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Effects of tempering on adhesion of liquid silicone rubber to thermoplastics

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Tempering improves the mechanical properties of liquid silicone rubber, but also decreases its ability to adhere to engineering thermoplastics.

Liquid silicone rubber (LSR) is a high-performance elastomer that has enjoyed high demand in recent years because of its outstanding characteristics (e.g., fast curability, excellent temperature stability, and physiological harmlessness). Consequently, LSR has found use in a range of products and parts, from medical tubes to automative applications. LSR consists of two components, A and B, whose main ingredients are vinyl-terminated polysiloxanes. Normally, component A contains a platinum catalyst, and component B includes a cross-linking agent (a silicon-hydrogen-functionalized polysiloxane) and an inhibitor (e.g., alkanol). Both components are combined in a 1:1 ratio and vulcanized at temperatures above 120°C. The combination of LSR with a rigid carrier material (thermoplastic) is increasingly important in industry. Therefore, the hard and soft parts are joined using two-component injection molding. The carrier material is typically an engineering thermoplastic resin such as polyamide (PA) or poly(butylene terephthalate) (PBT).

The adhesion of LSR to a thermoplastic is influenced by the injection-molding parameters and choice of neat polymer, and significantly by post-treatment steps such as tempering.[1,2] Indeed, post-treatment by tempering has the potential to further improve the mechanical properties of LSR, because it leads to post-cross-linking and removes volatile components such as siloxanes. Tempering of LSR products is normally carried out at 200°C for four hours.[3] In thermoplastic/LSR combinations, however, temperatures in this range would soften standard thermoplastics (i.e., PA). Consequently, if the glass transition temperature of the PA is about 155°C, the tempering temperature must be reduced to less than 150°C. So far, however, the effect of tempering at temperatures below 150°C has been studied only for semicrystalline PAs at a tempering temperature of 140°C for four hours.[1,2]

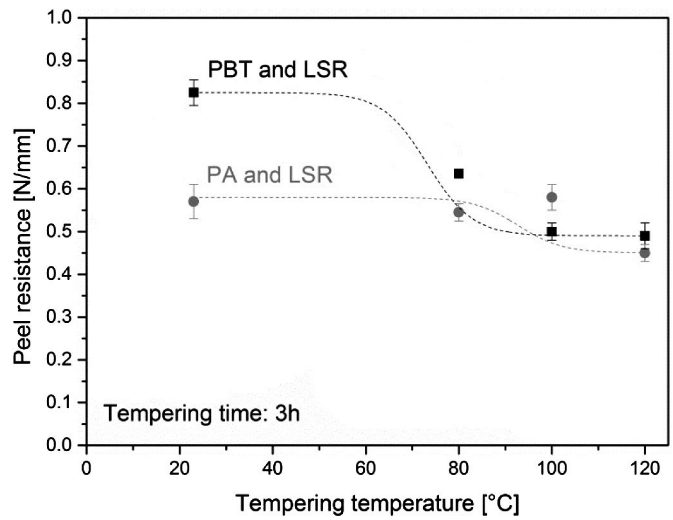

Figure 1. *Influence of tempering at a range of temperatures (80, 100, and 120°C) on the peel resistance of liquid silicone rubber (LSR) from poly(butylene terephthalate)—PBT—and polyamide (PA). The tempering time was three hours (3h). Reference combinations of PA/LSR and PBT/LSR (the first two points in the graph) were not tempered and were stored at room temperature.*

We wished to study different thermoplastics with alternative tempering conditions.[4] In our study we therefore started by using a batch mixer to mix the two LSR components (A and B) from a commercial grade system, in a 1:1 ratio, and we cross-linked them at a temperature of 150°C. We selected a semicrystalline PBT and an amorphous PA (PA 12) as the thermoplastic carrier materials. We produced test specimens—with dimensions according to the Association of German Engineers (VDI) directive 2019—via two-component injection molding. We then tempered both the single components (LSR and thermoplastic), as well the thermoplastic/LSR combinations, in a convection oven at three different temperatures (80, 100, and 120°C) for three

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Table 1. *Influence of the tempering process on the storage modulus (E′) of the LSR.*

	Tempering process			
	Without	80°C for 3h	100°C for 3h	120°C for 3h
E′ (Pa)	$5.9{\cdot}10^6$	$6.7{\cdot}10^6$	$7.4{\cdot}10^6$	$7.9{\cdot}10^6$

hours. We also subjected the test specimens to tensile tests, dynamic mechanical analysis, differential scanning calorimetry, and thermogravimetric analysis. To determine differences in the peel resistance, adhesion quality, and fracture pattern between the thermoplastic and LSR, we used a universal testing machine (Zwick Z2.5) to perform a peel test. During this test, the specimen was clamped in a test slide that was fixed via a tension rod, and the soft component (LSR) was pulled off at a 90° angle. We examined five samples for every peel-test series.

The effect of tempering on the adhesion of LSR to PBT and to PA is shown in Figure 1. The results indicate clearly that the peel resistance of the PBT/LSR combination decreases by about 30% when the tempering temperature exceeds 60°C. In contrast, for the PA/LSR combination, the peel resistance remains constant with tempering at temperatures below 100°C and decreases by about 22% with tempering above 120°C.

We attribute the deterioration of the adhesion between the PBT and the LSR to post-crystallization of the semicrystalline PBT. The post-crystallization is accompanied by an increase in crystallinity of 7% (from 25 to 32%) after three hours at 120°C (not shown). Post-crystallization makes fewer macromolecules available for entangling in the interphase between the two components. This is illustrated by the adhesion loss for the PBT/LSR combination at all tempering temperatures, whereas the peel resistance remains constant for the PA/LSR combination at temperatures up to 100°C. Tempering affects adhesion deterioration only at temperatures higher than 100°C because of post-cross-linking of the LSR. This is evidenced by decreased adhesion at 120°C for both combinations. The amorphous PA 12 material is only slightly affected by the tempering procedure.

We also find that tempering influences the storage modulus of LSR. As shown in Table 1, post-cross-linking in LSR is apparent from the 26% increase in the storage modulus, i.e., from 5.9MPa (without tempering) to 7.9MPa (tempering at 120°C for three hours). In addition, because the tempering process is used to release volatile components, we also investigated the composition of the liberated components using gas chromatography coupled with mass spectrometry. We identified the important volatile components as silanols, siloxanes, and silanes.

In summary, the mechanical and thermal properties of single thermoplastic and LSR components are improved by tempering. However, tempering negatively affects a semicrystalline thermoplastic-LSR combination. The roughly 30% decrease in adhesion, therefore, suggests that post-production tempering is ineffective. Our next step will be to examine the long-term behavior of thermoplastic/LSR combinations—as well as the single materials—at room temperature or higher (e.g., at 60°C).

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References

1. K. Pohmer, *Self-adhesive liquid silicones for inexpensive rigid/flexible composites: silicone composites*, **Kunststoffe 90**, pp. 32–33, 2000.
2. C. Ronnewinkel, **Multi-Component Injection Moulding of Liquid Silicone Rubber/Thermoplastic Combinations**, dissertation, RWTH Aachen University, 2001.
3. **Fest- und Flüssigsiliconkautschuk—Der Leitfaden für die Praxis**, Wacker Chemie, Munich, 2015.
4. C. Baumgart, D. Weiß, and V. Altstädt, *Influence of different tempering conditions on the adhesion properties of thermoplastic/liquid silicone rubber combinations*, **Polym. Eng. Sci. 56**, pp. 849–855, 2016. doi:10.1002/pen.24313