Peroxide cure

Facts on file

Most silicone PSAs will exhibit pressure sensitive behavior immediately after solvent removal. However, further crosslinking may be done to reinforce the adhesive network and improve performance properties.

To achieve additional crosslink density, the majority of silicone PSAs use a peroxide catalyzed (benzoyl peroxide or 2,4-dichlorobenzoyl peroxide) free-radical reaction. Cure takes place in a multi-zone oven. First, lower temperatures (60-90°C) are used to remove the solvent. Then, at elevated temperatures (130-200°C), the peroxide catalyst decomposes, forming free radicals, which primarily attack the organic substituents along the polymer chains, extracting protons and generating more free radicals. The free radicals then combine to form crosslinks.

The main benefit of the peroxide catalyzed system is the ability to control properties by varying the peroxide addition level from 0-4%.

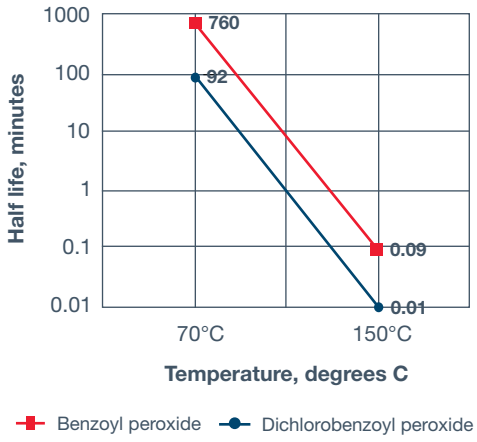
Factors affecting cure

Catalyst poisoning – To develop significant cohesive strength of the cured silicone PSA, it is necessary to catalyze the cure. Cure of an adhesive initiated by peroxides can be impaired by radical scavengers such as activated carbon or other materials that contain substantial amounts of compounds that can impair the formation and propagation of radical species for the crosslinking reaction.

Catalyst reactivity – Although other peroxides are appropriate, the catalyst most often used tocure silicone PSAs is benzoyl peroxide (BPO). BPO is typically purchased as a powder and dispersed to make a 10% solution in toluene or xylene. The catalyst solution is then added to the silicone PSA in the range of 1-3% BPO (on a solids basis). The solution will lose activity fairly rapidly and reactivity will diminish substantially in a few days if the solution is not refrigerated.

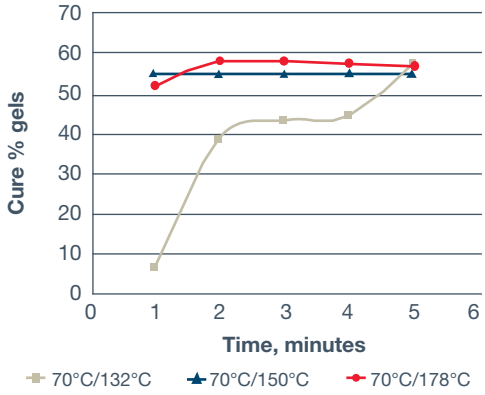
The half life of the peroxide – Figure 1 shows the relative half lives of the two peroxides typically used to cure silicone adhesives. Half life is defined as the amount of time it takes for half of the radicals contained in the peroxide to be released at any given temperature. If lower-temperature cure is required, 2,4 dichlorobenzoyl peroxide can be used. It is also possible to achieve lower temperature cure with benzoyl peroxide; however the adhesive must cure for a longer time.

Figure 1. Half lives of peroxides used to cure silicone PSAs



Time and temperature – Cure is measured by the extractable silicone portion of the adhesive, which levels off (indicating complete cure) at about 50%. Cure may be achieved at lower temperatures – an advantage when using temperature-sensitive substrates. However, optimum cure is achieved much more quickly at higher temperatures. (See Figure 2.)

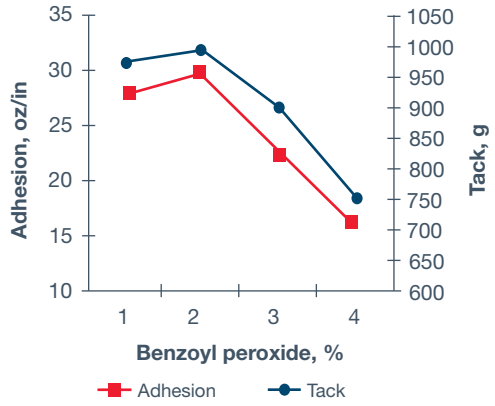
Figure 2. Effect of time and temperature on cure of a peroxide-cured silicone psa



Factors affecting adhesion to the substrate

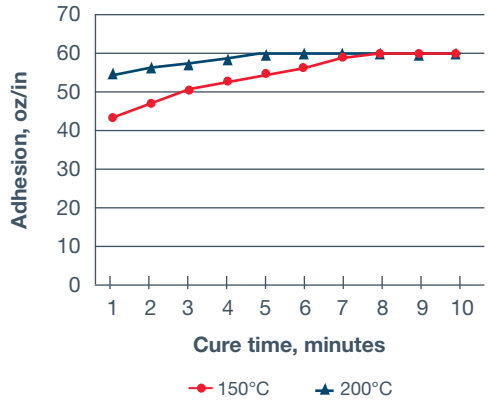
Peroxide level – Initially, increasing the peroxide level will increase adhesion due to greater crosslinking of the adhesive. However, further increases in peroxide level will decrease adhesion. Tack also decreases as the peroxide level is increased and the adhesive becomes harder. (See Figure 3.)

Figure 3. Effect of peroxide level on adhesive properties



Cure time and temperature – The higher the temperature, the more quickly optimum adhesion is achieved. (See Figure 4.)

Figure 4. Effect of time and temperature on adhesion of a peroxide-cured silicone PSA.



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