SPECIAL REPORT — Adhesives and Sealants

Adhesion of millable PU to general purpose rubber

By Tom Jablonowski
TSE Industries Inc.

Executive summary

Polyurethanes are known for their outstanding abrasion resistance and strength properties, properties that are important for applications such as conveyor belting for mining, footwear and other applications.[1]

Millable polyurethanes are often used for these applications, but their relatively high cost can be a disadvantage vs. general purpose rubbers like SBR and NR, which are more commonly used. Co-vulcanizing a thin layer of the millable polyurethane over a general purpose rubber gives a highly abrasion-resistant layer, resulting in improved performance and lower total cost compared to an all-polyurethane compound.

Bonding of these dissimilar polymer types has been difficult in the past, but the inclusion of a minor proportion of a polybutadiene-based thermoplastic polyurethane to either or both components has been found to result in excellent adhesion.[2,3]

Polyurethanes are well known for their outstanding properties, especially abrasion resistance, which makes this polymer family extremely useful for applications where the surface of the rubber article is subject to wear.

One such application is in conveyor belting for mining and material transport (**Fig. 1**). Conveyor belting for these applications is typically constructed of natural rubber, SBR or polybutadiene (BR) rubber types, often in blends of these, due to their very good properties and relatively low cost.

Another application is rubber-covered rolls, made from various rubber types (NR, SBR, NBR, etc.), depending on the requirements of the specific use of the roll. Polyurethanes, especially millable (solid, vulcanizable rubber) polyurethanes, also could be used in these applications, and would offer improvements in abrasion resistance, strength properties and ozone resistance, compared to the conventional rubber types, but are more expensive than the conventional rubber types, making them costly to use.

TECHNICAL NOTEBOOK
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One method used to minimize the expense of using a more expensive rubber is to apply a thin layer, a veneer, of the higher performing rubber on top of the conventional rubber. **Fig. 2** illustrates the practice and potential benefit for conveyor belts but this would apply as well to rubber covered rolls (**Fig. 3**) and other applications.

An important factor in this technique is obtaining excellent adhesion between the top, high-performance, and bottom, less-expensive conventional rubber, layers. Although this can sometimes be done post-vulcanization, by cold-bonding the two layers together, a better bond is usually achieved by curing the two rubber compounds together.

Polyurethanes, thanks to their chemical structure being different than most common rubbers, can be difficult to bond to other rubbers during curing. Polyurethanes are composed of polyols (ether or ester), isocyanates and chain extenders; these monomers are much different from the monomers making up conventional rubber types (isoprene, butadiene, styrene and others).

Also, the conventional rubber types typically contain double bonds in most, if not all, of the repeating units of the polymer, while sulfur-curable polyurethanes contain only a low level of double bonds, pendant to the polymer chain backbone.

It previously has been determined[2,3] that thermoplastic polyurethanes based upon polybutadienes can be used as bonding promoters for adhering dissimilar polymers. The double-bond functionality in these TPU polymers allows (co-)vulcanization with other polymers, and the polyurethane nature provides compatibility with millable polyurethanes.

This paper more fully explores the utility of this technology for bond improvements, primarily between millable polyurethanes (MPU) and other polymers (NR, SBR, NBR, EVA), during the vulcanization process.

Experimental

Ingredients used were common materials used in rubber compounding. The polybutadiene-based TPU (Safipol-brand TPU7840) was obtained from Chemspec Ltd., and used as received. Polyether millable polyurethanes, EU1 (Millathane-brand E34) and EU2 (Millathane E40), were from TSE Industries. Diene 140ND, a high cis, neodymium, polybutadiene rubber was from Firestone Polymers.

Compounds were mixed in either an internal mixer (BR Banbury-brand) or a miniature internal mixer (Brabender Prep-Mixer-brand). Compounds containing TPU7840 were mixed as a masterbatch (without curatives) to approximately 150°C, to melt/flux the TPU7840, and curatives were added on the mill.

Abrasion resistance was tested per ASTM D5963, using a rotating test piece. This abrasion test is commonly known as "DIN Abrasion."

Adhesion was tested per ASTM D413, Machine Method, using Strip Type A specimens, prepared by curing the two compounds together in a 25 mm x 150 mm x 6 mm mold, using a Mylar separator between the compounds, and testing peel adhesion at 0.8 mm/s.

Results and discussion

MPU-Natural Rubber

A standard NR compound, carbon black reinforced, with a CBS/sulfur cure was used for the initial bonding studies. This is a typical NR compound with very good physical properties and abrasion resistance (**Table 1**). A standard sulfur-cured polyether millable polyurethane (EU1) compound was evaluated for bonding to the NR compound.

The compound used the standard cure system used in sulfur-curable millable polyurethane: MBTS-4, MBT-2, ZM (Thanecure-brand ZM, an MBTS/zinc

Fig.1: Conveyor belt used in a quarry.

Fig. 2: Conveyor belt with abrasion-resistant surface layer.

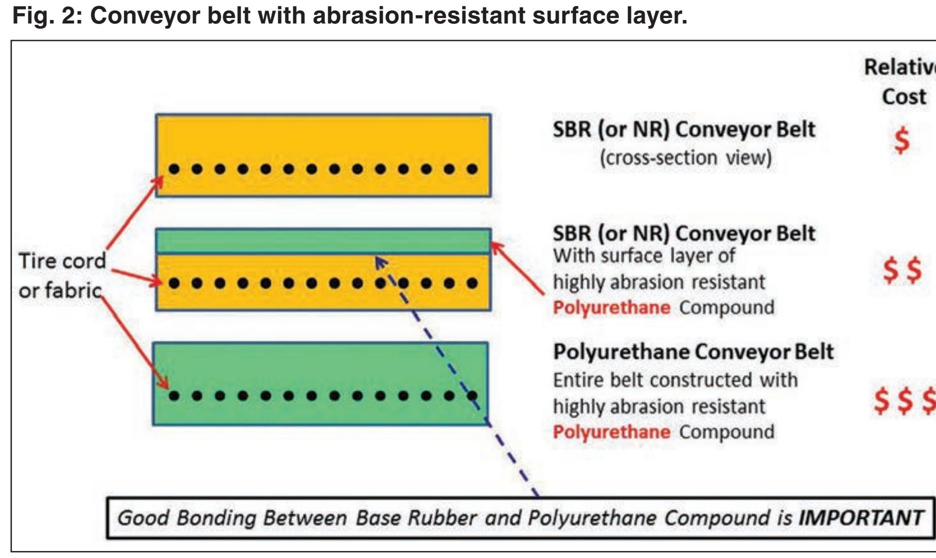
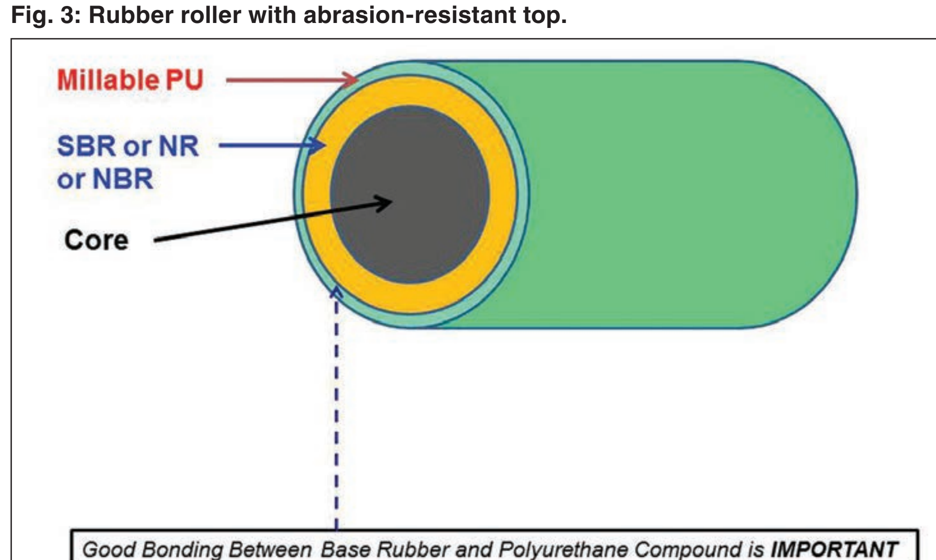
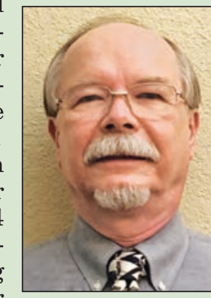


Fig. 3: Rubber roller with abrasion-resistant top.



The author

Tom Jablonowski has been with TSE Industries Inc. for 14 years and is the global technical service manager for Millathane-brand millable polyurethanes.


Jablonowski

He has been in the rubber industry for 44 years, previously working 20 years for Uniroyal Chemical/Crompton as senior research scientist, providing technical service for EPDM, millable polyurethanes and rubber chemicals. Prior to Uniroyal, he held technical positions at Master Processing Corp., Gates Engineering, Stowe Woodward and RM Roll Products.

Jablonowski has presented and had published numerous papers, and is a co-author of the "Polyurethane Elastomers" chapter of the 14th edition of the Vanderbilt Rubber Handbook. He also is co-inventor on three patents.

He has a bachelor's in chemistry from Penn State University and a master's in Internet Business from Mercy College. He is a member of the American Chemical Society, the Rubber Division of the ACS, ASTM and several rubber groups.

chloride complex)-1, and sulfur-1.5. This compound had similar tensile strength to the NR (both 24+ MPa), but it had much better abrasion resistance in the DIN abrasion test, losing 66 mm^3 mass while the NR compound lost 132 mm^3 mass.

This is the primary reason for wanting the millable polyurethane layer as the wear surface of the conveyor belt (or roller), as it would provide longer wear than the NR. Curing the two compounds together, however, gave very low adhesive strength (0.5 N/mm), with adhesive (interfacial) failure.

Replacing the carbon black with silica and adding a mercapto silane coupling agent, along with several other formula modifications, gave some improvement in adhesive strength, but the adhesion was still low (1.3 N/mm) and the failure mode was still adhesive. Adding 15 phr of TPU7840, along with a slight cure system modification (to better cure the TPU component) gave excellent adhesion, with the samples showing cohesive failure (within the NR layer).

MPU–SBR/BR

A similar study was done with an SBR/BR (80/20) compound, typical of a formula used for conveyor belting, with N330 black reinforcement and a CBS/sulfur cure (**Table 2**). The polyether polyurethane (EU2) used a similar cure system as the EU1 compound, but used silica and mercapto silane for reinforcement, as that seemed to improve adhesion somewhat in the previous study.

The polyurethane compound had much better properties and abrasion resistance compared to the SBR/BR compound, but the cured adhesion of these two compounds was poor (1.4 N/mm). Adding 5, 10 and 15 phr of the TPU to the EU2 compound, with a slight increase in sulfur level, did improve the cured adhesion somewhat (by 2x, 2.5x, and 3x), although the adhesion was still not 'excellent', with the failure at the interface between the two compounds.

Adding 10 phr of the TPU to the SBR/BR compound gave some improvement in adhesion to the base EU2 compound (1.8x, with adhesive failure), but the addition of 5 or more phr TPU to the SBR/BR compound resulted in excellent adhesion, with cohesive failure (within the SBR/BR compound), indicating that the bond was stronger than the SBR/BR compound.

This suggests that a small amount of TPU in both the substrate and the top layer compounds may be the most effective way to achieve the excellent adhesion and high abrasion resistance needed in demanding applications.

MPU-SBR

This improvement in adhesion was investigated more thoroughly in a follow-up study, where the TPU was evaluated as a polymer replacement for both the millable polyurethane (EU1) and the SBR, at 0, 5, 15 and 25 phr levels (**Table 3**). The data shows, as with the previous study, increasing adhesion strength to the SBR compound with the addition of the TPU to the millable polyurethane, with 5 phr TPU giving 8x better adhesion, but adhesive failure.

TPU levels of 15 phr and higher gave excellent adhesion, with cohesive failure (within the SBR compound). Adding 5 phr of TPU to the SBR compound also improved bonding to the MPU compound, giving higher adhesion to the base MPU compound, and cohesive failure to the 5 and 25 phr EU/TPU compounds.

Compounds with high levels of TPU in the SBR gave reasonably good adhesion, but didn't result in cohesive failure. This may be because of some incompatibility of the TPU with the SBR at higher TPU levels. Tensile strength and abrasion resistance were slightly adversely affected by the inclusion of the TPU, but low levels (up to 15 phr) did not have significant effects on these properties.

Overall, the best performance, physical properties, abrasion resistance and adhesion, was obtained when a small amount (5 phr) of the TPU was included in both the millable polyurethane and the substrate SBR compound.

MPU-NBR

Bonding of millable polyurethane (EU1) to NBR during curing also was investigated. NBR is a more polar rubber than NR and SBR, and generally is more compatible with MPU. A study similar to that used with the SBR was conducted, with levels of the TPU in both the MPU and the NBR ranging from 0 to 25 phr.

The data (**Table 4**) showed that the EU1 compound gave much better adhesion to the NBR than the NR, SBR/BR or SBR, and the addition of the TPU to the MPU only benefited adhesion moderately. The best adhesion, with cohesive failure (within the NBR compound) was obtained when the NBR compound contained 25 phr of TPU, and the MPU had 0-15 phr TPU.

MPU–Ethylene vinyl acetate

EVA is a thermoplastic material com-

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Table 1: NR to MPU adhesion with TPU7840.

	NR	MPU-Ctrl	MPU-MOD	MPU-TPU
NR (SMR CV60)	100			
EU1 (Millathane E34)		100	100	100
TPU7840				15
Carbon Black (N650)	50			
Carbon Black (N330)		30		
Precipitated silica			30	30
Mercapto silane			0.6	0.6
Aromatic oil	10			
Coumarone Indene Resin		10		
Ester Plasticizer			5	5
Liquid polybutadiene			5	5
Zinc oxide	5			
Stearic Acid	2			
Zinc stearate		0.5	0.5	0.5
CBS	1			
Sulfur	2	1.5	2.5	3.5
MBTS		4	4	4
MBT		2	2	2
ZM		1	1	1.5
Physical Properties				
Hardness, Shore A	63	63	70	67
Tensile Stress, 100%E, MPa	2.3	1.7	2.5	2.5
Tensile Strength, MPa	24.6	24.8	29.8	25.9
Elongation, %	625	780	590	500
Abrasion resistance, mm^3 loss	132	66	62	66
Adhesion to NR, N/mm	—	0.5	1.3	**>6.3**
Failure type	—	Adhesive	Adhesive	**Cohesive**

Table 2: SBR/BR to MPU adhesion with TPU7840.

	E40	E40 TPU5	E40 TPU15	E40 TPU25	SBR/BR	SBR/BR TPU10
EU2 (Millathane E40)	100	100	100	100	—	—
SBR 1500	—	—	—	—	80	80
BR (Diene 140ND)	—	—	—	—	20	20
Zinc stearate	0.5	0.5	0.5	0.5	—	—
Stearic acid	—	—	—	—	1	1
Zinc oxide	—	—	—	—	5	5
Precipitated silica	24	24	24	24	—	—
Mercapto silane	0.5	0.5	0.5	0.5	—	—
Carbon Black (N330)	—	—	—	—	50	50
Aromatic oil	—	—	—	—	8	8
Coumarone Indene Resin	5	5	5	5	—	—
Process Aid	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	4	4	4	4	—	1
MBT	2	2	2	2	—	—
ZM	1	1	1	1	—	—
Sulfur-80% dispersion	2.5	3.5	3.5	3.5	1.9	2.5
CBS	—	—	—	—	1.5	1.5
TPU7840	—	**5**	**15**	**25**	—	**10**
Physical Properties						
Hardness, Shore A	70	67	67	67	65	71
Tensile Stress, 100%E, MPa	2.2	2.0	1.8	1.8	2.1	3.2
Tensile Strength, MPa	33.3	35.0	33.2	27.3	19.0	15.7
Elongation, %	615	625	615	585	470	350
Abrasion resistance, mm^3 loss	59	58	64	69	91	114
Adhesion to SBR, N/mm	1.4	3.0	3.2	4.0	—	—
Failure type	Adhesive	Adhesive	Adhesive	Adhesive		
Adhesion to SBR/TPU10, N/mm	2.5	***>6.1***	***>6.1***	***>5.6***	—	—
Failure type	Adhesive	**Cohesive**	**Cohesive**	**Cohesive**		

Table 3: SBR to MPU adhesion with TPU7840.

Millable Polyurethane Formulation	
EU1 (Millathane E34)	100 - 75
Safipol TPU7840	0 - 25
Zinc Stearate	0.5
N330	25
Coumarone Indene Resin	5
Process aid	0.5
MBTS	4
MBT	2
Thanecure ZM	1
Sulfur (80% oiled dispersion)	2.5

SBR Formulation	
SBR 1500	100 - 75
Safipol TPU7840	0 - 25
N330	50
Sundex 790	8
Zinc Oxide	5
Stearic acid	1
CBS	1.5
Sulfur (80% oiled dispersion)	2.5

Millathane E34	100	95	85	75	—	—	—	—
SBR	—	—	—	—	100	95	85	75
Safipol TPU7840	—	5	15	25	—	5	15	25
Cured Properties								
Shore A	67	67	67	67	67	70	75	80
Tensile strength, MPa	33	32	26	26	21	20	20	19
Abrasion resistance, mm^3 loss	43	45	58	65	88	85	94	112

MPU/TPU	100/0	95/5	85/15	75/25
Adhesion, N/mm				
to SBR	0.7	5.6	**>10.3***	**>12.3***
to SBR/TPU7840 - 95/5	2.6	**>11.7***	8.2	**>13.1***
to SBR/TPU7840 - 85/15	6.5	**>11.4***	**>14.9***	8.7
to SBR/TPU7840 - 75/25	**>19.9***	7.7	7.9	7.7

* Cohesive failure (within SBR); others, adhesive failure

Adhesives and sealants M&A keeping a strong pace

By Kyle Brown
Rubber & Plastics News Staff

MILWAUKEE—Mergers and acquisitions likely will continue at a rapid pace in the adhesives and sealants industry for the foreseeable future, according to Andy Hinz, managing director for Grace Matthews Inc.

Most of the deals are bolt-on acquisitions, Hinz said, generally between $20 million to $200 million in enterprise value. At that level, acquisitions tend to be lower risk.

"Strategic buyers historically have had a generally stronger appetite for bolt-on deals that can be very valuable to them, but also can carry somewhat lower risk, just due to their size," he said.

Another major reason that much of the action centers on that price range is the overall complexion of the market, as assets between $100 million and $500 million have become scarcer, he said.

"You have the large strategic players, approaching $1 billion in revenue and above. Then you have a large number of smaller companies generally under $100 million in revenue," Hinz said. "But really there are not very many companies remaining in that middle-size range."

Hinz said the market is likely to continue to consolidate, and many companies left in the middle-size range will be sold. As that happens, it tends to drive up the prices of those companies in that market as they attract a lot of strategic buyer attention.

"It continues to be a strong seller's market, and owners of high quality companies tend to have the upper hand when selling their business," Hinz said. "Because of that, high quality companies can often expect interest from multiple strategic parties, and more broadly from private equity buyers as well. In today's market, sellers often have the ability to choose their own destiny to a greater degree than in the past."


Andy Hinz

In this market, strategic buyers should be decisive and ready to pay high prices for acquisitions, Hinz said.

"The simple advice we give to companies is that if you want to be a successful acquirer, you have to play by today's rules. You have to be prepared to pay a high value, and you have to be prepared to move quickly," Hinz said. "In most cases, you have to be prepared to participate in an auction process."

Hinz said he expects the market to continue at a high level of activity into the future.

"It's probably fair to say we are near or at a cyclical peak in M&A," he said. "But that's not to say a market correction is imminent. We believe M&A activity could remain elevated for some time."

One reason for that level of activity is the health of the overall economy, as the U.S. and most other major economies seem to be healthy right now, he said. The lending environment also is encouraging both in terms of interest rates and the banks' appetite to continue to lend money to support deals. Though interest rates are starting to creep up, they're not yet at a level that could significantly dampen M&A, though that could be an issue in upcoming years.

> **"Strategic buyers historically have had a generally stronger appetite for bolt-on deals that can be very valuable to them, but also can carry somewhat lower risk, just due to their size."**
>
> **Andy Hinz**

U.S. tax reform also will likely be supportive of M&A this year and beyond, Hinz said.

"I don't necessarily think it's going to be a big push, but I do think it could help support, or even possibly drive up, valuations a little bit, and also support some incremental activity," he said. "Acquirers can get some pretty attractive tax breaks in the first year of their acquisition."

Hinz said private equity groups have a huge desire to acquire companies in adhesives and sealants, and in the broader specialty chemicals market, but that is not necessarily translating into completed transactions. Many private equity groups struggle to pay the valuation that strategic buyers are more willing to pay for a business.

"A good example of that, for high-quality companies today, it's not uncommon for us to see double-digit multiples, or a buyer paying 10 times EBITDA or more," Hinz said. "Private equity buyers just tend to struggle to get to that level of valuation on a business."

Valuations continue to remain high, encouraging some adhesive and sealant company owners who normally would not be planning to sell to reconsider, Hinz said.

"I think what's happening, is the values that are being contemplated are so high that they're getting sellers who historically may not have ever considered selling their business to think much harder about the possibility," he said.

An aging population of adhesive and sealant company owners also is a fairly significant driver in the level of activity, as private company owners are getting ready to retire without having a natural transition in place with another generation, Hinz said.

He doesn't see signs of company valuation amounts coming down significantly anytime soon, as the current market backdrop supports high values into the foreseeable future. But it does add a level of risk to acquirers who are paying high prices.

"There's certainly going to be less margin of error with how they operate their acquired businesses going forward," he said. "Particularly in the first couple of years, there's zero tolerance when you're paying a double-digit multiple for a company."

Grace Matthews is a middle-market investment bank that provides M&A and corporate finance advisory services for chemical companies.

Adhesion

Continued from page 13

monly used as a cushioning agent or shock absorber in athletic footwear. As one of the applications of MPU is in shoe soles, good adhesion of MPU to EVA is desirable. As EVA is only peroxide-curable, peroxide-cured EU1 compounds were evaluated for adhesion during curing (**Table 5**). Compounds of both dense EVA and foam EVA were evaluated, with the foam compounds made with expandable microspheres (Expancel 920DE80 d30). An EVA with 18 percent vinyl acetate and 8 MFI (Elvax 450) was chosen for this work.

Adhesion testing showed the peroxide-cured MPU compound to have low adhesion to the EVA dense and EVA foam compound, but including 15 phr of the TPU7840 into the MPU resulted in a high strength bond, with cohesive failure (failure within the EVA compounds).

Table 4: NBR to MPU adhesion with TPU7840.

Millable Polyurethane Formulation	
EU1 (Millathane E34)	100 - 75
Safipol TPU7840	0 - 25
Zinc Stearate	0.5
N330	25
DBEEA	5
Process aid	0.5
MBTS	4
MBT	2
Thanecure ZM	1
Sulfur (80% oiled dispersion)	2.5

SBR Formulation	
Nipol DN3350	100 - 75
Safipol TPU7840	0 - 25
N330	25
DBEEA	5
Process aid	0.5
Agerite Resin D	2
Stearic acid	1
Zinc oxide	5
DTDM	1
TMTD (75% oiled dispersion)	1.7
Sulfur (80% oiled dispersion)	0.6

Millathane E34	100	95	85	75
Safipol TPU7840	—	5	15	25
Adhesion, N/mm				
to NBR	3.7	5.1	6.1	5.6
to NBR/TPU 95/5	4.6	4.4	5.3	4.7
to NBR/TPU 85/15	4.6	6.8	5.3	4.6
to NBR/TPU 75/25	**>8.4***	**>8.4***	**>8.4***	4.4

* Cohesive failure (within NBR); others, adhesive failure

Summary and conclusion

Abrasion resistant surfaces (veneers) can be useful in applications such as conveyor belting, rollers, footwear and other articles to improve wear characteristics without the need for 100 percent highly abrasion resistant materials.

Millable polyurethanes generally have much better abrasion resistance than conventional rubber types (e.g., NR, SBR, NBR), so they are useful for this practice.

Adhesion of MPU to conventional rubbers, without compound modifications, may be low, due to polymer and cure system differences.

Incorporating a minor amount of a BR-based TPU (TPU7840) into either the MPU or conventional rubbers (NR, SBR, SBR/BR, NBR, EVA), or both, can result in excellent adhesion between the two layers.

TPU7840 blends with millable polyurethanes or other polymers may require curative adjustments and mixing condition adjustments (to melt/flux the TPU).

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Table 5: EVA to MPU adhesion with TPU7840.

Millable Polyurethane Formulations		
EU1 (Millathane E34)	100	100
Safipol TPU7840	—	15
Precipitated Silica	30	30
Vinyl silane	0.6	0.6
Plasticizer	5	5
Stearic Acid	0.5	0.5
TAC	0.25	0.25
Dicumyl peroxide 40%	2	2
Adhesion, N/mm		
To EVA-Dense	2	>6.9*
To EVA-Foam	1.2	>3.9*

EVA Formulations	Dense	Foam
Elvax 450	100	100
Stearic Acid	0.5	0.5
Zinc oxide	1.5	1.5
Expancel 920DE80 d30	—	10
TAC	0.25	0.25
Dicumyl peroxide 40%	2.5	2.5

* Cohesive failure (within EVA); others, adhesive failure