

PROPERTIES OF POLYURETHANE & BRUSH POLYMER RELEASE AGENTS

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There are two types of generic compounds that are used as release agents for pressure sensitive adhesive tapes: Brush polymers, Figure 1a, and silicone-modified polyurethanes, Fig. 1b.

Brush Polymers

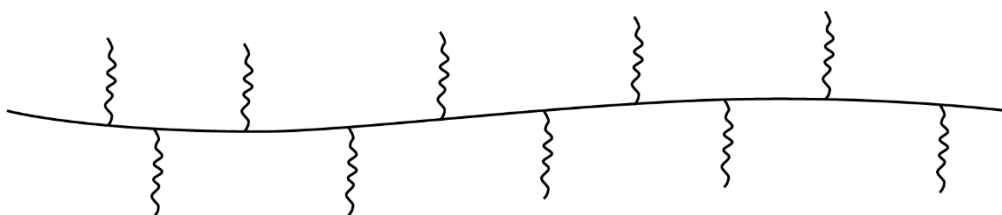


Figure 1a

PUR-Si

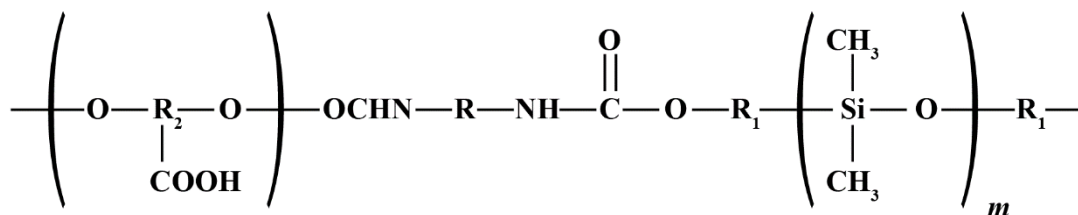


Figure 1b

A powdery brush polymer soluble in toluene, a recoverable solvent, and usable as a release agent was first developed in the early 1950's by Dahlquist in 3M Company's laboratory. Water base silicone-modified polyurethane release agents were developed by one of the authors (Shores) and became commercially available in 1994. Its toluene solution equivalent was made commercially available in 2011.

Brush Polymers

Figure 2 depicts a representation of brush polymer release agents. The polymers' common denominator is that they all contain a main chain characterized by strong polar groups and strait C₁₈-long hydrocarbon side chains R.

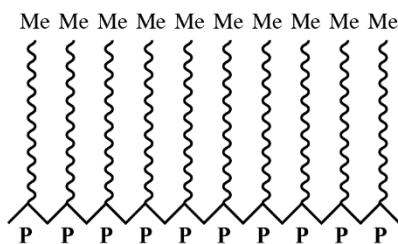


Figure 2

It has long been suspected that surface tension had a primary role in the effectiveness of brush polymer release agents. We chose brush polymers with various chemical compositions to measure their surface tension by a contact angle technique.

Surface Tension of C₁₈ Brush Polymers

We have determined the surface tension, as described by Schwarcz and Farinato^{1,2}, by measuring the contact angle of several liquids having various surface tensions on these polymers. By applying the Owens and Wendt³ equation we calculated their total surface tension γ_s which are the sum of their dispersion γ_s^d and polar contributions γ_s^p . The calculated total surface tension of these polymers is summarized in Fig. 3. They were between about 20 and 29 dyne/cm. Most of the surface tensions are attributed to their dispersion forces components and only about 0.2-5% for their polar components.

The #3 polymer in Fig. 3 is one of the few commercial brush polymer release agents. It is polyvinyl octadecyl carbamate, PVODC, synthesized by Dahlquist from polyvinyl alcohol and octadecyl isocyanate.

Surface Energies of Polymers with Long Unbranched Side Chains R

No.	R	γ_s	γ_s^p	γ_s^d
1.	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{OCO} \\ \\ \text{R} \end{array}$	20.4	0.5	19.9
2.	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{O} \\ \\ \text{R} \end{array}$	21.1	0.2	20.9
3.	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{OCONH} \\ \\ \text{R} \end{array}$	21.3	0.4	20.9
4.	$\begin{array}{c} \text{---CH}_2\text{---CH}_2\text{---CH---CH---} \\ \quad \\ \text{CO} \quad \text{CO} \\ \diagdown \quad / \\ \text{N} \\ \\ \text{R} \end{array}$	22.7	0.6	22.1

5.	$\begin{array}{cccc} \text{---CH}_2\text{---} & \text{CH---} & \text{CH---} & \text{CH---} \\ & & & \\ & \text{O} & \text{CO} & \text{CO} \\ & & \diagdown & / \\ & \text{R} & \text{N} & \end{array}$	23.5	0.7	22.8
6.	$\begin{array}{cccc} \text{---CH}_2\text{---} & \text{CH}_2\text{---} & \text{CH---} & \text{CH---} \\ & & & \\ & & \text{CO} & \text{COO} \\ & & & \\ & & \text{OH} & \text{R} \end{array}$	24.3	1.4	22.9
7.	$\begin{array}{cccc} \text{---CH}_2\text{---} & \text{CH---} & \text{CH---} & \text{CH---} \\ & & & \\ & \text{R} & \text{CO} & \text{CO} \\ & & \diagdown & / \\ & & \text{O} & \end{array}$	26.9	0.3	26.6
8.	$\begin{array}{cccc} \text{---CH---} & \text{CH}_2\text{---} & \text{CH---} & \text{CH---} \\ & & & \\ \text{C}_6\text{H}_5 & & \text{CO} & \text{COO} \\ & & & \\ & & \text{OH} & \text{R} \end{array}$	28.5	1.0	27.5

Figure 3

Hydrocarbon Chain Length

We measured the effect of the hydrocarbon length on the surface tension of EM-A, a polymer derived from the reaction product of poly(ethylene-maleic anhydride), EM, and amine A of various chain length R-A. A slow and gradual increase in the surface tension resulted from chain length C₁₈ to C₁₂ amines. At C₁₂ and less the surface tension increases rapidly by an amount attributed to increases in the polar forces, see Fig. 4.

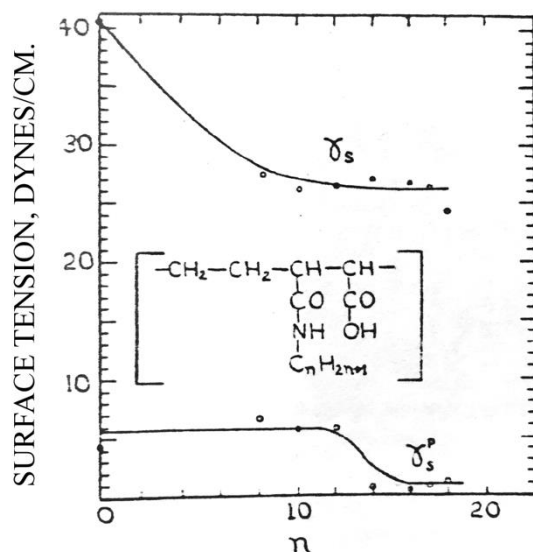


Figure 4. Surface tension γ_s and its polar component γ_s^p of styrene-N-alkylmaleamic acid copolymers as a function of the number n of carbon atoms in the alkyl group.

Side Chain Spacing

The effect of side chain spacing on surface tension was determined by gradually decreasing the

stoichiometric proportion of the C₁₈ amine from 100% to 0% in the R-A reaction with EM. The result plotted in Fig. 5, upper curve, shows a relatively sharp decrease in surface tension with initial increases of amine mole per cent, which is inversely proportional to side chain spacing, up to about 50% amine. Further increases have slower decreasing effect on the surface tension.

Polymer Mixtures

The lower curve in Fig. 5 represents the surface tension of the polymer mixtures of EM/EM-A as a function of EM-A mole%. There is a precipitous decrease of surface tension with as little as 0.8-1.6 mole per cent EM-A, about 1.5-3.0 weight per cent. Beyond this range of concentration the surface tension stays the same low level.

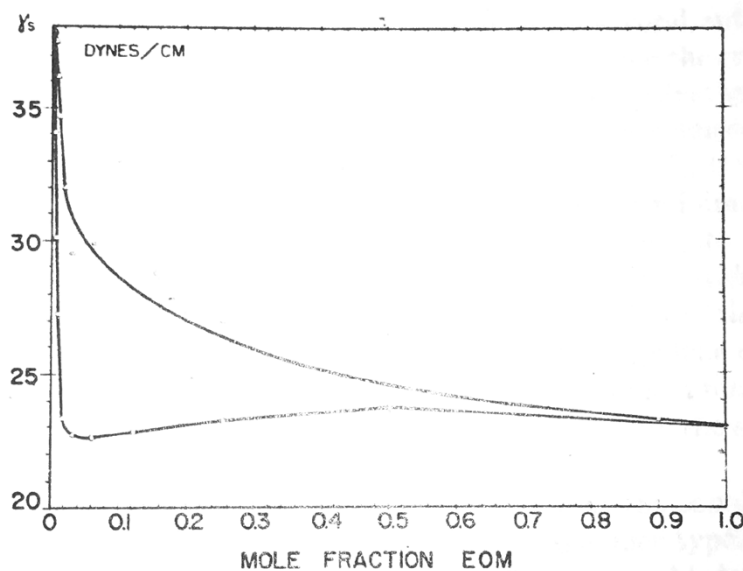


Figure 5. Surface tension γ_s as a function of EOM concentration: (O) mixtures EOM + EMA; (Δ) Copolymers EOM- EMA.

Molecular Weight

In another study the molecular weight of the brush polymer EM-A was varied Table 1. There was no change in surface tension between 20,000 and 80,000 molecular weight but a significant increase at 2,000.

TABLE 1
Surface Tension EOM with Various MW

EOM-EMA Copolymers	Average
100% EOM-0% EMA 2,000	24.3
100% EOM-0% EMA 20,000	21.4
100% EOM-0% EMA 80,000	20.9

Release Agent Properties

Contact angle measurements showed that brush polymers of various chemical compositions with C₁₈

side chains have low surface tension, the best ones are 20-21 dyne/cm, such as PVODC. Maximum side chain concentrations and molecular weights 20,000 and more yield the lowest surface tension possible with brush polymers, 20-21 dyne/cm.

It has been reported³ that maximum side chain concentrations yield to their dense packing and crystallization. This is the case with PVODC. It dissolves in toluene at elevated temperatures but precipitates from the solution at temperatures below at around 75°F or less. That makes the dissolved release agent feasible to ship, store and coat only with external heating and its blending with a lower alcohol. Dissolving the polymer and heating requires input of energy, takes up plant space and makes the release coating quality less reliable. Part of the alcohol in the solution does not get recovered and ends up in water that is difficult to dispose of. Furthermore, brush polymers are insoluble in water and their dispersion in water requires the use of a surfactant risking detackifying the adhesive.

Polyurethane Release Agents

Polyurethane release agents first became commercially available in water solution in the early 1990's and their equivalent toluene solutions in the early 2010's. They are synthesized by the reaction of a diisocyanate with an isocyanate-reactive silicone and optionally a diol containing carboxyl groups to provide water solubility, as in Fig. 1b. They contain in their repeating units carbamate, e.g. urethane, bonds and polydimethylsiloxane segments. They contain no free silicones.

Their surface tension due to their dimethylsiloxane group is about 20 dyne/cm, comparable to the best brush polymers, and necessary for providing effective release from pressure sensitive adhesives. Their degree of release can be engineered by varying the polysiloxane content.

Due to the carbamate and other polar groups they adhere to most films, paper and aluminum. Their high molecular weight and high softening temperature, ~90°C, allows their processing and use without crosslinking. Release properties immediately develop by flashing off the diluent water or solvent.

Since the polymers are amorphous they stay in solution in either water or toluene, they do not precipitate, at any concentration and any temperature, even under freezing conditions. Consequently, they may be shipped in solution without heating, which eliminates the dissolving process at the tape plant, and allows storing and coating without heating. That results, as compared to brush polymers, in reduced production time, labor, heat, mechanical energy, dusting, VOC emission, workers exposure to toluene and fire hazard. It circumvents waste due to potential precipitation of release agent on coating that may cause clogging of rotogravure roll and Mayer rod

Their amorphous nature also allows their application at high total solids, which in turn makes them suitable coating on rough and porous substrates.

Their water base variety completely circumvents problems and costs associated with the use of toluene, such as fire hazard, workers exposure, recovering cost and toluene loss.

They may also be coated from VOC-free solvents where the use of toluene is not desirable.

RELEASE PROPERTIES OF A BRUSH POLYMER AND SILICONE-MODIFIED POLYURETHANES

The following Table summarizes the release properties of PVODC and silicone–modified polyurethanes. Test specimen were prepared by depositing 2% total solids solutions of release agents on a 1.2 mil t-OPP, dried and laminated to 2.5” wide OPP standard and premium quality packaging tapes with adhesion to steel typically 55 and 85 ounce/2inch. Some of the laminates were aged in an oven at 150°F for 18 hours and both the aged and green samples were tested in T-peel mode at a separation speed of 2”/min (Low Speed) and at 180° angle at 300’/min (High Speed). Subsequent measurements indicated no significant loss of adhesion (ASS) due to the release agents. The separation force was reported in ounce/2inch.

Table 2 below shows release properties depending on the adhesive, aging and separation speed. The polyurethane release agents yielded better release values after heat aging.

TABLE 2
Release Properties, oz/2in

	<u>STANDARD TAPE</u>				<u>PREMIUM TAPE</u>			
	<u>Low Speed</u>		<u>High Speed</u>		<u>Low Speed</u>		<u>High Speed</u>	
	<u>Green</u>	<u>Aged</u>	<u>Green</u>	<u>Aged</u>	<u>Green</u>	<u>Aged</u>	<u>Green</u>	<u>Aged</u>
<i>Brush Polymer-Toluene</i>	12	15	2	9	11	15	3	35
<i>Polyurethane-Toluene</i>	6	15	1	4	13	21	2	4
<i>Polyur. 1st Gen-Water</i>	6	15	2	6	8	23	3	12
<i>Polyur. 3rd Gen-Water</i>	7	10	2	3	9	10	2	3

Conclusion

Brush polymers with main chains having highly polar groups and strait hydrocarbon side chains with at least 18 carbon atoms have low surface tension ranging 20-30dyne/cm. The lowest surface tension ones among them and the one with the best release properties was developed by minimizing side chain spacing and maximizing molecular weight over 20,000 Daltons, such as in PVODC, which can be dissolved at higher than ambient temperature in toluene in the tape plant. Due to side chain crystallization, their coating solutions require heating on storage and coating, which increases the possibility of metering roll clogging, uneven coating, energy dispensing and fire hazard.

Silicone-modified polyurethanes overcome all these problems. They predissolved by the supplier and shipped either in toluene, water or VOC-free solvents. They never precipitate from coating solutions at any temperature and any concentration. Their composition may be tailored to different adhesives. Unlike brush polymers, which have reached their structural limitations for further improvement, the versatility of polyurethane chemistry overcame their processing problems and optimized their release properties.

References

1. Andor Schwarcz and R.S. Farinato: *J. Polym. Sci., Polymer Phys. Ed.*, 10 (10), 2025 (1972), Surface tension of polymers with long unbranched side chains
2. A. Schwarcz, *J. Polymer Sci., Polymer Phys. Ed.*, 12, 1195 (1974), Surface Tension of Polymer Mixtures and Copolymers
3. D.K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 13, 1741 (1969)
4. Shireesh Pankaja and Mario Beiner: *Soft Matter*, 2010, 6, 3506-3516, Long-term behavior and side chain crystallization of poly(3-alkyl thiophenes)