubricant formulations require defoaming agents as well because a machine oil with a foaming tendency can lead to cavitation and inadequate lubrication. Foam testers are used to quantify the foaming characteristics of oils or the defoaming abilities of additives. Production of a cellular material or foam requires a foaming or blowing agent to create controlled porosity within the plastic or elastomer. The effectiveness of blowing agents for manufacturing foam materials can be evaluated using specific gravity and density instruments.

Regardless of what type of additive is being used, it is critical to fully characterize it, as well as any material it will interact with, before, during and after it is used for its specific function. Specifically, the additive purity before mixing, the interactions between the additive and material during the mixing and finally the stability and function of the final product are key. Plastics, lubricants and other organic or polymer products can degrade when exposed to sunlight (UV) or oxidize when exposed to air and heat. A variety of stabilizers or inhibitors are added to foods, polymers and other products to prevent reactions or to retard degradation such as UV stabilizers or UV absorbers, heat stabilizers, anti-oxidants, fragrance fixatives, color stabilizers, preservatives and corrosion inhibitors. Anton Parr provides several oxidation stability testers to evaluate liquid fuels (gasoline, diesel, biodiesel/FAME and blends), according to ASTM D7525, ASTM D7545, EN 16091 and IP 595 international standards.

First, it's important to test the incoming additives for purity and quality before they are incorporated into a material. Common techniques for testing incoming materials are nuclear magnetic resonance spectroscopy (NMR), refractive index, Raman spectroscopy, particle sizing, x-ray diffraction and zeta potential. Second, it is also important to monitor the interactions between the additive and the material during the mixing or adding process. Common techniques for this type of analysis are rheology, particle size and various forms of spectroscopy. Finally, it is critical to test additives and the resulting material after incorporation to ensure that proper mixing has occurred, to investigate the uniformity of the resulting dispersion and to characterize the final product to ensure that the additive is functional. Common tests for these properties include rheological analysis, hardness, scratch, tensile testing and other structural tests.

Figure 1. Particles in Suspension
Source: Anton Paar

In the following sections, we describe, in more detail, specific tests that are commonly used to characterize additives before, during and after their incorporation into various materials, processes and consumer products.

Particle and Surface Analysis in the Additives Industry

Reinforcing fillers or additives are widely used to enhance mechanical, thermal, electrical or optical properties of the final product. For example, TiO2, owing to its excellent optical properties, is widely used in printing inks, paints and cosmetics while carbon nanotubes are increasingly used in polymers due to their exceptional mechanical and electrical properties. In order to ensure and optimize the benefits of reinforcing fillers, it is important that the filler particles are individually dispersed before, during and after incorporation into the larger matrix. The presence of aggregates in a composite material may lead to poor quality, heterogeneity in the material or poor reproducibility in the manufacturing process. Various dispersing agents need to be evaluated and the effective particle size and occurrence of agglomerates need to be determined analytically.

Aggregation of additives may be monitored by analyzing the particle size. Dynamic light scattering (DLS) is a straightforward and reliable technique that is often employed to monitor particle aggregation in suspension (**Figure 1**). DLS involves probing the sample with a laser and monitoring the rate at which the intensity of the scattered light fluctuates. That rate is related to the speed of the particles due to Brownian motion that is, in turn, related to the particle size. The speed of the particles is mainly influenced by the temperature, viscosity of the medium and the size of the particle. Thus, if one maintains constant temperature and viscosity, the particle size can be determined using the Stokes-Einstein equation. A non-invasive method, DLS is a fast measurement of suspensions or colloidal systems and can analyze a large range of particle sizes from nanometers to micrometers. Improved algorithms that are employed in the latest analysis software can also help differentiate multiple population sizes within the sample space.

Although DLS can be used to monitor aggregation, it cannot help control it. Familiarity with the pair potential (the total potential energy of interaction between components) is key to realizing and achieving stable dispersions that do not aggregate. The DLVO theory summarizes the total interaction potential between two components as the net effect of the attractive and repulsive interaction. Thus, aggregation of additives and fillers may be prevented as long as the repulsive interaction between these particles is greater than the attractive interaction between them. Repulsive interactions are mostly electrostatic in nature (i.e. like charges repel each other). As such, having a high enough negative or positive surface charge on the additives will help ensure that they do not aggregate. While surface charges cannot be directly determined experimentally, they may be measured by analyzing the zeta potential (ζ) of the particles (as shown in **Figure 2**). Electrophoretic light scattering (ELS) is a technique that determines the zeta potential of colloidal systems by applying a voltage across the sample space. The movement of the particles under the influence of the applied voltage, known as the electrophoretic mobility, is determined and used to calculate the zeta potential. Zeta potential is a key indicator of the stability of colloidal dispersions. The higher the magnitude of the zeta potential (that is, highly positive or highly negative), the more stable the colloid. A lower-magnitude zeta potential indicates a less stable colloid; in other words, a tendency toward aggregation or coagulation. As such, knowledge of zeta potential is important in achieving a stable dispersion of particles

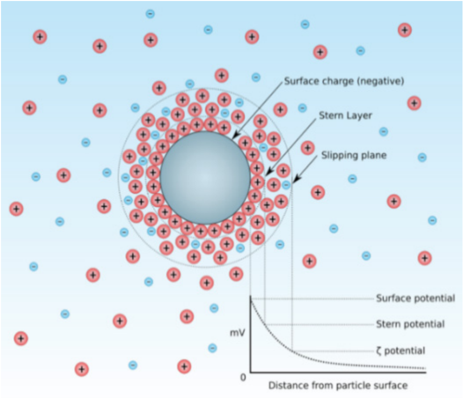

Figure 2: An electrical double layer. Source: Anton Paar

Contrary to traditional belief, zeta potential may also be used to determine the surface charge of the final, real-life material or product and to discern its interaction with surface coatings, treatments or other chemistries. The streaming potential measurement is a unique analytical method that determines the zeta potential and surface charge of larger solid surfaces (not colloidal systems). A surface-sensitive technique, streaming potential measurements only probe the outermost surface of the material to reveal its interfacial behavior. As such, it is ideal to investigate adsorption and coating behavior. It works by flowing a weak electrolyte past the sample surface, which results in a voltage due to charge displacement in the electrical double layer. The resulting voltage is related to the material's zeta potential using the Helmholtz-Smoluchowski equation.

Knowledge of the zeta potential of the larger final product is important to understand the behavior of this product in many technical and biological processes. In the cosmetic industry, for example, zeta potential of both the hair and the shampoo is important in understanding their interaction when brought together. In the petroleum industry, zeta potential analysis is applied to rocks and core samples to study the effect of surfactants as used for enhanced oil recovery. While ELS measurements reveal the zeta potential of the surfactants, streaming potential measurements are necessary to reveal the zeta potential of the core samples. Essentially, this information is of vital importance whenever a solid surface contacts a liquid during its application.

DLS and ELS together offer a straightforward solution to study and monitor the effectiveness of reinforcing filler or additive dispersion in a matrix, a parameter of vital importance in transferring the excellent properties of these fillers to the final product. Insight into the particle size, by DLS, and zeta potential, through ELS, can help improve the process of incorporating the additive into the matrix. Zeta potential through streaming potential analysis will further help understand the suitability of the final product for additional applications such as coating, adsorption, surface modification and more.

Rheological Analysis of Additives and Composite Materials

In industrial applications, a wide range of additives are used. Each additive incorporated into a product provides a unique function to the processing or the final customer experience. The signatures of these additives and their influence on the product can be monitored through an array of rheological techniques that analyze the deformation/flow characteristics of the product under a number of environmental conditions.

In consumer markets, the rheology of a product must be well understood in order to meet the demands of the end user. If the rheological properties are not fully characterized and understood, there is a significant risk that costly R&D investment and time will be spent on the release of a product that the market does not require or will not use.

When a contractor is applying thin-set to remodel a bathroom, they must move the sample from the bucket to the surface. If the bucket is tipped, the thin-set will not flow freely as would be expected. This response is known as a yield stress and is characteristic of a structured material. Essentially, the internal structure of the thin-set has enough force to maintain its shape even under the influence of gravity. However, by applying force, when using a trowel for example, the thin-set will move and can be applied to the surface.

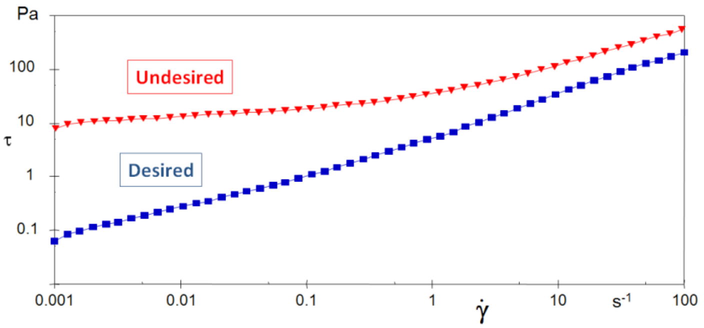

Figure 3: Rheological signature (Shear Stress, τ vs Shear Rate, γ) of two thin-sets with different additives. Source: Anton Paar

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Flow behavior of a material can be controlled by the addition of varying additives known as rheological modifiers. These can increase or decrease the viscosity without changing structure or they can add structure to the product, resulting in an increase or decrease in the yield stress. This phenomenon is shown in Figure 3 when comparing two thin-sets. Differences are clearly seen in the low shear rate range. The behavior of the thin-set with a much higher yield stress is undesired as it requires a much higher initial force to be applied to the sample in order to get it to flow. If the product does not readily break down or flow, it can be less desirable for a consumer as this may cause fatigue over time, making a product with a lower shear stress under low shear conditions more desirable. A product's viscosity needs to be increased in some cases. For instance, a paint that is runny or too thin may disappoint a consumer. A grease with too low a viscosity might not be properly retained within an industrial bearing.

Rheology or viscosity modifiers include thinners or flow promoters, leveling agents, pour point depressants, thickeners or gelling agents and thixotropic agents. A laboratory rheometer, or viscometer, is required to properly evaluate the performance of various flow control agents. An instrument capable of determining viscosity on a small sample can be very useful in the evaluation process because many variations can be mixed in on the benchtop without consuming products or pilot facility time. Oils, greases and lubricants require a viscometer capable of measuring kinematic or dynamic viscosity and a viscosity index such as a Stabinger SVM series viscometer. The effectiveness of pour point depressants on a fuel or lubricant can be gauged using a cold flow tester. A high throughput rheometer, or inline viscometer, is required for quality testing of the product after the additive becomes part of the formulation and is released to production.

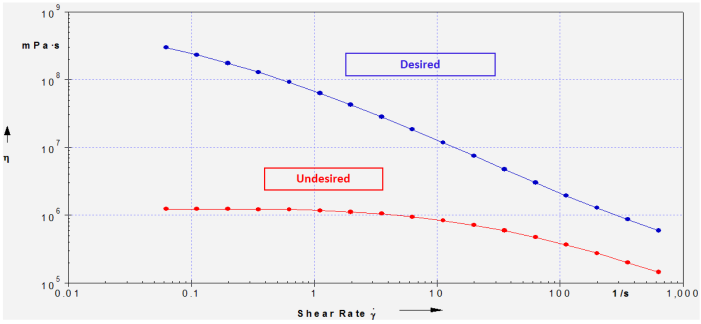

Figure 4: Rheological signature (viscosity vs. shear rate) of skin creams with different additives. Source: Anton Paar

However, after initially causing the product to flow, the ease at which it flows is also considered. This resistance to flow is known as viscosity and can be assessed under varying applications. Figure 4 shows the response of two different skin creams under varying shear conditions. A consumer would like for the skin cream to not only be applicable with minimal effort but also to remain in place (i.e. not run). It is clearly observed that both samples have a similar viscosity at high shear rates, which is the range that would mimic the process of applying the cream to the body. However, the lower shear rate is what is more relevant and important to the customer. If the sample viscosity is too low under low shear conditions, it will appear to be too runny and thus less likely to be used, making the more viscous product the preferable one

Additionally, understanding the recovery kinetics is crucial to provide a desirable end product. Recovery kinetics, also known as thixotropy, are particularly important in the paint industry. When painting a room, it is desired that after a brush stroke the paint levels out smoothly and then sets. However, in some cases, brush strokes can be seen that indicate that the paint has set before it could level out. This can occur due to the improper balance of additives in the paint and can result in it recovering too quickly (an example of this behavior is shown in Figure 5). Alternatively, if a sample recovers too slowly, it will sag or run, which is also undesirable. Through the use of thixotropic or leveling agents one can fine-tune this behavior. This is illustrated in Figure 6 where the use of rheological additives changes a paint from being free flowing after application (G" > G') to a paint that has a short period of flowing (G" > G') before setting up (G' > G"). The time in which this setting up occurs can be further adjusted through additives to meet the customer's end need.

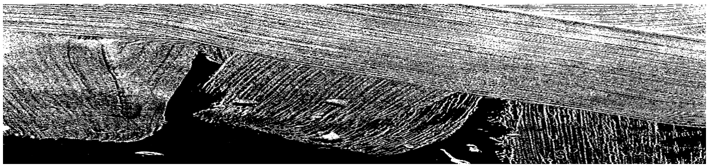

Figure 5: Improper balance of additives in paint. Source: Anton Paar

Rheology offers a means in which a formulation can be "fingerprinted" and further tuned. A host of other rheological techniques can be used to fine tune the recipe of the final product, however, these three techniques show the most benefit to the additives industry. These rheological techniques offer the means to better understand the underlying issues occurring from both a processing standpoint as well as its end use.

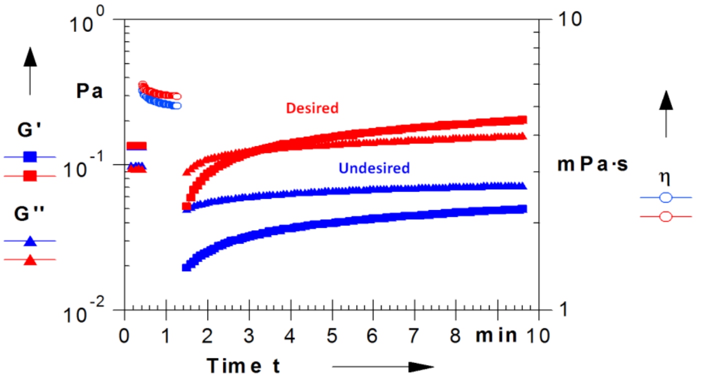

Figure 6: Use of rheological additives to modulate paint samples. Source: Anton Paar

Mechanical Surface Testing of Particle Reinforced Materials

Additives and fillers have been developed for materials like paints, clear coats and molded plastics to improve resistance to wear, scratch and environmental degradation and to extend their working lifetime. The ultimate goal of coating formulation is to create everlasting surfaces that retain their initial properties and appearances. In order to achieve high-performance products fibers and nanoparticles are often used. For example, silica, alumina, ceria and zinc oxide nanoparticles are commonly used to improve wear resistance in coatings. When designing such materials, it is necessary to accurately quantify the effectiveness these additives will have on increasing durability. For many industries, the most important types of mechanical surface characterization include wear and scratch resistance as well as resistance to permanent surface deformation. The hardness and strength improvement from nanoparticle additions to thin coatings is impossible to measure using conventional test equipment. Nanoindentation and scratch testers provide a unique tool for evaluating how the nanoparticles and other chemical additives modify hardness, elastic modulus and other mechanical properties of thin coatings.

A commonly used technique to characterize adhesion and cohesion behavior is the controlled scratch test. In this test, a sphero-conical diamond stylus is drawn across a material's surface with a linearly increasing normal force (Figure 7a). As the scratch is made on the material, a displacement sensor is used to monitor the scratch depth. Other signals often used include acoustic emission sensors for measuring the onset of cracking and tangential force sensors for determining frictional properties. Once a scratch has been created, an optical microscope is used to take a panoramic image of the resulting scratch. By syncing the panoramic image of the scratch with the data (Figure 7b), one can identify critical load to failure (Lc) points along the scratch length and quantify adhesive and cohesive characteristics of the material or coating. Since coatings are often designed to self-heal or recover over time, the scratch tester has been developed to run multiple timed profiles post-scratching in order to evaluate the elastic recovery behavior of coatings. Post-scratch scan capabilities have allowed the automotive industry, for instance, to develop self-healing high-end clear coats that greatly extend the lifetime of their products and maintain aesthetic appeal.

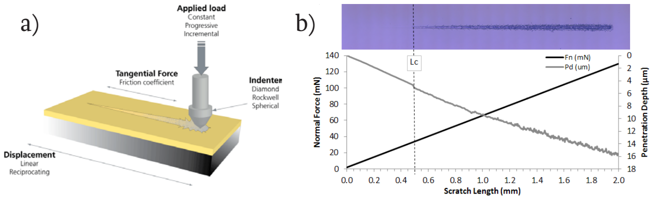

Figure 7: Controlled scratch test schematic (a) and panoramic image of scratch on polymeric material synced with normal force and scratch penetration depth data (b). Source: Anton Paar

Other material properties in which additives and fillers are used include hardness, elasticity and creep. The instrumented indentation tester has become an effective tool in measuring multiple properties of materials within one test and then automatically analyzing the measurements with software. During an instrumented indentation test (IIT), a three-sided pyramid diamond indenter is loaded normal to the sample surface to a prescribed maximum force. The indenter is then held at a maximum force for a brief pause and then unloaded from the material. Throughout the loading-unloading sequence (**Figure 8a**), the indentation depth is measured from a capacitive displacement sensor. Indentation hardness is then automatically analyzed as a function of indentation depth and elasticity is computed using the slope of the unloading curve that is proportional to the stiffness of the material. Many nanoparticles are specifically selected to function as hardness modifiers by creating dense elastomeric structures within the coating or matrix. Instrumented indentation is also useful for comparing local properties (matrix between particles) and average properties (testing a larger volume of material).

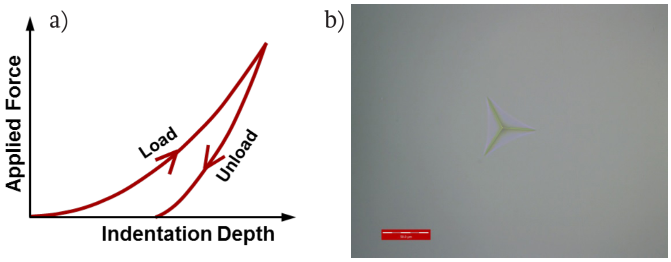

Figure 8: Loading-unloading curve example during instrumented indentation test (a) and residual imprint of indentation on polymer coating (b). Source: Anton Paar

Combining scratch testing with indentation testing allows chemists and material engineers to test formulations and to determine how well their chosen additives are improving the material performance. By having highly precise instrumentation to test the surface characteristics, it is possible to discern small changes in additive amounts as well as the materials being used for the additive. Thus, indentation and scratch tools are widely used in research and development and quality control settings.

To summarize, chemical additives are a large, diverse industry with a wide range of applications and industrial uses. Characterizing additives before, during and after their use or incorporation into a final product is critical for ensuring the optimal performance of the material. Specific technologies useful for characterizing additives and the resulting compounds, formulations and composite materials include particle analysis of the raw materials, rheological analysis of the composite material during mixing or processing as well as surface analysis to ensure proper incorporation of the additive, structural integrity and optimal performance.

Useful Resources

Books

Applied Rheology, Thomas G. Mezger

The ZETA Guide, Thomas Luxbacher

Application Reports

Printing Ink: Gauging the Viscosity to Fine-Tune the Particle Size Calculation

Silica Particles: Size and Colloidal Stability

Surface Characterization of Reinforcing Fibers for Fiber Reinforced Polymers

Quality Assurance—Rheological Testing of the Sagging Behavior of Coatings

Determination of the Mechanical and Thermal Stability of Skin Cream

Rheology of Thickeners in Pharmaceuticals: Xanthan

Mar Resistance of Paint Coatings by Nano Scratch Testing

Characterization of the Surface Mechanical Properties of Paints and Polymeric Surface Coatings

Finer Particle Size Allows Better Coating Characterization
On the Use of Nanoindentation for the Determination of Visco-elastic Properties of Polymers

Standards

ISO 14577	Metallic Materials—Instrumented Indentation Test for Hardness and Material Parameters
ISO 13099-2	Colloidal Systems—Methods for Zeta-Potential Determination
ISO 13321	Particle Size Analysis—Photon Correlation Spectroscopy
ISO 22412	Particle Size Analysis—Dynamic Light Scattering (DLS)
ISO 3219	Plastics—Polymers/Resins in the Liquid State or as Emulsions or Dispersions
ISO 6721-1	Plastics—Determination of Dynamic Mechanical Properties
ASTM D7027	Evaluation of Scratch Resistance of Polymeric Coatings and Plastics Using an Instrumented Scratch Machine
ASTM D7187	Standard Test Method for Measuring Mechanistic Aspects of Scratch/Mar Behavior of Paint Coatings by Nanoscratching
ASTM E2490-09	Standard Guide for Measurement of Particle Size Distribution of Nanomaterials in Suspension by Photon Correlation Spectroscopy (PCS)
ASTM E2865-12	Standard Guide for Measurement of Electrophoretic Mobility and Zeta Potential of Nanosized Biological Materials
ASTM D4440	Standard Test Method for Plastics: Dynamic Mechanical Properties Melt Rheology
ASTM D4473	Standard Test Method for Plastics: Dynamic Mechanical Properties: Cure Behavior
ASTM D5279	Standard Test Method for Plastics: Dynamic Mechanical Properties: In Torsion

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