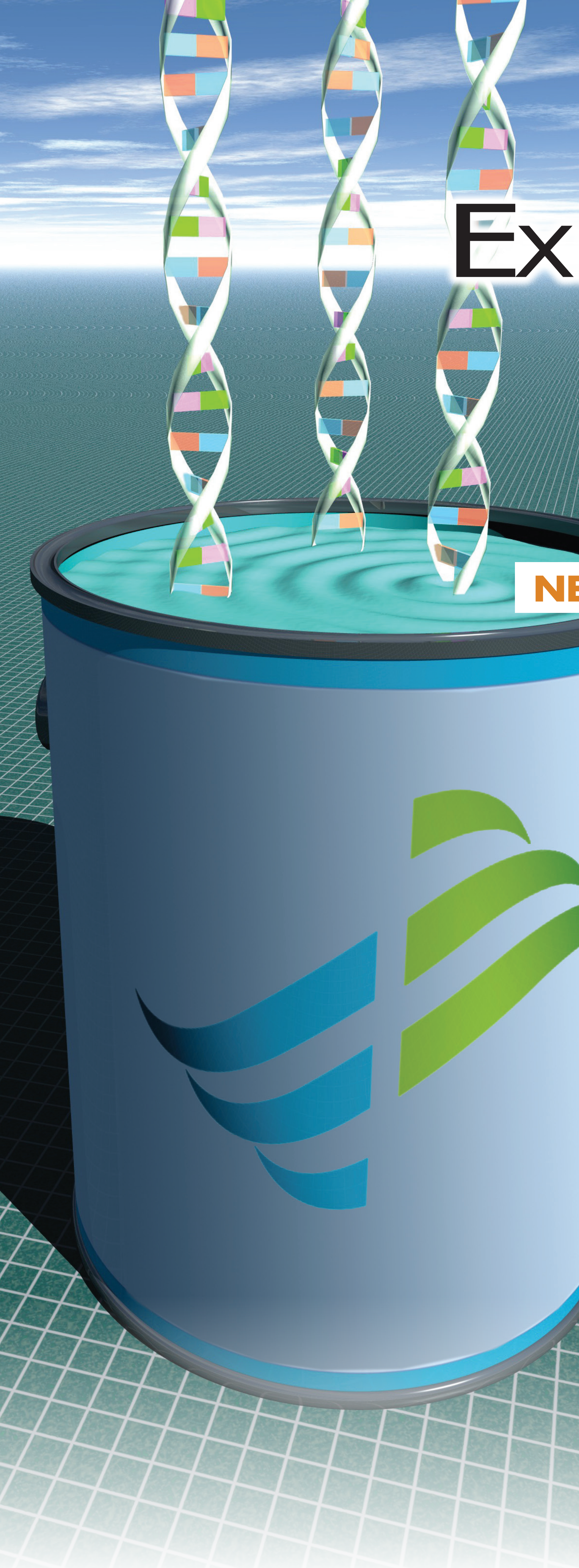

Expanding Opportunities for Functional Surfaces: NEW Self-Degreasing Laminates

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Surfaces that simply protect and/or beautify will no longer meet the expectations of the end user in the near future. Today's customers—from individual consumers to industrial users—demand enhanced functionality, from antimicrobial capability to self-cleaning and self-healing properties. Leaders in the coatings market are beginning to appreciate that unique functionality can be used to ensure not only continued, but highly profitable, growth of the industry. To provide these features cost effectively, they have sought assistance from resin and additive suppliers.

Use of bioengineered additives in particular has been demonstrated to be an effective means for incorporating such unique functionality into paint formulations. The fact that bio-based ingredients are naturally derived, environmentally friendly materials with non-persistent, non-accumulating, and non-toxic profiles makes them a very attractive solution. Recently, it has been demonstrated that enzymes can also be incorporated into laminates, dramatically expanding the opportunities for creating uniquely functionalized surfaces.

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Photo courtesy of Reactive Surfaces.

BIOACTIVE ADDITIVES DELIVER NOVEL FUNCTIONALITY

Bioengineered materials—including enzymes, peptides, proteins, antibodies, and other biologically active molecules—impart highly specific and targeted functionalities to coatings and materials. Such biomolecules are attractive for several reasons:

- They are naturally derived, environmentally friendly materials with non-persistent, non-accumulating, and non-toxic profiles;
- There is a vast array of biological compounds with widely varying activities, providing almost limitless functionality from which to choose;
- Advanced genetic and polymer engineering techniques make it possible to carefully tailor bioactive compounds to perform very specific actions under certain conditions; and
- Enzymes, peptides, antibodies, and other biological actives can be incorporated into formulations using existing manufacturing systems without the need for significant investment in capital or additional operator or applicator training.

These features have led a number of groups—both in academia and industry—to develop bioengineered additives for use in materials and coatings. Bioengineered additives that act as broad-spectrum antimicrobial agents, break down phosphate-based pesticides and chemical warfare agents, de-grease surfaces, serve as antifoulants for marine and medical devices, and are designed for use in protective food packaging applications and self-healing coatings are all being commercialized. Despite initial concerns over the durability of biological components under industrial use conditions, extensive tests have shown that when properly designed and engineered, bio-based additives retain their desired functionality throughout processing and application of the coatings and continue to perform in the applied state as well.

ADDRESSING INDUSTRIAL CONCERNS

Even with such high levels of interest, there does remain some skepticism about the practicality of using biomolecules in applied coatings. Active bioadditives such as enzymes and proteins are intended to function in the complex and fully hydrated environment present in living systems in which they evolved. It is widely accepted that biomolecules are generally susceptible to extremes of temperature and pressure, and thus may not be very durable and/or suitable for many applications due to the unfavorable conditions required for manufacturing. Furthermore, because specific conformations of these compounds are often required for them to interact effectively with reactants, their use was thought to be limited due to the polymeric matrix in paint films and composites causing denaturation of the specific protein conformation.

Fortunately, these concerns have proven to be unfounded.[1] Reactive Surfaces and other companies and research groups have discovered that when the bioactive compound and the polymeric resin are properly engineered together, these biomolecules can indeed withstand a range of industrial processing conditions and maintain their activities for extended periods in applied films.[2-12] Most importantly for coating formulators, existing manufacturing systems typically can be utilized without the need for significant investments in capital or additional operator or applicator training.

The ability to design bioengineered additives to perform under very specific conditions increases the potential applications for these uniquely functional ingredients in many different markets, such as the automotive, textile, paper, appliance, architectural, and furniture sectors, to name a few. It also opens possibilities for their use in other surface materials. This thinking led to the investigation of the use of de-greasing enzymes in laminates.

PUSHING THE LIMITS WITH LAMINATES

Even though enzymes have been shown by us and others to tolerate typical manufacturing processes for paints and coatings, it was uncertain whether activity could be maintained after exposure to the high temperatures and pressures used in the production of thermosetting materials such as laminates, heat-cured coatings, and plastics. Extensive laboratory testing has confirmed, however, that in thermosetting laminates such materials not only survive the extremes of temperature and pressure, but also can exhibit surprisingly high levels of long-term functionality such as the ability to self-degrease.

Composite laminates are prepared by combining multiple thin layers of paper impregnated with a resin—typically overlay and Kraft papers treated with melamine and phenolic resins—and heating them under pressure to harden them. Laminates were originally developed by the electronic industry for use as insulating material on which to mount electronic components. When decorative paper was incorporated in the top layer, a new market was born. In today's composite industry, paper-based decorative laminates are used to impart decorative and protective properties to countertops and backsplashes, workstations, cabinets and furniture, wallboard, flooring, and other building materials. Kraft paper-based phenolic industrial laminates are also designed to provide structural and functional performance for circuit boards, concrete forms, and wood paneling overlays.

The composite laminates market is in fact quite large, and provides a significant new opportunity for the use of bioengineered additives. The global decorative laminate market was estimated by Global Industry Analysts (GIA) to exceed $21.2 billion in 2009.[13] Demand for laminates suffered during the recent economic downturn, but is expected to grow at a modest rate as the recovery takes hold and residential construction revives.[14] Like the coatings industry, however, much of the laminate market has become commoditized, with Big Box retailers taking significant market share while product differentiation disappears and profits decline, except in high-end specialty offerings.[15] Laminates that are attracting attention offer unique designs and textures or incorporate novel materials into the top layer such as microscopic aluminum oxide particles, which improve abrasion and scratch resistance as well as gloss and color retention, according to GIA.[13-14] Clearly, the addition of novel functionality will help laminate manufacturers maximize their growth and profit potential as the market recovers.

Our approach involves the use of a lipolytic enzymatic additive (DeGreez™) that has been shown to be effective at self-degreasing when incorporated into paints and coatings.[12,16] The enzyme is a lipase (triacylglycerol acylhydrolase, E.C. 3.1.1.3) (*Figure* 1).

Lipases (triacylglycerol acylhydrolase, E.C. 3.1.1.3) are natural lipid hydrolyzing enzymes that enable auto-decontamination and removal of oil and grease from surfaces. These enzymes have been shown to be quite robust, functioning over a wide range of temperatures and are also highly specific for a wide range of natural greases, oils, and fats. In addition to hydrolyzing long-chain triacylglycerols, they can catalyze esterification, transesterification, acidolysis, alcoholysis, and aminolysis reactions.

Given the growing demand for higher performing products in many decorative laminate applications, the potential market for self-cleaning laminates could be quite large and would likely include end uses such as countertops, kitchen backsplashes, tabletops, and cabinet doors.

MARKET-READY RESULTS

To evaluate the market-readiness performance of the enzyme in laminates, it was formulated as a drop-in liquid additive containing 2 wt% enzyme. A commercial laminate supplied by WilsonArt, Inc., Temple, TX and prepared from Kraft paper and melamine resin was used as the representative test laminate (*Figure* 2).

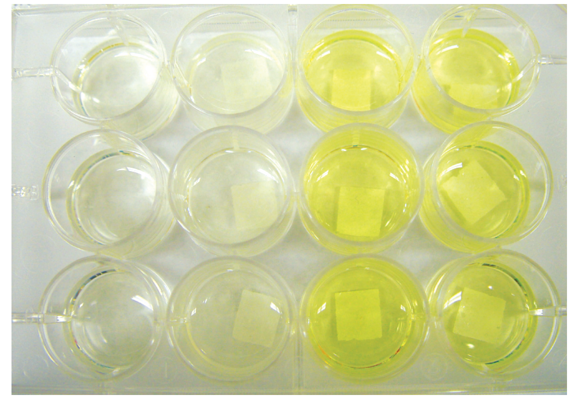

Figure 2—Kinetic evaluation of overlay paper treated with DeGreez. Samples conditioned at 120°C for 20 min prior to pressing overlay paper into composite. From left to right: Column 1: Control assay buffer; Column 2: Overlay paper with 65 polymer wt% (Pwt%) control; Columns 3 and 4: Overlay paper plus two different lots of DeGreez. Photo was taken 15 min after initial challenge.

For these tests, laminates were prepared by first infusing a resin formulation into Kraft paper and then conditioning the resin in a forced air oven. Manual pressing of samples between aluminum panels (4.6 in. x 4.6 in.) was carried out at commercially-acceptable pressures and temperatures. The activity of the enzyme was then determined by following the hydrolysis of the oil-analog *p*-nitrophenyl acetate using a colorimetric method. The product of this reaction representing hydrolysis of the ester bond is *p*-nitrophenol, which has a λ_{max} of 405 nm, and causes the solution to change from clear to yellow (*Figure* 3).

Initial results indicated that the enzyme retained complete activity in the resin alone up to 105°C for two hours. When properly conditioned, the lipolytic enzyme not only remained catalytically active after being pressed under typical manufacturing conditions (temperature and pressure), but also remained stable in pressed composites stored at room temperature. Additionally, the overlay

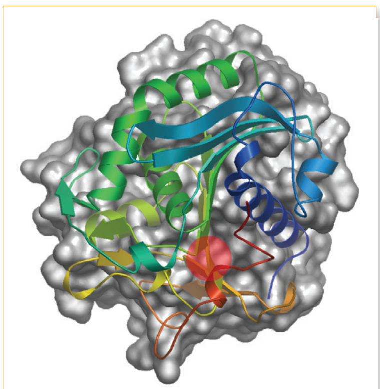

Figure 1—3D model of the lipase enzyme used in the composite laminate material. The monomeric wild-type enzyme is a 269 amino acid, single domain triglyceride lipase of *Thermomyces (Humicola) lanuginosus*.[17] The surface profile of the enzyme is shown in the gray background and is overlaid with a rainbow-colored coded structure: blue indicates the beginning of the molecule, an N-terminal (amino functional) amino acid, while red indicates the end of the molecule, a C-terminus (carboxyl functional) amino acid. The red circle shows the active site. The program AstexViewer™ was used to generate this view.[18]

paper can be treated and stored for extended periods prior to incorporation into laminates. Samples containing the enzyme solution have been pressed up to two weeks after initial conditioning (roll-to-roll processing).

These results were highly encouraging. Prior to the investigation, it was anticipated that the enzyme would become denatured when exposed to the temperatures and pressures required for laminate manufacturing. The initial experiments, however, clearly confirmed that the enzyme retained its activity throughout the processing of the laminates and when incorporated into the composite structure.

At this point, it was expected that further stability could be achieved with the use of dry additive formulations. Therefore, this approach and other possible ways to optimize the performance of the enzyme in the laminate system were explored next.

OPTIMIZATION

First, it was necessary to learn more about the effect of the location of the enzyme in the various layers required to prepare the laminates. Typically there are four layers of paper used to manufacture laminates. The Kraft paper makes up the bottom two layers. On top of that is the decorative paper, and the top layer is an overlay layer. The melamine resin is impregnated into the top overlay layer, typically at 65–90 Pwt%, and during the pressing process penetrates into the decorative and Kraft paper layers, binding them together to form the laminate (*Figure* 4).

The composite material is made of several components; for simplicity we will discuss the relationship between the polymer matrix, the fiber, and the enzyme.

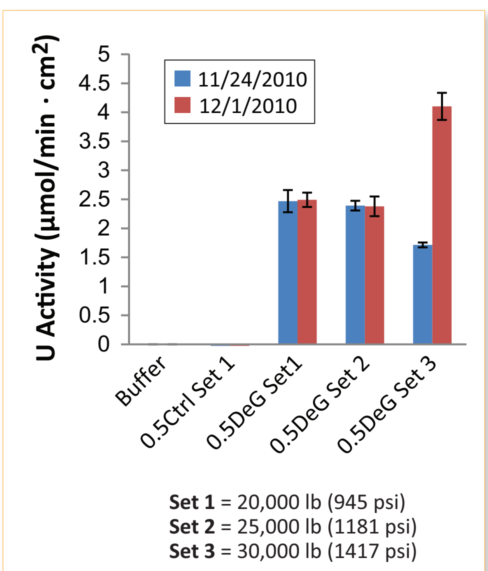

Figure 3—Kinetic activity of DeGreez in simple laminate conditioned at 110°C for 20 min and pressed at 120°C for 15 min.

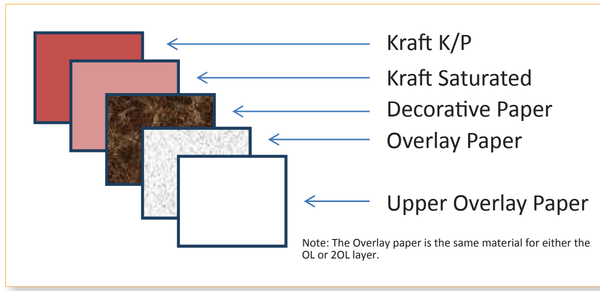

Figure 4—Breakout of layers used to prepare composite laminates.

When manufacturing laminate composite material, the polymer matrix is infused into the paper fiber resulting in weight fractions of each component. For this study we investigated the material with the polymer weight fraction at 65 wt% and 35 wt% of the overlay paper. The enzyme added to the composite material was based on the total resin solids of the polymer weight fraction only. The wt% reported herein represents the weight fractions for the overlay paper and not the composite material total. The resin infused overlay paper is placed on the decorative, Kraft, and release papers to form the final composite laminate by heated pressing.

To determine in which layer the enzyme is most effective, the amount of enzyme additive, resin saturation level, and number of overlay layers was varied (see *Figure* 4). The press temperature was also increased to 126°C for these evaluations. The pertinent results are presented below. The control laminate was made with an overlay paper (OL) containing melamine resin at a 65 Pwt% and an enzyme concentration of 0.5% based on TRS of the polymer fraction. Variations from the control included the following:

- An overlay layer (OL) with 65 Pwt% with a second overlay layer (2OL) placed on top that has 35 Pwt% and 0.5% TRS of enzyme
- An OL with 65 Pwt% with a 2OL placed on top that has 35 Pwt% and 1.0% TRS of enzyme

In both cases, the samples were placed in the press at a final temperature of 126°C and exposed for a total of 15 min at 1400 psi. Before liberating the laminate from the aluminum press plates, each sample was cooled to ambient temperature.

In all of the samples tested during this evaluation, the maximum polymer weight percent in any one layer was reduced from the typical level of 70–90%. By doing so, the fiber content in these layers was increased. To compensate for the reduced amount of resin, a second overlay layer containing some resin was added to the top of the composite, resulting in a total amount of resin similar to that used in a typical laminate. Importantly, because a roll-to-roll process is used to manufacture laminates, adding the additional layer does not add any significant time or cost to the production process.

A noticeable improvement in the activity of the enzyme was observed by adding the second overlay with

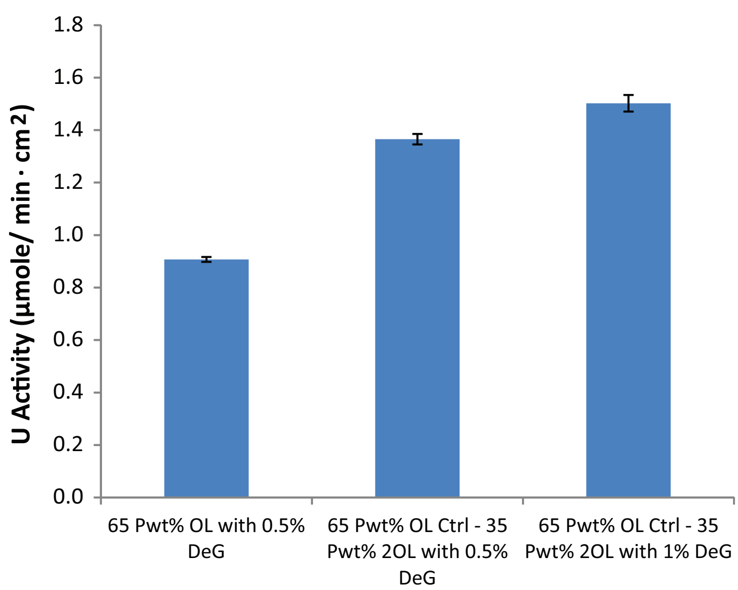

Figure 5—Lipase activity in laminates with second overlay layer.

reduced polymer solids. (Analysis of activity was determined using the same colorimetric method described previously.) In fact, activity increased by as much as 50 to 70% in the samples containing 35 Pwt% and the lipolytic enzyme (*Figure* 5). Interestingly, increasing the enzyme content from 0.5 to 1.0% based on TRS did not significantly increase the retention of activity in the laminate material. It is possible that the functionality of the enzyme is surface area-dependent in the laminate material, and even at 0.5 wt% TRS, the available surface area of the laminate is possibly saturated with enzyme.

Having established that activity was improved by incorporating the additive into a second overlay layer, it was then important to evaluate the effect, if any, that the bioengineered material had on key physical properties of the composite laminates. For these studies, a control laminate composite made using a single overlay with 65% total resin solids was compared to an active laminate composite also prepared with a 65 Pwt% overlay and a second overlay containing 35 Pwt% and 0.5% enzyme on TRS (*Figure* 5).

Hardness was measured according to ASTM D 3359-02. The control sample with a single layer of 65 Pwt% was found to be 2H, while the control and active system of the split-overlay formulation was evaluated as 6H. No flaking was observed in the adhesion of the samples, which were each rated at 5B. The measured hardness and adhesion results indicate that the additive did not impact the physical properties of the composite laminate.

Results of gloss measurements are shown in *Figure* 6. Gloss was measured at three angles according to ASTM D 523-85. As can be seen, no significant difference in gloss was observed for the control and active composites at all angles.

FUTURE DIRECTIONS: IMPROVING EASE OF USE AND REACTIVITY

New product introductions are most successful when the products are easy to use and do not require any investment in additional equipment or training. At this point we had demonstrated that incorporating a properly designed and formulated lipolytic enzyme additive into laminates provides a self-degreasing material that can be prepared using conventional, established production equipment. To maximize the commercial potential of the additive, however, it was determined that the user-friendliness of the material should be improved.

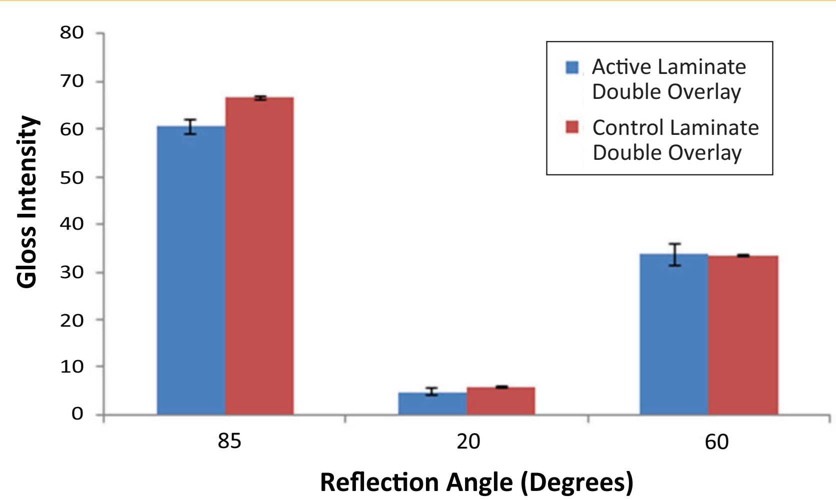

Figure 6—Gloss comparison of a control and active composite laminate.

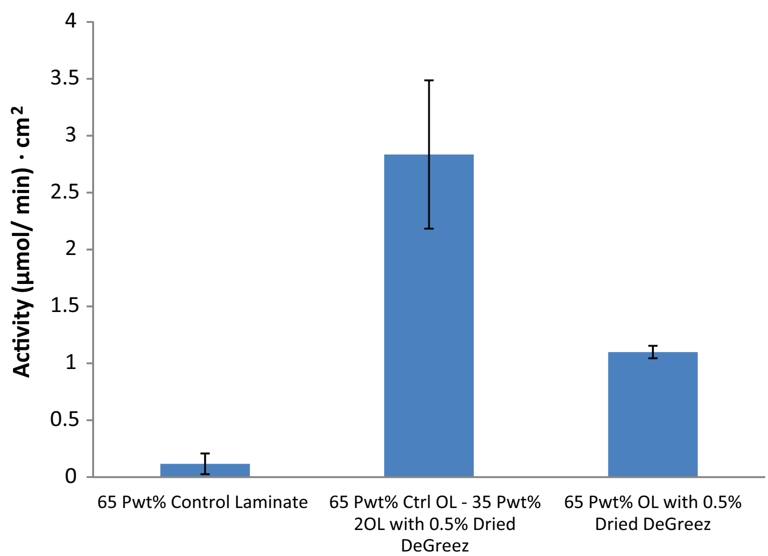

Figure 7—Kinetic activity of dry DeGreez in laminates conditioned at 120°C for 20 min and pressed at 1400 psi for 15 min.

Table 1—Activities of Various Laminate Formulations Containing the DeGreez Enzyme

Sample	Activity (µmole/min/cm²)	Std
Control sample	0.12	0.09
≈65 Pwt% OL with 0.5% DeGreez	0.91	0.01
≈65 Pwt% Ctrl OL - ≈35 Pwt% 2OL with 0.5% TRS DeGreez	1.37	0.02
≈65 Pwt% Ctrl OL - ≈35 Pwt% 2OL with 1.0% TRS DeGreez	1.50	0.03
≈65 Pwt% Ctrl OL - ≈35 Pwt% 2OL with 0.5% TRS Dried DeGreez	2.83	0.65
≈65 Pwt% OL with 0.5% TRS Dried DeGreez	1.10	0.05

One approach involved preparation of the additive in a dry powder formulation suitable for addition to laminate materials that cannot tolerate additional water. The dried additive raw material was shown to have comparable activity in solution to the solution-based enzyme formulation. Specifically, when the dry additive was used to produce laminates, not only was the activity of the enzyme retained in the composites, but its functionality was actually improved (*Figure* 7). Compared to the laminate prepared with 65 Pwt% overlay and 35 Pwt% second overlay containing 0.5% liquid-based enzyme, the same laminate with the dried enzyme exhibited slightly over a two-fold increase in activity (1.35 vs. 2.8 mmol/min-cm^2, respectively).

These latter results represent only an initial study with the dried enzyme. Given the increase in enzyme functionality in the laminate composites, however, this approach certainly appears to be the correct path to further optimization of performance (*Table* 1).

SCALING UP AND MOVING BEYOND

The success of the laboratory testing of the specialty lipolytic enzyme in various laminate designs and with the various forms of the enzyme additive has intrigued laminate manufacturing companies, and many are hoping to schedule in-plant trials with the new additive in the near future. Further pursuit of optimization strategies in order to develop the most effective additive for production of self-degreasing laminates also continues. Incorporation of other bioactives is being explored as well.

These data are encouraging to the degree that they demonstrate that careful attention to the details of bioactive additive and polymer matrix chemistries can result in successful compatibilization and engineering of both components, even in applications that require extreme processing conditions. Furthermore, these results demonstrate that purposefully designed biological additives can withstand strenuous industrial processing environments.

Indeed, with the right tool set, commercially viable high-performance bioengineered additives can be developed that dramatically enhance the functionality of a variety of surfaces using some familiar and some not-so-familiar techniques:

- An extensive understanding of state-of-the-art genetic engineering technologies,
- Knowledge of various polymer-based product formulations and their desired characteristics, and
- Familiarity with relevant production processes and application techniques.

Clearly, the possibilities for the development of novel, highly functional advanced materials using bioengineered additives encompass applications well beyond paints and coatings. In fact, the opportunities for creating uniquely functionalized surfaces with bioactive agents are truly limitless. CT

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