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Material Reinforcement

## Storage-Stable, Fiber-Reinforced Adhesive Films

# Storage-Stable, Fiber-Reinforced Adhesive Films

The desire for lightweight yet strong composite materials is echoed by various industries confronted with new, often extreme, requirements. With this in mind, Nolax has developed fiber-reinforced adhesive films that combine toughness and high tensile strength combined with low weight and outstanding flexibility.

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Sailing involves many physical phenomena and begins with the force of the wind in a sail. A sail in action is typically curved, and air flows around it with different flow paths on each side, resulting in unequal air pressure. This phenomenon, the so-called Bernoulli principle, is exploited by sailors to sail outside the wind direction or even faster than the wind [1].

The more the Bernoulli principle is applied in sailing, the stronger a sail must be. The quest for ever more potent and, at the same time, lighter sails led to the striking development of membrane sails (*Figure 1*) [2]. These consist of several layers of unidirectional thin-ply prepregs, or fiber-reinforced adhesive films (*Figure 2*), laid down in specific directions and laminated together at elevated temperature and pressure, taking into account the exerted force in the finished membrane.

### From fabric to yarn and filament

Traditionally, fibers are primarily applied in a twisted form, such as in yarns, or are woven, as in fabrics. Due to the zigzag path of yarns in fabrics or textiles, their performance decreases significantly compared to untwisted and precisely arranged filaments (*Figure 3*). Fiber-reinforced adhesive films and components made from arranged filaments, such as a membrane sail, exploit high-performance fiber's full potential. During the manufacturing of fiber-reinforced adhesive films, multi-filament yarns are spread such that their filaments are arranged without twisting or zigzagging, side by side in one direction (unidirectionally), and impregnated with a binder. Compared to the classic impregnation of textiles, spread fibers can be wet better with a binder, resulting in higher fiber content and higher performance of the composite [3].

The principle of manufacturing these unidirectional fiber-reinforced adhesive films is as shown in *Figure 4*. Continuous multi-filament yarns are unwound and spread over either metal or ceramic rods. Impregnation is achieved by roller application with a binding agent. Spreading and impregnation can also be carried out in a nip roll filled with a binder [4]. Depending on the chemistry, the binder solidifies or dries, enveloping the individual filaments and embedding them as a matrix. This method produces lightweight, unidirectional, high-performance adhesive films with typical weights of $<100\ g \cdot m^{-2}$, which can be further processed at elevated temperature and pressure to produce composite or hybrid components.

The mechanical performance of these adhesive films is highly anisotropic due to the unidirectional arrangement of the fil-


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**Figure 1** > A membrane sail in action

aments: In the direction of the filament orientation (0° direction), the mechanical performance is high; in the transverse direction of the filaments (90° direction), it is low. *Figure 5* shows the angular dependence of Young's modulus of the adhesive film T52.5110 from Nolax. The anisotropy can be reduced by stacking and laminating such adhesive films in different directions. Furthermore, the angle-dependent performance of a cross-ply laminate with two layers with fiber directions (0°/90°) and a quasi-isotropic laminate with four layers with fiber directions (0°/45°/90°/135°), both produced with adhesive film T52.5110, is depicted.
The strong angle dependence of the mechanical properties thus has consequences for the design of a final part. However, this is also an advantage because (quasi-)isotropic reinforcements are often unnecessary, and selective reinforcing in the direction of the applied force can save weight and costs in the final component.


**Figure 2** > Fiber-reinforced adhesive films from Nolax. Unidirectionally arranged filaments are embedded in an adhesive and can be processed at elevated temperature and pressure, for example, into membrane sails.

## The Nolax matrix: solvent-free and storage-stable

The fibers are responsible for the mechanical performance of a composite material. The matrix plays another vital role by:

- holding the fibers together,
- transmitting the applied force to the fibers,
- conferring durability because it supports and protects the fibers from external mechanical and chemical influences.

The matrix has a significant influence on the manufacture and further processability of the fiber-reinforced adhesive films. Traditional binders used to produce conventional filament prepregs contain solvents (a typical solvent is butanone) and/or have a pot life, involving a two-component system of hardener and polymer (e.g., a polyester-based system such as Adcote 122-HV) [6]. In such prepregs, the two components are not storage-stable at room temperature and, such reactive systems must be stored at low temperatures (at about -20 °C) to avoid crosslinking. Furthermore, such prepregs have to be thawed prior to further processing.
Nolax proposes a new way to increase workplace safety during production by using only water-based dispersion adhesives to impregnate the spread fibers. These adhesives are solvent-free. Furthermore, Nolax uses adhesive thermoplastic or latent-reactive (the crosslinker may be encapsulated) systems, offering a larger processing and storage window. After careful drying, even with a crosslinker present, these adhesive systems can be stored at room temperature for an extended period (of >12 months) without extra effort [7].

## Crosslinking on demand

In addition to a thermoplastic matrix, latent-reactive systems can be used when exceptionally high workloads are expected, such as high heat resistance and alternating climate under stress. Storage-stability for reactive systems can be achieved by the physical separation between the resin and the crosslinking agent [8]. In Nolax fiber-reinforced adhesive films, encapsulated or surface-deactivated (poly-)isocyanate particles (crosslinking agent) are finely dispersed in polyurethane (resin) [9]. In this case, the crosslinker is present; however, crosslinking has not yet occurred. Only a short activation impulse

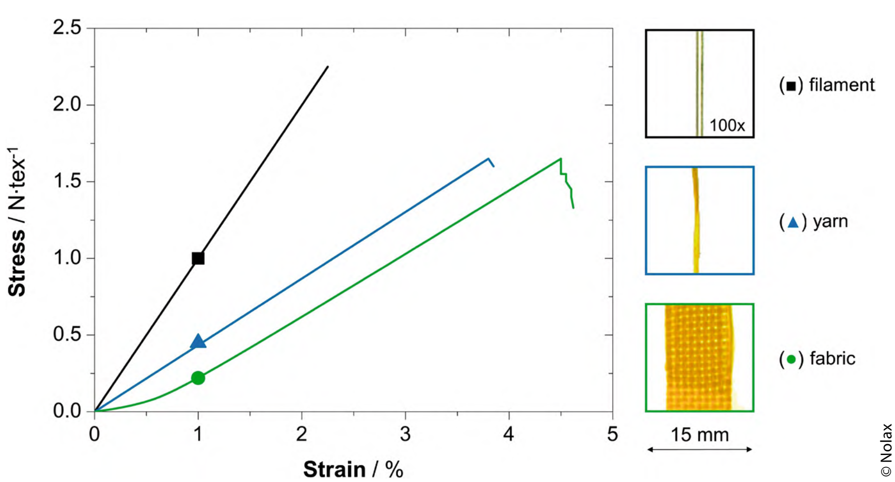


**Figure 3** > Stress-strain diagram of a filament, yarn and fabric made of aramid. The zigzag path of yarns in a fabric significantly reduces their performance compared to a single filament.

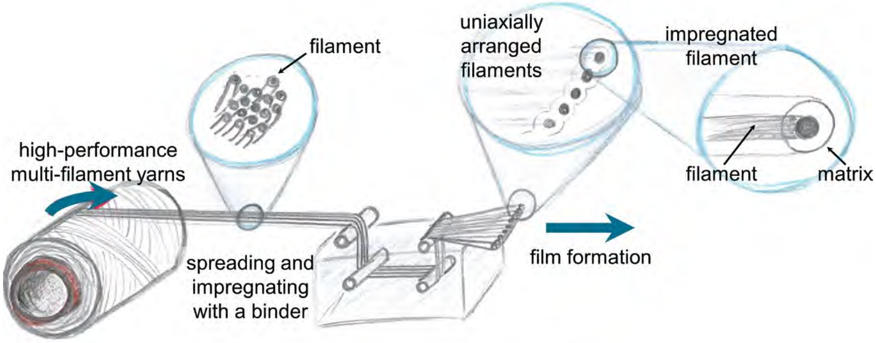


**Figure 4** > Continuous multi-filament yarns are unwound, spread and impregnated. This process produces fiber-reinforced adhesive films with typical weights of <100 g·m$^{-2}$.

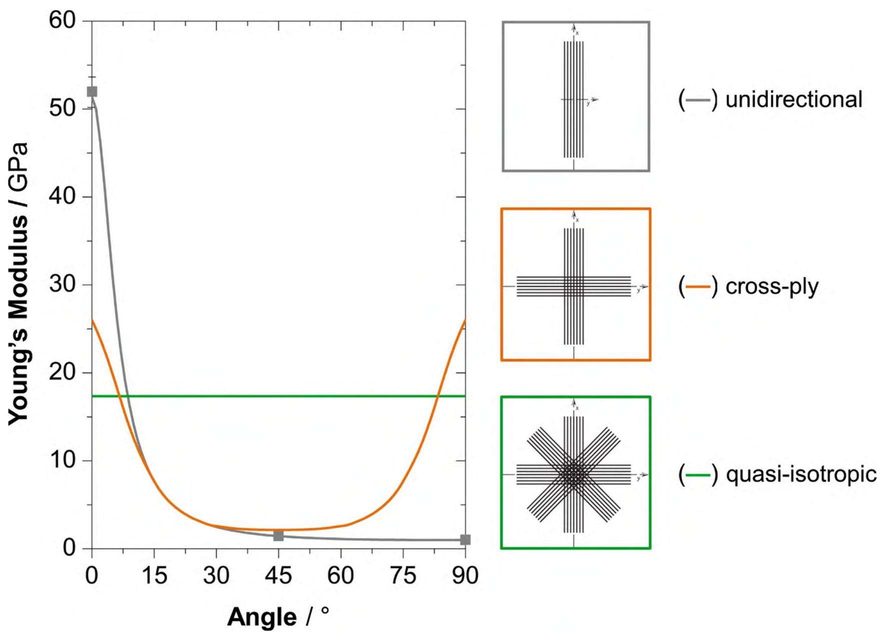


**Figure 5** > Calculated off-axis Young's moduli of the fiber-reinforced adhesive film T52.5110 and their laminates – unidirectional: one layer of fiber-reinforced adhesive film, cross-ply laminate: two layers in fiber directions (0°/90°), quasi-isotropic laminate: four layers with fiber directions (0°/45°/90°/135°), (■) measurements of Young's modulus at 0°, 45° and 90° to the fiber orientation in T52.5110. The Tsai-Hill criterion [5] was used to calculate the off-axis Young's moduli.

| Name | Matrix | Fiber | Mechanical properties | | | Density | Temperature |
|---|---|---|---|---|---|---|---|
| | | | E / GPa | σ / GPa | ε / % | ρ / g·cm$^{-3}$ | T / °C |
| nolax T51.5000 | LRPU | LCP | 30 | 1.0 | 3.0 | 1.4 | 100–140 |
| nolax T52.5110 | EAA | UHMWPE | 50 | 1.5 | 3.0 | 1.0 | 100–120 |
| nolax T53.5000 | LRPU | Aramid | 50 | 1.5 | 1.5 | 1.4 | 100–140 |

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**Tabelle 1** > Overview of the mechanical properties (in fiber direction), density and application temperature of three different fiber-reinforced adhesive films. The films have a fiber content of about 55–60 vol.-% and can currently be produced to weights of 15–75 g·m$^{-2}$ and 600 mm width. (LRPU: latent-reactive polyurethane / EAA: ethylene-acrylic acid copolymer / LCP: liquid crystalline polymer / UHMWPE: ultra-high molecular weight polyethylene / E: Young's modulus / σ: tensile strength /ε: elongation at break / ρ: density / T: laminating temperature)

during the bonding process at relatively low temperatures (>90 °C) can start the crosslinking between the isocyanate groups and the free OH-groups of the polyurethane. In other words: crosslinking on demand. In some cases, production cycle times can be shortened by a factor of ten, and interestingly, such a matrix system still has heat-sealing properties. Given the low crosslinking temperature of the matrix, it is possible to use low-melting fiber types such as ultra-high molecular weight polyethylene (UHMWPE). Also temperature sensitive substrates such as leather can be similarly reinforced.

## Customized properties

For the Nolax's fiber-reinforced films, different matrix systems and high-performance fibers can be combined to meet individual requirements and needs. This building-block principle allows tailored properties for the fiber-reinforced films, depending on the final usage. *Table 1* provides an overview of possible compositions, mechanical tensile properties, densities, and typical bonding temperatures of these films. The high-performance fibers of liquid crystalline polymer (LCP), UHMWPE, and aramid are embedded in two different base matrix systems: latent-reactive polyurethane (LRPU) or ethylene-acrylic acid copolymer (EAA) [7].
It is simple to process the fiber-reinforced adhesive films into composite or hybrid components by employing hot and double belt presses, simple laminators, a vacuum bag, or heat gun and hand roll application. Thanks to the heat-sealing properties, the composite is formed within just a few minutes.

## Advantage: 30 times lighter, same strength

In addition to sail membranes, there are many other applications for the fiber-reinforced adhesive film T51.5000. The application areas are typically where elements need to be lightweight, and nevertheless, strong, as well as durable. One example is selective reinforcements in belts. Here, the fiber-reinforced adhesive film can take over a tensile component's function and replace the heavy core fabric in belts. In *Figure 6*, the tensile force k1% value (the force at 1 % elongation) is plotted against the number of layers. This shows that one layer of the adhesive film with a basis weight of about 15 g·m$^{-2}$ can replace a polyester fabric with a weight of 450 g·m$^{-2}$. Both the polyester fabric and the fiber-reinforced film have a k1% value of

| Name | Matrix | SAFT initial / °C | SAFT after alternating climate / °C |
|---|---|---|---|
| nolax T51.5000 | LRPU | >150 | >150 |
| nolax T52.5110 | EAA | 80 | 80 |
| nolax T53.5000 | LRPU | >150 | >150 |



**Tabelle 2** > SAFT values before and after the climate change test
(LRPU: latent-reactive polyurethane / EAA: ethylene-acrylic acid copolymer)

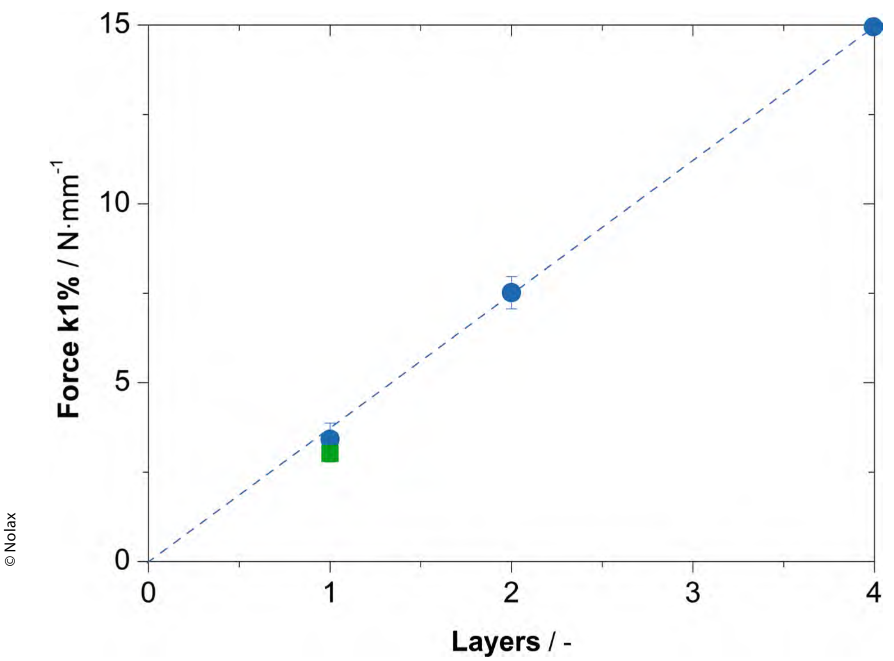


**Figure 6** > Tensile force k1% value (the force at 1% elongation) versus number of plies of (●) Nolax T51.5000 with 15 $g\cdot m^{-2}$, in comparison with a (■) standard polyester fabric 450 $g\cdot m^{-2}$, single layer

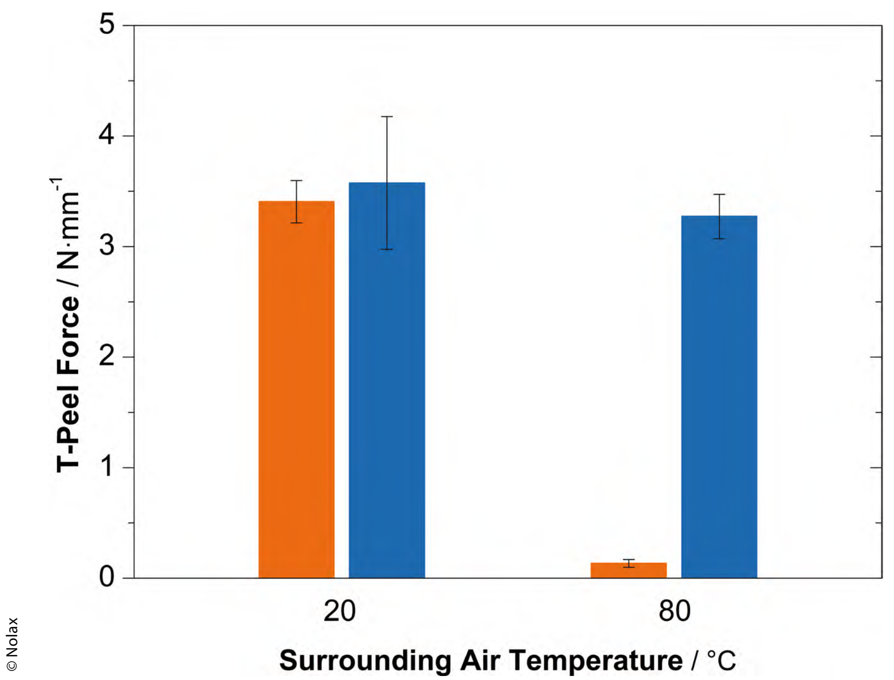


**Figure 7** > T-peel force at 20 °C and 80 °C of laminates with two layers of fiber-reinforced films: (■) fiber-reinforced film (weight 25 $g\cdot m^{-2}$) with a thermoplastic PU matrix, (■) Nolax T51.5000 (weight 25 $g\cdot m^{-2}$) with a latent-reactive crosslinked PU matrix

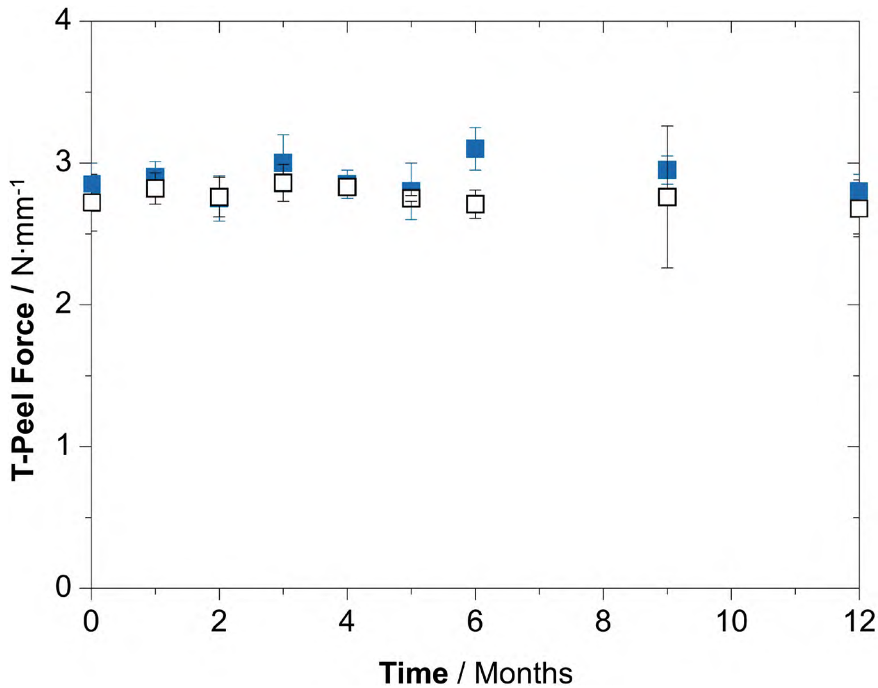




**Figure 8** > Plotting the T-peel force of laminates against the storage time of the fiber-reinforced adhesive films. The unidirectional laminates consist of 10 layers of T51.5000 (weight 15 g·m$^{-2}$) dried at (■) 50 °C or (□) 60 °C – with a line speed of 8 m·min$^{-1}$ and a drying section of approx. 25 m

~3.5 N·mm$^{-1}$. If two or four layers of the adhesive film are applied, the tensile performance increases linearly.

## Thermal and alternating climate resistance

The latent-reactive matrix used for the T51.5000 and T53.5000 fiber-reinforced adhesive films shows a high heat resistance after crosslinking. *Figure 7* shows the T-peel force of unidirectional laminates (2 plies, consolidated at 110 °C during 10 min and 4 bar) at 20 °C and 80 °C. One laminate was made with the T51.5000, and the other laminate with the related but thermoplastic matrix. At 20 °C, the peel force for both laminates is at the level of about 3.5 N·mm$^{-1}$. When the temperature is increased to 80 °C, the laminate with the thermoplastic matrix can be peeled off without noticeable force input. The latent-reactive matrix remains at a peel force of about 3.4 N·mm$^{-1}$. In many outdoor applications, materials need to resist alternating temperature and humidity changes. With significant temperature differences (membranes can reach a surface temperature of 70–80 °C in direct sunlight) and high humidity, the matrix systems of these soft composites can age severely. As a result of water immersion and absorption, delamination and eventually early failure of the component occurs. A good indication of whether a matrix has a high resistance to alternating climate changes is the combination of determining the shear adhesion failure temperature (SAFT; test at 0.5 °C·min$^{-1}$ heating rate, 1000 g applied weight, 12.5 x 25.0 mm$^2$ bonded area) before and after a climate change test, for example, PV 1200 (Volkswagen AG group standard with 20 cycles, one cycle 12 h, T = 25 °C / 80 °C / 40 °C / 25 °C, RH = 40 % / 80 % / 0 % / 40 %). *Table 2* shows the SAFT values before and after the climate change test of laminates (shear specimens with five layers each and an orientation 0°/90°/0°/90°/0°; consolidated at 110 °C for 10 min and 4 bar) from T51.5000, T52.5110 and T53.5000. In all cases, the values show no degradation after the alternating climate tests.

## Storage-stable for over 12 months

Unlike many other reactive adhesive systems, Nolax's fiber-reinforced adhesive films are storage-stable for at least one year at room temperature. In *Figure 8*, the T-peel strength of laminates made from T51.5000 is plotted against the storage time at room temperature of the fiber-reinforced adhesive films (laminates consist of 10 layers, consolidated at 110 °C for 10 min and 4 bar). Over the course of 12 months, the reactivity remains at a level where the same peel force of about 3 N·mm$^{-1}$ is obtained. As long as the latent-reactive, fiber-reinforced adhesive films do not reach temperatures above 50 °C, the adhesive film remains reactive.

## Conclusions

This article provides an insight into the subject of fiber-reinforced adhesive films and their potential applications as lightweight, high-performance components, such as a membrane sail, or as selective reinforcement of components, such as belts. In Nolax's fiber-reinforced adhesive films, high-performance fibers are impregnated with innovative, water-borne adhesives, where the property profiles can be tailored. The new thermoplastic, as well as the new reactive matrix systems, can be stored at room temperature for up to one year and have heat-seal properties. Moreover, lightweight and robust composite or hybrid components can be manufactured in just a few minutes. Time savings of up to a factor of ten are possible here.

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