

15. Silicones in the Plastics Industry

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Silicones are used in the plastics industry as additives for improving the processing and surface properties of plastics, as well as the rubber phase in a novel family of thermoplastic vulcanizate (TPV) materials. As additives, silicones, and in particular polydimethylsiloxane (PDMS), are used to improve mold filling, surface appearance, mold release, surface lubricity and wear resistance. As the rubber portion of a TPV, the cross-linked silicone rubber imparts novel properties, such as lower hardness, reduced coefficient of friction and improved low and high temperature properties.

Low molecular weight PDMS polymers, with viscosities less than 1000 cSt, are used extensively by the plastics industry as external release agents applied on the mold surface prior to injection molding. To eliminate an external application during processing, higher molecular weight PDMS materials, with viscosities ranging from 10,000 cSt to 60,000 cSt, have been used as internal additives in thermoplastic polymers to give processing advantages and surface property improvements [1-2]. Due to the incompatibility between dimethyl siloxanes and most thermoplastics, the PDMS is driven to the surface. For example, the solubility parameter for dimethyl siloxane is $14.9 \text{ MPa}^{1/2}$ and the solubility parameter for nylon 6 is $27.8 \text{ MPa}^{1/2}$ [3]. A concentration of the PDMS at the surface results in the observed processing and surface property benefits.

A more recent advancement in the field of PDMS additives is the use of ultra high molecular weight (UHMW) PDMS, with viscosities ranging from 10 to 50×10^6 cSt [4]. Additives are now available with 50 weight percent UHMW PDMS in various thermoplastic carriers and as pellets so as to allow easy addition of the additive directly to the thermoplastic during processing. An important improvement obtained using UHMW PDMS is that the loading of PDMS in the concentrated additive is increased from approximately 20 to 50 weight percent. As seen in Figure 1, the UHMW PDMS forms stable droplet domains in the thermoplastic carrier, with an average particle size of 2 microns.

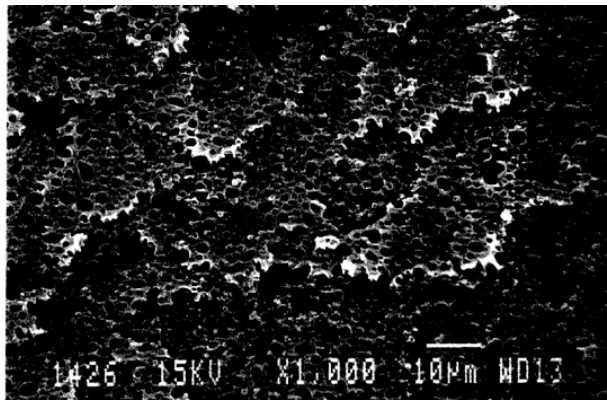


Figure 1. Photomicrograph of a 50% UHMW PDMS dispersed in polypropylene and showing the fine dispersion of the silicone into the organic phase.

UHMW PDMS results in the same processing benefits such as improved mold release, easier

mold filling, and lower extruder torque as compared to lower molecular weight PDMS, but it eliminates the “bleed-out” that can occur after processing. This benefit is clearly seen when comparing the print adhesion to polypropylene films containing various additives (see Figure 2). Low molecular weight PDMS (30,000 cSt) and common organic mold release additives significantly reduce the print adhesion due to their migration to the surface and eventual blooming or bleed-out from the plastic part. Conversely, the UHMW PDMS does not reduce the print adhesion because its high molecular weight reduces its mobility and effectively anchors the additive into the plastic.

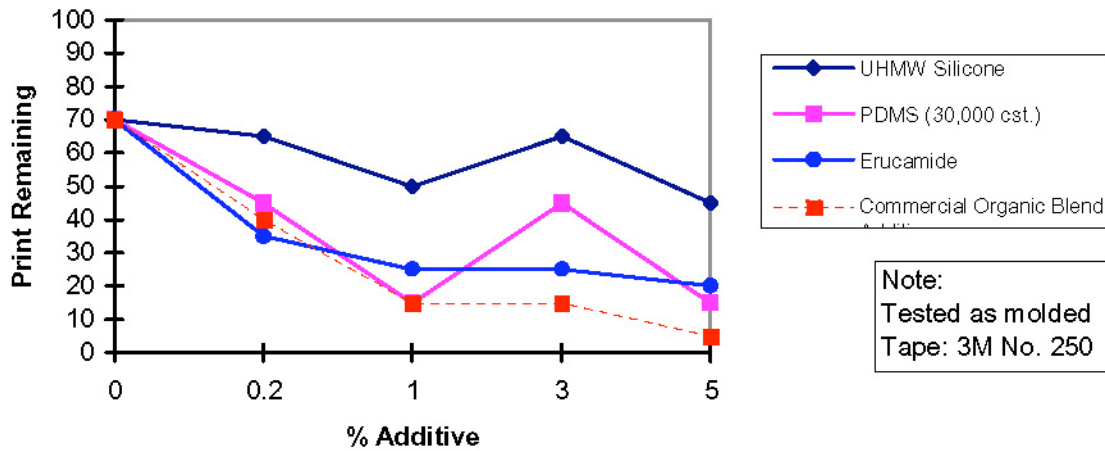


Figure 2. *Print adhesion to polypropylene films containing various additives and tested with 3M tape no. 250 per ASTM D3359.*

UHMW PDMS additives are often used to improve the wear or abrasion resistance or to reduce noises generated by the motion of plastic parts. These benefits are reflected by the decrease in the coefficient of friction (see Figure 3). A rotating cylinder method was used to generate the coefficient of friction results, with a constant force of 2 kg and a varying velocity until sufficient heat generation occurred and the cylinder and barrel fused. The addition of 3 weight percent UHMW PDMS significantly reduced the coefficient of friction as well as delayed the fusing until much a higher velocity.

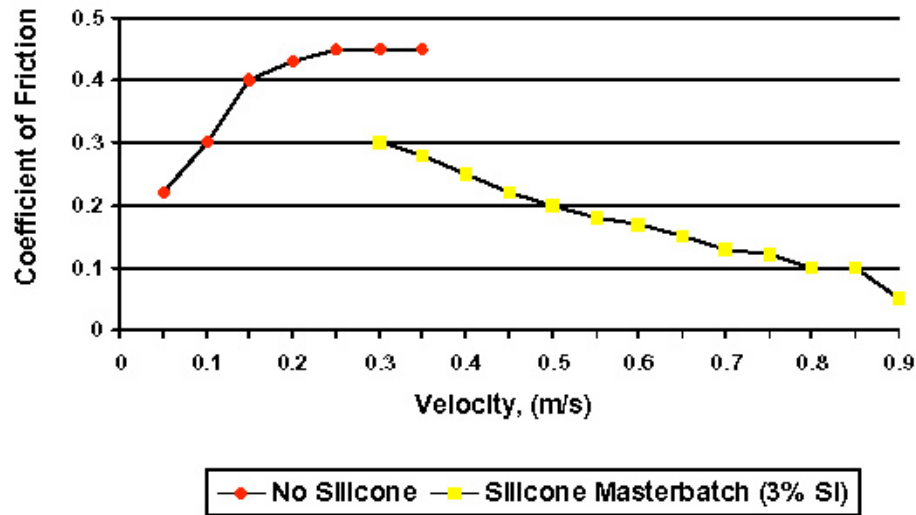


Figure 3. Coefficient of friction measurements from pressure-velocity plots for polypropylene without or with UHMW PDMS additive.

Recently, a novel family of TPV products has been introduced and is based on crosslinked silicone rubber dispersed into various engineering thermoplastics [5]. The dispersion of the silicone internal phase is produced by dynamic “vulcanisation” or cross-linking of silicone polymers within the thermoplastic organic phase and results in a stable droplet type morphology (see Figure 4).

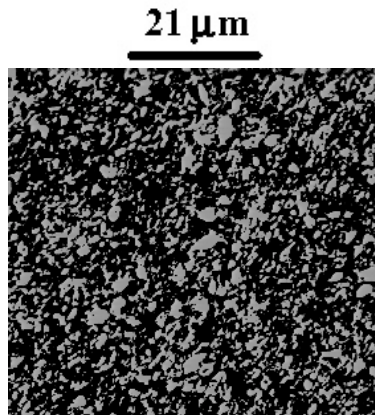


Figure 4. Transmission electron micrograph depicting the morphology of a silicone-based TPV (light gray areas are silicone rubber particles dispersed within the organic continuous phase).

Such a stable morphology is achieved only by using appropriate compatibilizers to ensure compatibility between the silicone and organic thermoplastic phases, which have very dissimilar solubility parameters. As for other TPVs, such thermoplastic compounds are melt processable and fully recyclable.

Silicone TPVs have been commercialized using various engineering thermoplastics, but of greatest interest are polyamide and polyurethanes thermoplastics. Silicone polyamide TPV

has found use as the jacketing material in automotive brake cables due to its excellent temperature and chemical resistance [5]. Silicone polyurethane TPV combines the benefits of excellent abrasion resistance from the polyurethanes as well as the lower coefficient of friction and improved temperature properties from the silicone rubber. The properties of silicone polyurethane TPV vs. a well known EPDM-PP TPV are compared in Table 1. In particular, the silicone polyurethane TPV outperforms the EPDM-PP TPV in oil resistance due to the miscibility of oils in polypropylene.

Table 1. Comparison Between a Silicone Polyurethane TPV vs. a EPDM-PP TPV: Initial Properties and After Aging in Air or Oil at Elevated Temperatures

<i>Property</i>	<i>Testing Method</i>	<i>Silicone polyurethane TPV</i>	<i>EPDM-PP TPV</i>
Initial: Hardness, <i>Shore A</i> Tensile strength, <i>MPa</i> Elongation at Break, %	ASTM D2240 ASTM D412, Die D ASTM D412, Die D	71 16 600	66 6.5 457
70 hours in air at 175°C: Change in hardness, <i>Shore A</i> Change in tensile strength, % (*) Change in elongation at break, % (*)	ASTM D573-99 for heat aging. Same methods as above for testing	+7 +6.3 +12	-5 -32 -20
70 hours in IRM 903 oil at 100°C: Change in hardness, <i>Shore A</i> Change in tensile strength, % (*) Change in elongation at break, % (*) Volume swell, %	ASTM D471-98 for fluid immersion. Same methods as above for testing	-9 -23 -2.5 +23	-19 -29 -40 +80

(*) change expressed as percentage of initial value.

Compared to thermoset silicone rubber, a silicone TPV offers the added benefit of bondability to various thermoplastics without the use of primers or adhesives via coextrusion and comolding/overmolding. Silicone polyurethane TPV was overmolded onto “cold” (i.e., room temperature) inserts of various thermoplastics and the bond strength was testing according to ASTM D1876. An example of the peel force is shown in Figure 5.

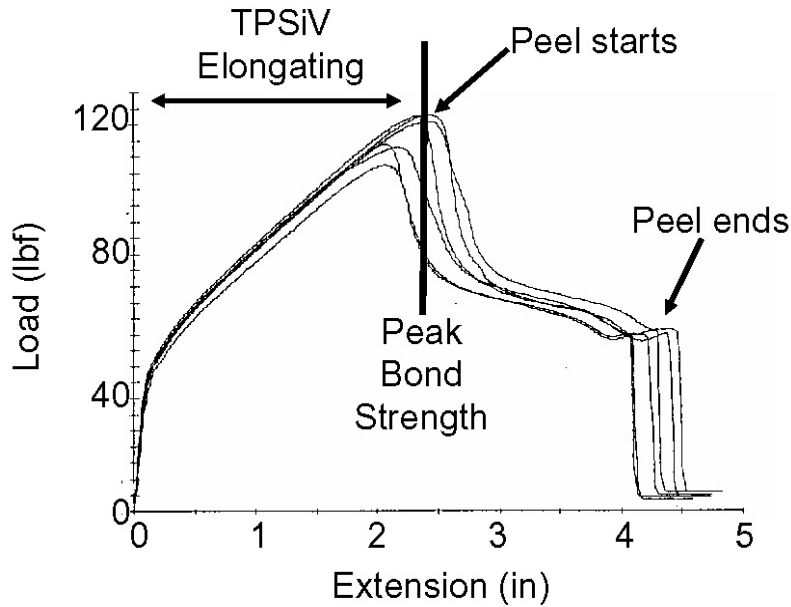


Figure 5. *Peel force of a silicone polyurethane TPV molded on polycarbonate substrate (multiple curves representing 6 repeats).*

The soft TPV first elongates until the bond begins to peel at the peak force. A bond strength of approximately 20 N/mm was observed on PC and ABS, while a bond strength of approximately 8 N/mm was observed on nylon. The bonding failure on PC/ABS is cohesive, while the bond failure on nylon is adhesive. This excellent bond strength has resulted in silicone TPV being an ideal material for applications that require the combination of soft and rigid plastics, such as overmolded electronic equipment (soft-touch grips and buttons) and overmolded seals.

The applications of silicones in the plastics industry continue to grow as more benefits are identified by combining the unique properties of thermoplastics and silicone.

References

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