

## THE CASE OF LATEX REMOVAL FOR CARPET AND ARTIFICIAL TURF RECYCLING

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### Introduction

For the recycling of carpet and artificial turf the latex backing is often a real stumble block. Many strategies have been developed like freezing the carpet, followed by grinding and subsequent separation of the milled particles. Once it has been separated from its backing materials, PA 6 is relatively easy to depolymerise. This produces fresh caprolactam that can be used to manufacture PA 6 with no loss in quality, and is suitable for further recycling [1]. The comparable process for PA 6,6 is not as easy, but DuPont and Polyamid 2000 have developed and patented a process that depolymerises any mixture of PA 6 and 6,6 using ammonia. The result is fresh caprolactam and 1,6 diaminohexane for manufacture of PA 6 and 6,6 respectively [2]. Obviously a lot of research has been devoted to avoiding latex as a backing like e.g. polyurethane carpet backing systems based on natural oil polyols and polymer polyols [4]. Still carboxylated styrene butadiene is the leading synthetic latex polymer used in EU-27 for carpet backing, followed by styrene-acrylics and pure acrylics. This contrasts with Eastern Europe, Russia, and Turkey where styrene-acrylics dominate, followed by PVAc and redispersible powders [3]. In addition there has been a lot of research into developing alternative backing systems where the backing can easily be removed. Examples are the use of gecko technology [5] or using click chemistry (reversible Diels Alder reactions) [6]. But the best option for recycling is of course to develop carpets based completely on monomaterials.

Nevertheless a huge amount of carpet and artificial turf is around and still being produced that is backed by latex. Research has been devoted to depolymerisation of the latex using a phenylhydrazine-ferrous chloride system [7] or using supercritical water [8]. Other techniques studied are laser ablation and UV radiation [9].

An obvious way of getting rid of the latex would be to dissolve it in a suitable solvent. We have to take into account however that carpet is increasingly made of polyolefin like polypropylene or polyethylene. The same holds for artificial turf. Thus selective dissolution is required in order to develop a suitable system. But it all starts with dissolution of the latex. A suitable method for the assessment of solubility is the concept of solubility parameters developed by Hildebrand and later on refined by other scientists. There is a rule of thumb that says "like dissolves like". Hildebrand quantified this rule by calculating solubility parameters  $\delta$  and the theory is that compounds with similar  $\delta$  values attract each other to form solutions or stable mixtures [17]. Small, Van Krevelen, Hoftyzer, and Hoy further developed the solubility parameter concept by introducing more accurate calculation methods based on dispersion forces, hydrogen bonding and dipole interactions. In their work the concept was refined for polymers and calculation systems were developed that enable the assessment of solubility of polymers [12,15].

In this research we want to test the hypothesis that these systems hold true for styrene butadiene latex. In addition we want to find a route for the dissolution/release of latex from carpet backing to make recycling of carpet more easy.

### Experimental

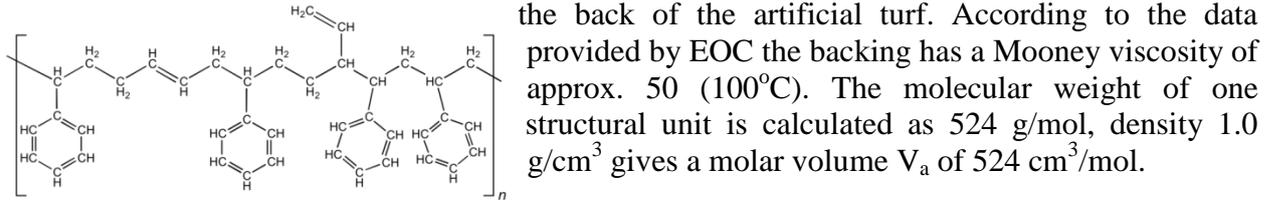
The material used in our research was artificial grass produced by TenCate-Thiolon, the tufted yarn was Polyethylene, pile height 60mm, 12 stiches per 10 cm. The tuft cloth was a double layer of woven polyethylene made by TenCate -Thiobac. At the back a thin non-woven fleece as

applied made of a mixture of PE and recycled natural/ synthetic material of undefined composition. The latex was provided by EOC BELGIUM Compound Division and was coded as EUR 1252 GB. After hardening the latex backing had a surface tension in the range of 25 – 29 mN/m, assessed by the standard water/isopropylalcohol droptest method.

The solvents were used as received from several suppliers and were of p.a. quality.

We also performed a few tests on the effect of commercial detergents on latex. The idea behind this was that the surface tension of a standard detergent solution is in the range of 30 mN/m and the presence of surfactants might promote the breaking of bonds between the latex and the tuft cloth.

For the overall molecular structure we adopt the generally described structure for Styrene butadiene latex [16]. After hardening a black dense and relatively impermeable layer is formed on the back of the artificial turf. According to the data



### Molecular structure of styrene butadiene latex

Following the method described by Van Krevelen the following basic data can be compiled [15]:

Table 1. cohesive energy data for styrene butadiene latex

Structural element	Nr. count	E <sub>coh</sub> (J/mol) per unit	Total contribution to E <sub>coh</sub>
>CH-	5	420	2100
-CH <sub>2</sub> -	7	4190	29300
Phenyl	4	31000	124000
-CH=CH-	1	10200	10200
-CH=C<	1	4860	4860
sum			170490

The overall solubility coefficient  $\delta t$  was calculated using Eq.1 [15]:

$$\delta t = \sqrt{E_{coh}/V} \quad \text{Eq. 1}$$

Thus  $\delta t = 18.0 \text{ (J/cm}^3\text{)}^{1/2}$ .

However to study the effect of polar, dispersion and hydrogen bonding forces a more detailed analysis has to be made. We apply the Hoftyzer/van Krevelen system again based on additivity of group contributions [15].

For this analysis we calculate the molar attraction constant F ((J/cm<sup>3</sup>)<sup>1/2</sup>.mol<sup>-1</sup>) based on group contribution using the following set of equations:

$$\delta d = \frac{\sum Fd}{va} \quad \delta p = \frac{\sqrt{\sum Fp^2}}{va} \quad \text{and} \quad \delta h = \sqrt{\frac{\sum Fh}{va}} \quad \text{Eq. 2 to 4}$$

In addition the following equation holds:  $\delta t^2 = \delta d^2 + \delta p^2 + \delta h^2$  Eq. 5

The following data set can be compiled:

Table 2. Bounding energy data for styrene butadiene latex, Hoftyzer/van Krevelen system

Structural element	Nr. count	Fd (J/cm <sup>3</sup> ) <sup>1/2</sup> .mol <sup>-1</sup> per unit	Total contribution to Fd	Fp (J/cm <sup>3</sup> ) <sup>1/2</sup> .mol <sup>-1</sup> per unit	Total Contribution to F <sub>p</sub> <sup>2</sup>	Fh (J/cm <sup>3</sup> ) <sup>1/2</sup> .mol <sup>-1</sup> per unit
>CH-	5	80	400	0	0	0
-CH <sub>2</sub> -	7	270	1890	0	0	0
Phenyl	4	1430	5720	110	193600	0
=CH-	3	200	600	0	0	0
=CH <sub>2</sub>	1	400	400	0	0	0
sum			9010		193600	

Applying equations 2 to 5 and using the data in table 2 we find for the respective parameters the following values:

$\delta d = 17.2 \text{ (J/cm}^3\text{)}^{1/2}$ ,  $\delta p = 0.8 \text{ (J/cm}^3\text{)}^{1/2}$ , and  $\delta h = 0 \text{ (J/cm}^3\text{)}^{1/2}$ . With Eq. 5 we find for  $\delta t$  a value of  $= 17.22 \text{ (J/cm}^3\text{)}^{1/2}$ , which is close to the overall factor we found for the  $\delta t$  based on  $E_{\text{coh}}$  calculations. From this calculation we see that the effect of hydrogen bonding is minimal which is understandable considering the fact that no polar groups are present in the molecule. To confirm the above analysis we also apply the more complex analysis developed by Hoy.

Hoy introduced the molecular aggregation number  $\alpha$  which describes the aggregation of molecules. Hoy also introduces the number of repeat unit per chain segment  $n$ . He also used a base factor  $B$  that has for our purpose the value of 277. In addition Hoy uses the Lydersen factor  $\Delta_T$  that takes non-ideality into account.

The following set of equations is applied [15]:

$$\alpha = 777 \Delta T / V \quad n = 0.5 / \Delta T \quad \text{Eq. 6 and 7}$$

$$\delta t = (F_i + B/n) / V \quad \text{Eq. 8}$$

$$\delta p = \delta t \left( \frac{1 - F_p}{\alpha F_t + B/n} \right)^{1/2} \quad \text{Eq. 9}$$

$$\delta h = \delta t ((\alpha - 1) / \alpha)^{1/2} \quad \text{Eq. 10}$$

$$\delta d = (\delta t^2 - \delta p^2 - \delta h^2)^{1/2} \quad \text{Eq. 11}$$

The following dataset was compiled:

Table 3. Interaction energy data for styrene butadiene latex, fine tuning by Hoy

Structural unit	Nr. count	$F_t$ ( $J/cm^3$ ) <sup>1/2</sup> /mol per unit	Total $F_t$	$F_p$ ( $J/cm^3$ ) <sup>1/2</sup> /mol) per unit	Total $F_p$	$\Delta_T$	Total $\Delta_T$	V ( $cm^3$ /mol)	Total V
>CH-	5	176	880	0	0	0.013	0.065	9,56	47.8
-CH <sub>2</sub> -	7	269	1883	0	0	0.020	0.14	15.55	108.85
=CH-	3	249	747	59,5	178.5	0.0185	0.0555	13.18	39.54
=CH <sub>2</sub>	1	259	259	67	67	0.019	0.019	19.17	19.17
CH <sub>ar</sub>	20	241	4820	62,5	1250	0.018	0.36	13.42	268.4
C <sub>ar</sub>	4	201	804	65	260	0.015	0.06	7,42	29.68
<b>sum</b>			9393		1755.5		0.6995		513.44

Applying above equation 6 and 7 and the data in table 3 we conclude for  $n = 0.717$ , the molecular aggregation number  $\alpha = 1.059$ .

Applying equations 8 to 11 and using the data in table 3 we find for  $\delta_t$  a value of  $= 19 (J/cm^3)^{1/2}$ , and subsequently for  $\delta_p = 7.8 (J/cm^3)^{1/2}$ ,  $\delta_h = 4.48 (J/cm^3)^{1/2}$ , and for  $\delta_d = 16.7 (J/cm^3)^{1/2}$ .

The table below shows the results grouped in one overview.

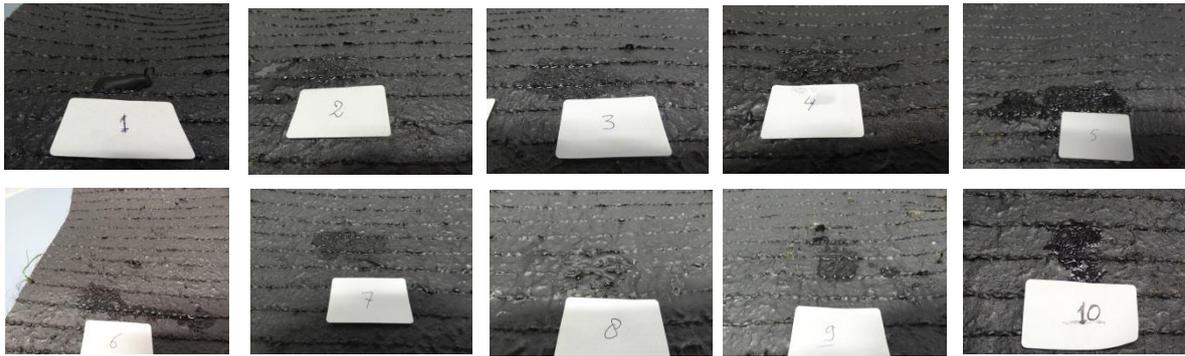
Table 4. Solubility parameters for styrene butadiene latex calculated by the three methods.

	Hoftzyer/van Krevelen	Hoy	Total average	Direct calculation via $E_{coh}$
$\delta_t$	17.22	19	18.1	18
$\delta_d$	17.20	16.7	16.9	
$\delta_p$	0.8	7.8	4.3	
$\delta_h$	0	4.48	2.24	

The Hoy method is more elaborate and puts more emphasis on potential polarity effects. There is good agreement between these data. The overall solubility parameter  $\delta_t$  of 18 is within accuracy boundaries about  $18 (J/cm^3)^{1/2}$ . It is also clear that the latex has very weak polarity and that hydrogen bonds are very weak indeed, as may be expected. Finding a good solvent for this latex means a solvent with a similar  $\delta_t$ , or more precise less than  $\pm 5 (J/cm^3)^{1/2}$  deviation from the value of 18.

To test this hypothesis a number of solvents were selected, listed in table 5. Water was taken as a reference. The solubility parameters ranged from 48 for water, 26.2 for Ethanol/stearic acid, 18.6 -18.2 for a range of organic solvents, 16.8 for cyclohexane, and 14.9 for n-hexane. Apart from water and ethanol, we aimed to include the effect of conjugated  $\pi$ -systems, thus solvent with C=C bonds present as opposed to solvents that only contain C-C bound in their structure.

The surface tension of the latex backing was found to be 25 – 29 mN/m. A quick reference test showed that indeed the organic solvents with surface tension in the range of 20 to 30 mN/m readily moistened the latex, whereas water did not show any tendency to spread. See Fig 1. pictures 1-10.

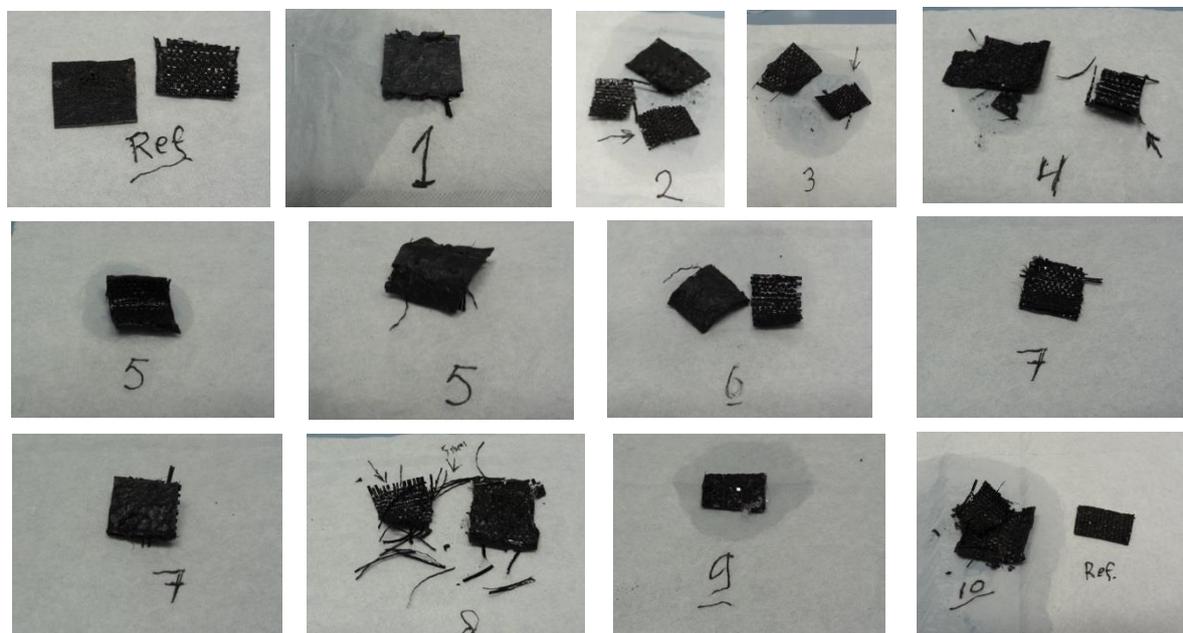


**Fig. 1. Quick test on wetting. 1=water, 2=ethylbenzene. 3=benzene, 4=carbontetrachloride, 5=cyclohexane, 6=ethylacetate, 7= n-hexane, 8=toluene, 9=stearic acid dispersed in EtOH, 10=tetrachloroethylene.**

The next set of experiments was conducted to test the hypothesis that solvents with a solubility parameter close the calculated one for latex (18H) would be able to dissolve the latex or at least should be able to disintegrate the consistency of the latex so that it can easily be removed from the tuft cloth.

Out of the sample material small samples of roughly 1x1 cm, weighing between 0.5 and 0.55 g were prepared. These were placed in Erlenmeyer flasks and 10 ml the solvents were added. The samples were left standing at ambient temperature of 20-22°C for 100h. This relatively long time span was chosen since that latex layer was very hard and had a closed/dense structure and time is needed for the solvent to be able to penetrate the material. After 100 h the samples were removed and dried. The integrity of the latex, bounding to the tuft cloth and swelling was assessed by visual observation and manual peeling off using tweezers and with minimal mechanical force.

The results are shown in Fig.2 pictures 1-10 and are summarized in table 5.



**Fig. 2. testing the impact of solvents on Latex backing. Ref= reference untreated, backside and cloth side, 1=water, 2=ethylbenzene. 3=benzene, 4=carbontetrachloride, 5=cyclohexane, 6=ethylacetate, 7= n-hexane, 8=toluene, 9=stearic acid dispersed in EtOH, 10= tetrachloroethylene. For 5 and 7 on the left: cloth side, on the right backing side.**

Table 5. Summary of solvability tests on latex backing

Solvent system	Surface tension $\gamma$ (mN/M) [14]	Solubility parameter, $\delta$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup> [12,13]	Effect on latex backing	Effect on the (doublelayer) Tuftcloth, Polypropylene
1. Water (demi)	72	48	Slightly discoloured	No effect
2. Ethyl benzene	29	18.6	Swollen, falls apart, loose from tuftcloth	No effect
3. Benzene	29	18.7	Swollen, falls apart, loose from tuftcloth	No effect
4. Carbon tetrachloride	27	18	Swollen, disintegrated, falls apart, loose from tuftcloth	No effect
5. Cyclohexane	25.5	16.8	Slightly swollen, loose from tuftcloth	No effect
6. Ethyl acetate	24	18.2	No or marginal effect on latex, but loose from tuftcloth	No effect
7. N-hexane	18.4	14.9	No or marginal effect, not loosened	No effect
8. Toluene	28	18.3	Swollen, disintegrated, falls apart, loose from tuftcloth	Tuftcloth falls apart
9. EtOH dispersion of stearic acid (1g/15ml)	23.6	26.2	Slightly discoloured, stearic acid crystals deposited	No effect
10. Tetrachloroethylene	31,7	18,9/20,1	Fully swollen and disintegrated, falls apart, loose from tuftcloth	No effect

We also performed a few tests on the effect of commercial detergents on latex. The idea behind this was that the surface tension of a standard detergent solution is in the range of 30 mN/m and the presence of surfactants might promote the breaking of binding between the latex and the tuft cloth.

#### Discussion and conclusions.

The results for the tested solvents and the results of the solubility tests are summarized as follows:

- Analysing the results is it clear that water ( $\delta_t = 48$ ) and ethanol/stearic acid dispersion ( $\delta_t = 26.2$ ) have no effect on the latex. This is in line with the high values for both the surface tension and the solubility parameter of these solvents.
- Furthermore our hypothesis that solvents containing double bounds have a profound effect on the latex was confirmed: complete disruption of the latex integrity was observed. Thus solvents of the type benzene ( $\delta_t = 18.7$ ), ethyl benzene ( $\delta_t = 18.6$ ), and toluene ( $\delta_t = 18.3$ ), are suitable solvents for the removal of latex form artificial turf.
- A special case is carbon tetrachloride ( $\delta_t = 18$ ). Due to the presence the four chloride atoms symmetrically positioned along the central carbon atom in the structure,  $\text{CCl}_4$  is a suitable solvent for many organic substances, and as shown here also for latex.

- A second special case was ethyl acetate ( $\delta_t = 18.2$ ). It did not really disintegrate the latex, but removed the bounding between latex and the polypropylene tuft cloth. Its lower surface tension (24 mN/m) probably promotes creeping between the latex and the polypropylene cloth thereby disrupting the bounding between latex and the tuft cloth.
- Solvents with no double bonds clearly did not perform. So cyclohexane ( $\delta_t = 16.8$ ) and n-hexane ( $\delta_t = 14.9$ ) are not suitable for latex removal.
- Tetrachloroethylene ( $\delta_t = 19.5$ ) proved to be very efficient for latex removal. The combination of the double bond and the 4 chloride atoms at the carbon atoms creates an efficient molecular structure for the dissolution of latex and removal from the polypropylene ( $\delta_t = 17$ ) tuft cloth.

However, most solvents used in these tests are unfavourable or even forbidden because of environmental- or human toxicity. But in the market closed loop systems are available used for chemical (dry-) cleaning that use tetrachloroethylene and that could be suitable for our purpose [18]. These systems utilize high performance filtration units and avoid leakage of the liquid or vapour into the environment and their functioning is subjected to strict rule and regulations [19]. Further research should be directed to development of this potential large scale process for the removal of latex from artificial turf.

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**Key Words:** Latex, removal, solvents, solubilityparameter, artificialturf

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**Biography Ir. Ger Brinks**

Ger Brinks studied textile engineering at the Saxion University of Applied Sciences, the Maere, and chemical engineering, with a major in biomedical materials science at the University of Twente. He held several prominent positions in the field of research and development. Ger Brinks was inter alia Group and Section Leader at Organon pharmaceutical research, R & D manager at Otares, Development Executive at Lever Industrial, Head of Research Division detergents at Unilever Research and R&D Director at Stork Prints. Brinks was global R&D director at Bonar. He is founder and director of BMA Techne, specializing in technology assessments and roadmapping. Brinks was associate at Boer & Croon and is currently program manager at MODINT. Since 2007 he is part-time Professor Smart Functional Materials at Saxion University of Applied Sciences, Research Centre Design and Technology. Responsive smart materials, biomaterials, digital processes and sustainability/recycling are key research areas.