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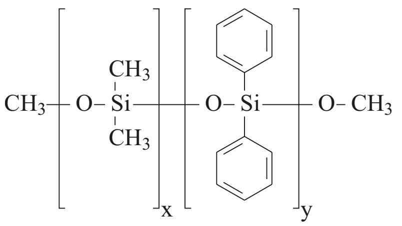
Characterization of the crosslinking process of silicone pressure-sensitive adhesives

RAPID COMMUNICATION

Summary — The process of thermal crosslinking of silicone pressure-sensitive adhesives, catalyzed with dichlorobenzoyl peroxide, was investigated using DSC method. Crosslinking temperature as well as energy evolved during crosslinking process were measured. Peel adhesion and shear strength of thermally crosslinked silicone pressure-sensitive adhesives dependently on crosslinking agent concentration were determined. IR investigations confirmed the course of crosslinking reaction *via* formation of chemical bonds between methyl groups of silicone pressure-sensitive adhesive.
Key words: silicone pressure-sensitive adhesive, thermal crosslinking, DSC, peel adhesion, shear strength, heat of crosslinking.

Silicone pressure-sensitive adhesive (PSA) formulations have been developed to perform well in their lots of application. The silicone PSA are normally prepared by the controlled condensation and capping of silicate hydrosols. Silicone and hydroxyl functionality is determined by reaction conditions including pH, temperature, silica concentration and capping conditions [1].

Silicone monomers are polymerized to yield silicone polymers that show adhesive and cohesive properties. Since silicones are expensive, their market use is normally limited to special fields of extremely high temperature resistance. Silicone PSA are high performance adhesives that can be used in a wide range of temperature, from -40 to 300 °C. They bond to both low energy and high energy surfaces. They can be used for producing masking tapes for printed circuit board plating as well as in electrical insulation tapes made of etched teflon-coated fabrics, extruded teflon, polyester and glass fabrics. Solvent-borne silicone polymers contain dimethylsiloxy and diphenylsiloxy groups [see Formula (I)] [2]:



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The molecular weights of such polymers are preferably in the range 500 000 to 1 500 000 Da [3].

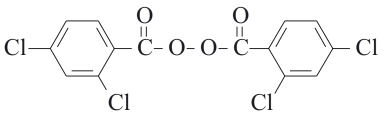
Silicone PSA were initially developed as solvent based materials. The adhesives patented by Dexter [4], in 1956, were described as silicone resin and polymer mixtures cured by the removal of the solvent carrier and the use of metal oxide or titanate catalysts. These products were initially introduced for high temperature environment adhesive tapes used for electrical insulation. The development of these adhesives directly followed the development of a commercial silicone resin process. The resin is important for the modification of polydimethyl silicone materials and created the basis for many types of pressure-sensitive adhesives.

The crosslinking of silicone PSA containing methyl or/and phenyl groups can be reached at temperature between 120 and 150 °C using organic peroxide. Silicone PSA are typically cured by diacyl peroxides. Dibenzoyl peroxide is normally the catalyst of choice. The use of peroxide catalyst does require a two stage cure. Free radical mechanism is not specific to silyl methyl sites as desired [5].

EXPERIMENTAL

Materials

The solvent-borne silicone pressure-sensitive adhesive trade name Q2-7735 was delivered by Dow Corning



(II)

(USA). As a catalyst of crosslinking reaction bis-2,4-dichlorobenzoyl peroxide (DClBPO) [(Formula (II)] purchased from Peroxid-Chemie (Germany) was used.

Coating and crosslinking

The commercial silicone PSA Q2-7735 was — after addition of various amounts of DClBPO, between 0.5 and 3.0 wt. % — put (in amount 60 g/m^2) on 36 μm special dehesive film CL PET 6J/000 from Rexam (USA) and dried for 10 min at 100 ^{o}C. Silicone PSA coated on PET film was thermally crosslinked for 10 min at about 140 ^{o}C.

Methods of testing

Differential scanning calorimetry (DSC)

The controlling and course of the thermally initiated chemical crosslinking of silicone PSA were determined by quantitative DSC with TA Instruments Q 100. Silicone PSA uncrosslinked layers containing crosslinking agent were investigated in the temperature range between 20 ^{o}C and 200 ^{o}C. The temperatures and heat flows associated with transitions in self-adhesives as a function of temperature or time in a controlled nitrogen atmosphere were measured. This technique provides quantitative and qualitative information on chemical changes that involve exothermic crosslinking processes.

Infrared spectroscopy

IR spectroscopy was performed using IR Negus spectrometer from Nicolet Corp. (USA).

Peel adhesion and shear strength

After crosslinking peel adhesion and shear strength of silicone PSA coated on PET film were measured according to AFERA 4001 and AFERA 4012 [6], respectively (AFERA — *Association des Fabricants Europeans de Rubans Auto-Adhesifs*). Shear strength was determined at 20 ^{o}C, 70 ^{o}C, 120 ^{o}C and 180 ^{o}C.

RESULTS AND DISCUSSION

Influence of the crosslinking agent concentration on crosslinking run

Fig. 1 demonstrates the DSC ability to detect the crosslinking process in a thermosetting silicone PSA for 0.5 and 3.0 wt. % of DClBPO.

Having known the heat of reaction of 100 % unreacted non-crosslinked but crosslinking agent containing silicone PSA, universal analysis calculated automatically heat of the crosslinking reaction. For this maximal heat reaction the optimal crosslinking temperature is calculated. For all investigated silicone PSA with various amounts of crosslinking agent the maximum of heat reaction for about 120 ^{o}C was observed.

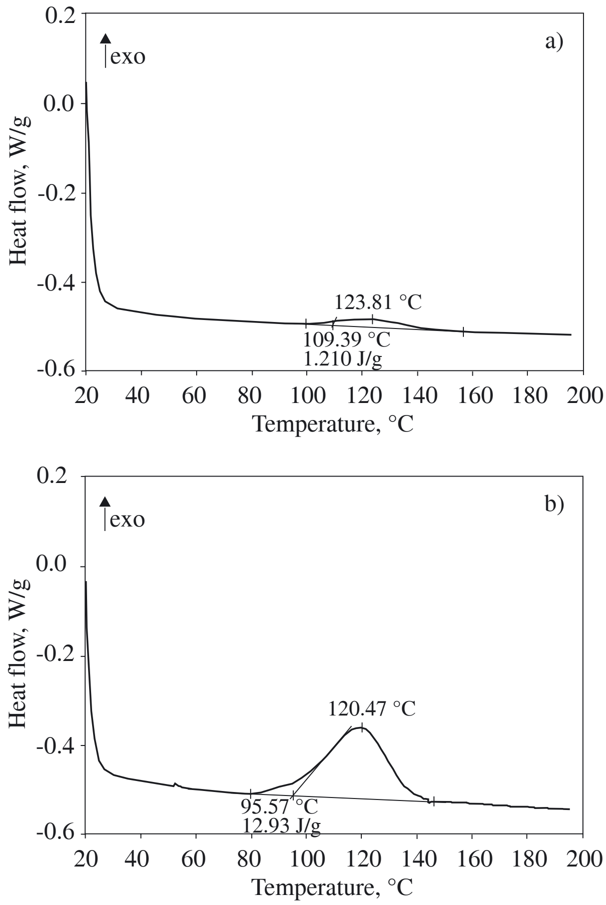


Fig. 1. Thermodynamic characteristic of silicone PSA crosslinking process catalyzed by: a) 0.5 wt. % of DClBPO, b) 3.0 wt. % of DClBPO

T a b l e 1. Influence of DClBPO content on heat of silicone PSA crosslinking

DClBPO concentration, wt. %	Heat of crosslinking, J/g
0	0
0.5	1.21
1.0	4.57
1.5	6.52
2.0	8.43
2.5	10.93
3.0	12.93

The heat arisen of crosslinking reaction of silicone PSA containing various contents of thermal crosslinking DClBPO is shown in Table 1 and Fig. 2. The increase in the concentration of crosslinking agent corresponds with directly proportional increase in heat of crosslinking reaction of silicone PSA. This relation allows controlling of thermally induced crosslinking of various adhesives at

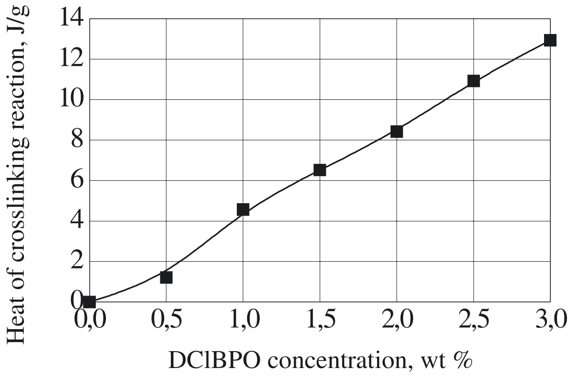


Fig. 2. Effect of DClBPO concentration on the heat of crosslinking reaction of silicone PSA

higher temperature and comparison of commercial self--adhesives with post reaction potential.

Influence of the crosslinking agent amount on silicone PSA performance

Peel adhesion and shear strength of the thermally crosslinked silicone PSA depend on concentration of crosslinking agent used. As can be seen in Fig. 3 the increase in thermal crosslinking agent DClBPO concentration from 0.5 to about 1.5 wt. % improves peel adhesion performance by a factor of about 2.5 in comparison to the initial value. The further increase in this crosslinking agent concentration considerably reduces the peel adhesion.

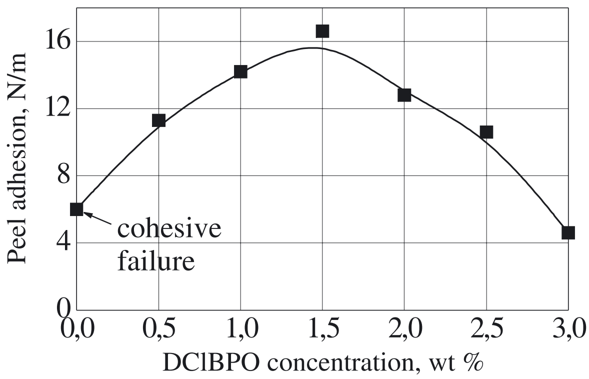


Fig. 3. Effect of DClBPO concentration on peel adhesion of silicone PSA

However, the increase in DClBPO concentration improves the shear strength at all elevated temperatures, what is shown in Fig. 4. The high cohesion of silicone PSA containing thermally by reactive peroxide DClBPO is caused by the reaction between methyl groups from

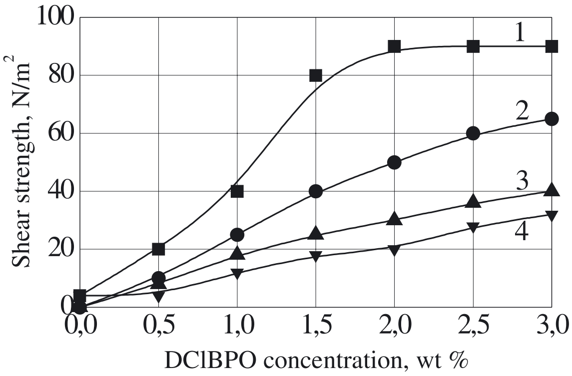
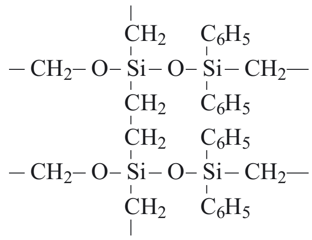


Fig. 4. Effect of DClBPO concentration on shear strength of silicone PSA at different temperatures: 1 — 20 °C, 2 — 70 °C, 3 — 120 °C, 4 — 180 °C



(III)

silicone polymer giving crosslinked product [Formula (III)]. This phenomenon was documented by IR spectrum of crosslinked silicone PSA Q2-7735, characterized for formed -CH_2- groups at about 2930 cm^{-1} and 2850 cm^{-1}.

CONCLUSIONS

Differential scanning calorimetry (DSC) is very interesting method to control the run of crosslinking processes of thermally crosslinked PSA systems. From the examined silicone PSA Q2-7735 the best balance of peel adhesion and shear strength was obtained for about 1.5 wt. % of peroxide crosslinking agent (bis-2,4-dichlorobenzoyl peroxide). This crosslinking agent can be used for silicone PSA crosslinking at elevated temperature about 120 °C.

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