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Reliable Adhesion on Snow

Skis should be robust against humidity and temperature fluctuations and have a long service life. Reliable adhesion in multi-material laminates can be achieved by employing high-performance multi-layer adhesive films. They significantly reduce the failure rate, thereby eliminating delamination between aluminum and the glass fiber-reinforced epoxy.

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The ski has been used for transportation for thousands of years and even predates the wheel. The use of skis dates to pre-Christian times, with the oldest evidence dating back to 6000 BC. Rock carvings show the early use of skis for hunting and transporting goods [1]. With the metamorphosis from transportation to sporting equipment, skis have experienced, from a materials science perspective, a remarkable development over the last 100 years. Simple, bulky wooden slats emerged as modern high-performance laminates (*Figure 1*). The latter comprises different, affiliated materials that ensure driving comfort, performance, and less weight [2]. The multi-material laminate construction is the most widely used method for producing skis to date and was introduced in the 1950s by Howard Head, an aircraft engineer and designer [3]. At that time, he had used the I-beam design, in which a lightweight core was connected to a stiff top and bottom chord. With that, Head accomplished pioneering work and built the Head Standard, which consisted of aluminum top and bottom chords, a wood core, steel edges, and a polymer running surface [4]. In the 1960s, Rossignol followed and launched the first million-selling ski model: the Strato [5]. By using epoxy resin, Rossignol introduced another class of material in the ski construction (*Figure 2*).

A significant challenge is joining these dissimilar materials which have different polarities and thermal expansion coefficients. Moreover, skis are exposed to extensive humidity and temperature changes, which often leads to delamination between the various components, especially between the aluminum and epoxy.

Failures due to low adhesion

Delamination is a constant challenge for ski manufacturers. Although careful attention was paid to potential sources of error during the manufacturing process, the ski start-up Anavon still experienced delamination between the aluminum and epoxy in a new ski model. Factors such as sanding the aluminum sheets, careful cleaning, eliminating release agents, recording manufacturing conditions, as was the use of carefully stored glass-epoxy prepregs were always given close attention. Nevertheless, random failures of skis due to delamination occurred repeatedly. *Figure 3*a shows that the aluminum top chord has separated from the substructure close to the ski tip. Another characteristic of low interlaminar adhesion between aluminum and epoxy is shown in *Figure 3*b. Circular delamination marks occurred at the drill holes for attaching the ski fittings. These typical punctiform indentations appear in multi-layer laminates in the event of an impact load and are more prominent, as the adhesion between the individual layers becomes weaker [6]. The

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Figure 1 > A typical ski: multi-material laminate of wood, aluminum, steel, and polymers

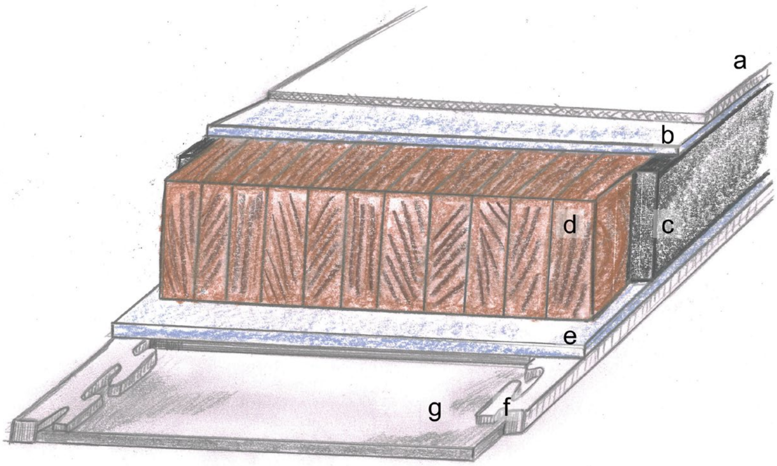

Figure 2 > Schematic of a typical ski layout. a) Top sheet, b) top chord, c) sidewall, d) core, e) bottom chord, f) edge and g) running surface. Since the 1960s, epoxy (as liquid resin or as prepreg) is widely used to bond the individual materials for skis.

residue on the aluminum top chord and the epoxy are further indicators of poor adhesion to the aluminum. To keep the design and shape and thus the riding comfort of the ski, a technique from the automotive industry was used to improve the adhesion between aluminum and epoxy. For manufacturing metal-polymer hybrid components for car interiors, metal sheets are coated first with a thermoplastic high-performance adhesive film before the polymer is rear-injected. Decrypted to skis, the aluminum top and bottom chords are coated first with adhesive films before further processing in the standard ski manufacturing process.

Methods from the automotive industry

Using multi-layer adhesive films, materials such as metals and polymers can be firmly bonded. Adhesive films replace labor and time intensive pre-treatments of the metal surface. These elaborate pre-treatments include primers, structuring, roughening, treating with plasma, or a combination of these. The so-called rear-injection molding process enables affordable and efficient production of structural or decorative metal-plastic hybrid components for the automotive industry [7][8]. In this case, the process essentially consists of three steps:

- The surface of a metal sheet is coated with an adhesive film at elevated temperature and under pressure in a flatbed laminator or double-belt press.
- If the metal sheets have not already been shaped before coating, they can be processed in standard stamping and forming procedures.
- The coated and formed metal parts are placed in an injection molding tool. The polymer is injection-molded directly onto the coating, thereby activating the adhesive film, and bonding the polymer to the metal.

As with rear-injection molding of metal, aluminum sheets for ski production can be coated first with adhesive films on a flatbed laminating machine and then processed into multi-material laminates in a ski press. The adhesive film forms the ideal bridge and creates reliable interlaminar adhesion between the different materials. Further, it protects the aluminum sheets from dirt, damage, or oxidation and can be stored at room temperature for up to two years. Due to the high elasticity, these adhesive films can absorb stresses at the aluminum/epoxy interface caused by the different thermal expansion coefficients. Adhesive films are durable, and multiple alternating climate cycles do not affect the multi-material laminate. Careful tuning of the adhesive film chemistry ensures optimal wetting during the bonding process and prevents water from migrating into the interfaces of the aluminum and epoxy. Furthermore, because they are thermoplastic, adhesive films can be thermally activated during the standard process for manufacturing skis.

Manufacturing of multi-material laminates

Four multi-material laminates were prepared to study the adhesion between the aluminum chords and glass-epoxy prepregs. The construction of the multi-material laminates (*Figure 4*) remained unchanged, varying only in the pre-treatment of the aluminum (*Table 1*). The 0.4 mm thick aluminum sheet was a high-strength alloy composed of approximately 1.7 % copper, 2.5 % magnesium, 7 % zinc, and 0.1 % zirconium. As a wood core, ash with 3.0 mm thickness was used. The prepreg used, 0.5 mm thick, consisted of a non-woven glass fabric with an epoxy resin content of around 40 mass-%. Other materials used: 0.5 mm co-polyamide cover sheet, 0.2 mm neoprene rubber inserts, 0.1 mm ash cut veneer, and 1.7 mm thick ultra-high molecular weight polyethylene running surface.

	Pretreatment aluminum	Remarks/Details
ML-1	Ground and cleaned	Reference
ML-2	Smooth and uncleaned	The aluminum has been used as delivered.
ML-3	Smooth, uncleaned, and coated with TPU adhesive film	The TPU monofilm nolax A21.4502 with 50 g/m^2 has been applied to the aluminum at 170 °C using a flatbed laminator.
ML-4	Smooth, uncleaned, and coated with TPU/PE adhesive film	The PE side of the multi-layer adhesive film nolax A22.5010 with 50 g/m^2 has been applied to the aluminum at 170 °C with a flatbed laminator.

Table 1 > Overview of manufactured and tested multi-material laminates (ML). The layout and preparation of the laminates are identical. The pretreatment of the aluminum alters.

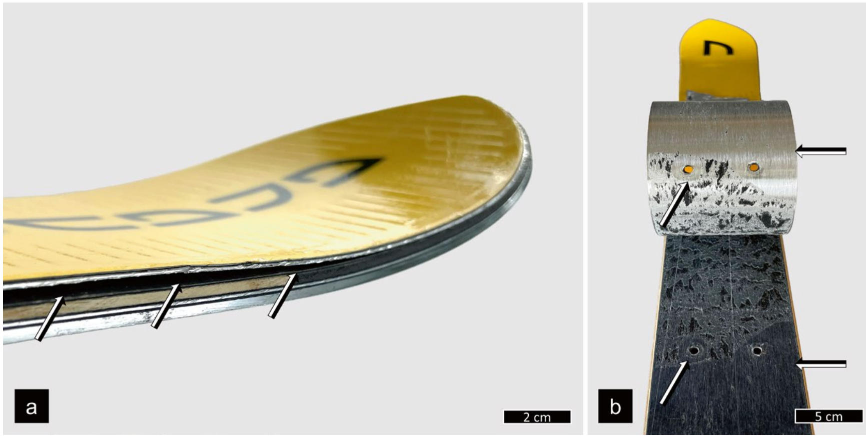

Figure 3 > a) Delamination near the tip of a used ski (see arrows), b) after removing the aluminum top chord, the failure mode shows a primarily adhesive character (see arrows)

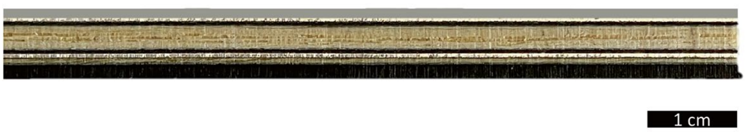

Figure 4 > Cross-section of a multi-material laminate; materials from top to bottom: copolyamide top sheet, aluminum top chord, neoprene rubber, ash core, neoprene rubber, aluminum bottom chord, ash cut veneer, ultra-high molecular weight polyethylene running surface

The aluminum sheets used to prepare the multi-material laminates (ML) were prepared as follows: sanded and cleaned with isopropanol (reference ML-1), smooth as delivered (ML-2), or smooth as delivered and coated with adhesive films (ML-3 and ML-4). Two different adhesive film formulations were used. In order to provoke and investigate a defined poor adhesion, the aluminum was coated with an adhesive film consisting of only one layer (mono-adhesive film) of thermoplastic polyurethane (TPU); in this case, the product Nolax A21.4502 with 50 g/m². This adhesive film can only provide good adhesion for the epoxy resin (ML-3). The adhesive film Nolax A22.5010 with 50 g/m² was used to achieve high adhesion between the different substrates. This consists of several layers (multi-layer adhesive film): a layer of TPU for bonding the epoxy resin and a layer of functionalized polyethylene (PE) that ensures good adhesion to aluminum (ML-4).

Where an adhesive film was used, it was first applied to the untreated aluminum on a Meyer flatbed laminating machine. The aluminum sheets were not sanded or cleaned beforehand. Coating the aluminum took place at temperatures of 160 to 170 °C and using a pressure of 1.5 bar, with subsequent cooling to approximately 25 to 30 °C at a speed of 1 m/min.

The laminates in A4 size were produced on a ski press of the company Langzauner in a multi-stage process:

- Heating up to T = 100 °C.
- Pre-fixing at T = 100 °C and p = 1 bar for t = 8 min.
- Pressing at T = 120 °C and p = 20 bar for t = 20 min.
- Cooling down to approximately T = 30 °C.

Using a belt saw 260 mm long and 20 mm wide test specimens with a thickness of about 8 mm were first cut out of the A4 laminates. The specimens showed no delamination after sawing. The 90° peel tests, before and after exposure to multiple alternating climate cycles, were carried out after seven days of storage at an ambient temperature of 20 °C and relative humidity of 65 %. The starting point for peeling the laminates was between the aluminum top chord and the layer of glass-epoxy on the wood core.

Testing of multi-material laminates

Figure 5 shows the initial peel resistance versus displacement of the multi-material laminates. The peel resistance was measured by a 90° peel test (according to DIN EN 1372) with an Instron universal testing machine at a test speed of 10 mm/min, at 20 °C room temperature and 65 % relative humidity.

The time-consuming grinding and cleaning of the aluminum showed slight improvements in adhesion within the composite compared to the aluminum top and bottom chords used directly in the as-delivered condition and without pretreatment. The average peel resistance for both ML-1 and ML-2 was close to 6.5 N/mm. Only the maximum peel resistance showed a noticeable difference and climbed from 8.9 ± 0.5 N/mm to 9.8 ± 0.7 N/mm when the aluminum sheet was sanded. For both, the peeling resulted in a cohesive fracture in the glass epoxy.

To obtain and investigate a defined poor adhesion, as in composite ML-3, the aluminum was coated in advance with a TPU adhesive film with 50 g/m² weight. Here, the lowest values of 6.4 ± 2.2 N/mm and 4.1 ± 1.0 N/mm for the maximum and average peel resistances with an adhesive failure to the aluminum were obtained. There was no residue of the TPU adhesive film on the aluminum. The initial adhesion was sufficient, as no delamination occurred when the laminate was cut into test specimens.

The best values were achieved when the aluminum was coated with a TPU/PE multi-layer adhesive film with a weight of 50 g/m² (and PE side against the aluminum) before the production of composite ML-4. Maximum and average peel resistances of 16.4 ± 2.2 N/mm and 7.5 ± 1.0 N/mm were measured. The adhesion between aluminum and epoxy could be improved in such a way that the fracture was directed into the wood core. The results of the initial peel resistances are summarized in *Table 2*.

For simulating the influence of humidity and temperature cycle on skis, the test specimens of the multi-material laminates were subjected to alternate climate cycle tests according to a Volkswagen standard, the so-called VW PV 1200. The 260 × 20 mm² (length × width) test specimens were exposed to 20 cycles of alternated temperature and humidity in a Weiss climate chamber. One cycle lasted 12 h with minimum temperature and humidity of T_{MIN} = 40 °C and RH_{MIN} = 0 % and maximum temperature and humidity of T_{MAX} = 80 °C and RH_{MAX} = 80 %.

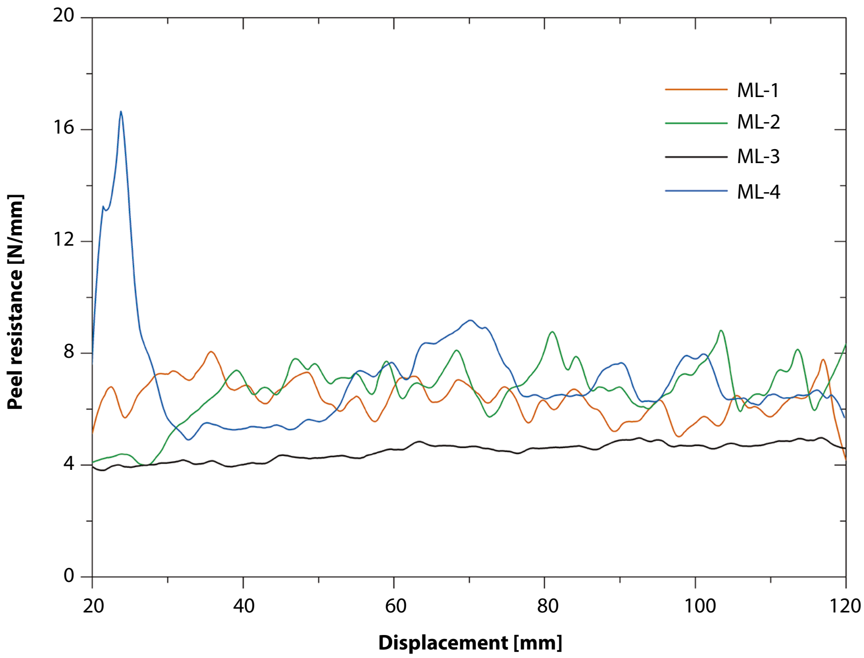

Figure 5 > Initial peel resistance versus displacement of the multi-material laminates during the 90°-peel test (DIN EN 1372)

Figure 6 and *Table 3* summarize the results of the 90° peel tests after the alternating climate test. The peel resistance deteriorated by about 25 % after the VW PV 1200 aging when the aluminum chords were sanded and cleaned, respectively, used in the as-delivered condition. The maximum and average peel resistances are about 7.0 N/mm and 5.0 N/mm. Before the 90° peel tests were performed, the first delamination between aluminum and epoxy could already be observed in the test specimens. After peeling, the fracture pattern revealed a mixed fracture: adhesive to the aluminum and cohesive in the epoxy resin.

The peel resistances just mentioned are also close to the initial value of ML-3, the laminate with the aluminum that was coated with the TPU adhesive mono-film. The ML-3 lost structural coherence after climatic cycling. The water could easily migrate between the aluminum and TPU adhesive film interface and provoke delamination. Some of these test specimens already fell apart in the climate chamber.

The test specimens from ML-4, in which the aluminum was pre-coated with the TPU/PE multi-layer adhesive film Nolax A22.5010, showed impressive improvements. After exposure to climate cycles, the average and maximum peel resistance improved by 50 % and 100 %, respectively, compared to the initial value. The peel resistances were determined at 11.0 ± 2.4 N/mm and 35.3 ± 2.2 N/mm. The test specimens produced multi-material failures with even a failure in the aluminum.

Figure 7 shows a pictorial summary of the failure behavior of ML-1, ML-2, ML-3, and ML-4 before and after exposure to climate cycling.

	Maximum peel resistance	Average peel resistance	Failure behavior
–	N/mm	N/mm	–
ML-1	9.8 ± 0.7	6.3 ± 0.4	Cohesive in epoxy
ML-2	8.9 ± 0.5	6.4 ± 0.1	Cohesive in epoxy
ML-3	6.4 ± 2.2	4.1 ± 1.0	Adhesive to aluminum
ML-4	16.4 ± 2.2	7.5 ± 31.0	Cohesive in wood core

Table 2 > Overview of the initial maximum and average peel resistances of the laminates. The start for peeling is located between the aluminum top chord and the epoxy.

	Maximum peel resistance	Average peel resistance	Failure behavior
–	N/mm	N/mm	–
ML-1	7.0 ± 0.2	4.8 ± 0.1	Mixed fracture: Adhesive to aluminum and cohesive in epoxy
ML-2	7.1 ± 0.1	4.9 ± 0.4	Mixed fracture: Adhesive to aluminum and cohesive in epoxy
ML-3	1.8 ± 0.3	0.1 ± 0.01	Lack of structural coherence
ML-4	35.3 ± 5.0	11.0 ± 2.4	Structural with multi-material failure

Table 3 > Overview of maximum and average peel resistances after the alternating climate cycle test (VW PV 1200). The starting position for peeling is located between the aluminum top chord and the glass epoxy.

Good wetting and high elasticity

Remarkably, a sanded aluminum sheet did not improve adhesion significantly when compared to a smooth one. After exposure to the alternate climate cycle test, peel resistance was significantly reduced for both multi-material laminates ML-1 and ML-2. Sanding the surface did not result in reliable adhesion [9]. This means that time-consuming aluminum sanding and cleaning is not a suitable pre-treatment solution.

If the adhesion is low and adhesive failure occurs when performing initial 90° peel tests, water penetration and delamination during the use can likely occur, as was the case with ML-3.

A TPU/PE multi-layer adhesive film, such as that applied in the ML-4, can be used to achieve strong adhesion between aluminum and epoxy. The wetting on aluminum is outstanding. In this case, water cannot subvert the interfaces during the application if the multi-layer adhesive

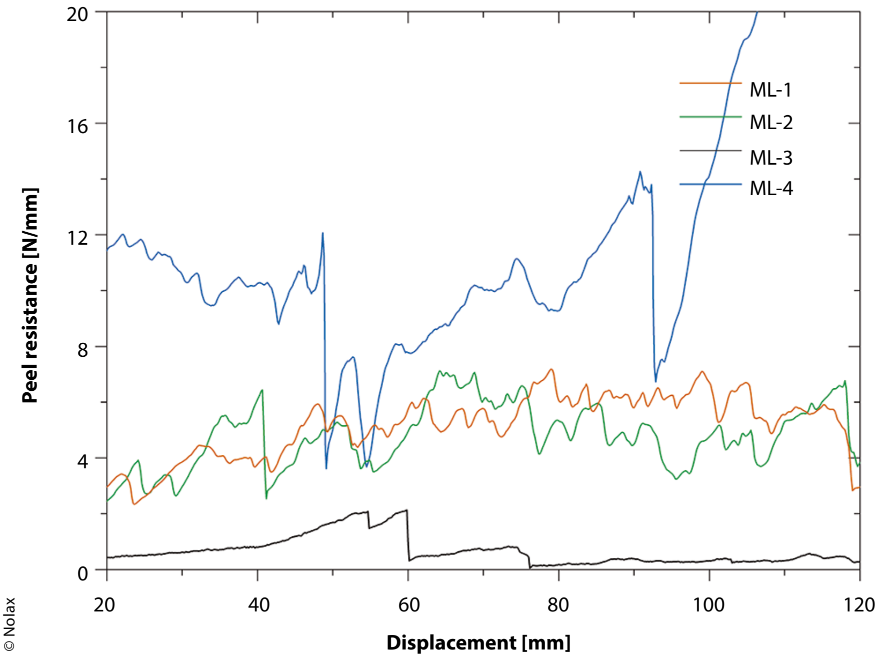

Figure 6 > Peel resistance versus displacement of the multi-material laminates during the 90°-peel test (DIN EN 1372) after the alternate climate cycle test (VW PV 1200)

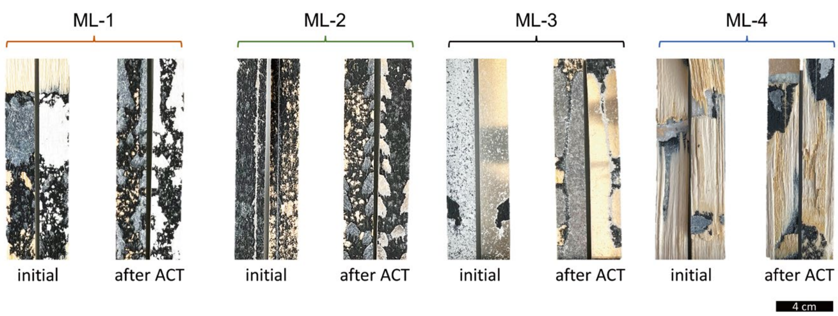

Figure 7 > Failure behavior during the 90°-peel test of ML-1, ML-2, ML-3, and ML-4 before (initial) and after the alternate climate cycle test (after ACT). The test specimens show the lower structure (left) and the upper chord (right).

film is applied to the aluminum sheet with the PE side first. Furthermore, the TPU side develops strong adhesion to the epoxy resin. The elastic adhesive film can also absorb the stress caused by temperature changes while skiing and the different thermal expansion coefficients of aluminum and epoxy resin.

Conclusions

For achieving reliable interlaminar adhesion in the multi-material laminate of skis, attention should be paid to optimal wetting and an elastic interface between dissimilar materials such as metals and polymers. This can be achieved with a multi-layer adhesive film – such as the product Nolax A22.5010 with 50 g/m² – which forms the best possible bridge between aluminum and glass-epoxy. They also make the skis more robust against moisture and temperature fluctuations, thereby increasing their service life and significantly reducing failure due to delamination. //

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