

Low Temperature Flexibility of Silicone Fusible Tapes

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Abstract

Low temperature flexibility of silicone rubber fusible tapes is studied by measuring the stress-strain relationship at sub-ambient temperatures. Observations are correlated to thermal transitions identified through differential scanning calorimetry. It is found that silicone fusible tapes based on phenylvinylmethylsiloxanes offer superior low temperature flexibility and elastic recovery as compared to tapes based on vinylmethylsiloxane. The difference is attributed to crystallization of vinylmethylsiloxane beginning at -70°C by DSC. Steric hindrance within PVMQ reduces or eliminates crystallization to maintain low temperature flexibility.

Keywords: fusible tape, silicone, crystallization

Introduction

Supported or unsupported, silicone rubber, fusible tapes consist of crosslinked vinylmethylsiloxane (VMQ) and an additive package that promotes fusing into a single homogeneous mass without application of heat. Fusible tape is widely used for dielectric protection of electrical cable assemblies over an operating temperature range of -50 to 200°C. Low temperature application is limited by polymeric crystallization resulting in loss of elastomeric properties. High altitude and space applications necessitate the need to extend the low temperature operating range to -100°C without sacrificing desirable elastomeric properties.

Crystallization of methylsiloxane (MQ) is well documented. Sundararajan examined MQ at -70°C by scanning electron microscopy and found approximately 100 micron crystals with spherulitic morphology attributed to linear MQ and approximately 1 micron single crystals attributed to cyclic MQ [1]. Jones and Torkelson examined low molecular weight MQ (≤ 25 kg/mol) and found that crosslinking reduces crystallization by reducing chain mobility [2]. For each crosslink, approximately eight adjoining monomer units are precluded from crystallizing.

The crystallization of copolymers of MQ and phenylmethyl siloxane (PMQ) and/or diphenylsiloxane (PQ) are also well researched. Balazs and Maxwell investigated MQ/PQ copolymers

and found the rate of crystallization decreased with increasing crosslink density but that the total amount of crystallization remained constant [3]. These findings are in contrast to those of Jones and Torkelson who reported crosslinking caused a decrease in the amount of crystallization for pure MQ [2]. The discrepancy may be due to the presence of PQ in the copolymer or differences in molecular weight or crosslink type or density. Chien et al. reported silica reinforced random block copolymers of MQ/PQ with 11.2 mol% phenyl crystallized at (-80°C) after a 30 minute incubation/nucleation period over a duration of 1.8 hours [4]. The duration of crystallization increased to 2.8 hours for the same non-reinforced copolymer. The increase in crystallization rate for the reinforced copolymer is in agreement with Dollase et al. who reported enhanced rates of crystallization when submicron particles were included with MQ [5]. Dollase et al. reported that the enhanced rate is independent of particle surface chemistry and suggested the effect is entropic, i.e. the conformational space of the polymer chains is modified by the mere presence of the surfaces [5].

Experiment

The fusible silicone rubber formulations examined in this study are blends of silica reinforced VMQ and silica reinforced copolymers of phenylvinylmethylsiloxane (PVMQ) (Table 1). All formulations contained an additive package to impart fusibility and peroxide to allow crosslinking at

elevated temperature. Also present is a small amount of iron oxide as pigment. Formulations were extruded into 1 in. wide x 0.020 in. thick profiles and thermally crosslinked.

Formulation	VMQ	PVMQ
	% wt	% wt
A	100	0
B	50	50
C	25	75
D	0	100

Table 1 – Silicone fusible tape formulations.

The stress-strain relationship in tension per ASTM D1708 of each cured formulation was measured on an InstruMet Corp. (Union, NJ) Instron 1130 tensile tester equipped with a 100 lb load cell with 0.1 lb resolution in an ATS Test Systems (Butler, PA) environmental chamber with liquid nitrogen cooling accessory. Ultimate tensile strength and ultimate elongation were measured on each cured formulation at 21°C, -33°C, -66°C, and -100°C. The hysteresis loss of formulations A, C, and D were calculated at 21°C and -70°C. Hysteresis is the lack of elasticity measured as the difference in two subsequent elongations over the same strain range. Specimens were elongated to 100%, returned to 0%, and again elongated to 100%. The area of each stress-strain curve was calculated by fitting the curve to a 3rd degree polynomial and integrating across the strain range. The area of the second elongation was subtracted from the first to calculate hysteresis loss.

A TA Instruments (New Castle, DE) Q100 differential scanning calorimeter (DSC) with liquid nitrogen cooling accessory was used to measure sub-ambient thermal transitions of each fusible tape formulation. The DSC was programmed to cool from 40°C to -150°C at 15°C/min. then heat at 15°C/min. to 0°C. This allowed for the analysis of the glass transition temperature, crystallization temperature, enthalpy of crystallization, melting temperature, and enthalpy of fusion. The DSC was also used for isothermal crystallization analysis performed on cured formulations A, C, and D. For the isothermal crystallization experiments, the DSC was programmed to hold the sample isothermally at -87°C before cooling to -135°C and ramping to -25°C at 2.5°C/min. The experiment was run in modulated mode using a modulation temperature of 1°C with a period of 60 seconds. The isothermal periods were 1 minute and 60 minutes. Modulated mode imposes a sinusoidal temperature profile over the temperature ramp that allows the complex signal obtained by DSC to be separated into the heat capacity and kinetic components. This is useful for separating transitions that occur simultaneously in polymers

such as glass transition temperature and enthalpic relaxation.

Results and Discussion

The retention of room temperature ultimate elongation at -100°C for fusible tape formulations A – D is shown in Figure 1. The retention of room temperature elongation increases as the concentration of PVMQ increases. Formulation A, with only VMQ polymer, has an ultimate elongation of 210% and a tensile strength of 2424 PSI at -100°C. This corresponds to 40% retention of room temperature elongation and 268% increase in room temperature tensile strength. This indicates VMQ retains at least some amorphous regions at -70°C since a completely crystalline structure would be brittle and have very low elongation. Formulation D, with 100% by weight of PVMQ, has an elongation of 452% and a tensile strength of 2131 PSI. This corresponds to 92% retention of room temperature elongation and a 197% increase in room temperature tensile strength. Formulation D is the most stable across the temperature range of 21°C to -100°C.

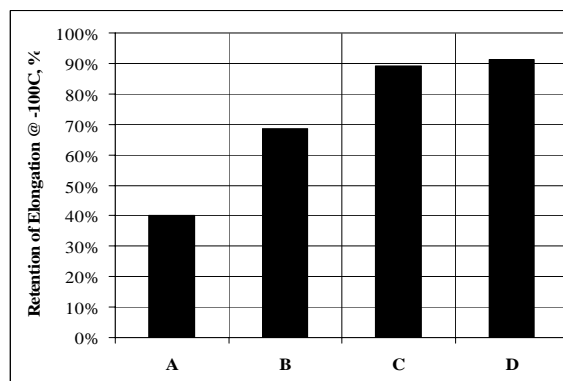


Figure 10 – Retention of room temperature elongation at -100°C of fusible tape formulations A – D.

The hysteresis loss of fusible tape formulations A, C, and D was calculated at 21°C and -70°C and is shown in Figure 2. Formulation A has the least hysteresis loss at 21°C. Increasing the concentration of PVMQ increases the hysteresis loss at 21°C. This is expected since VMQ has inherently better resilience than PVMQ. However, at -70°C formulation A has the highest hysteresis loss and formulations C and D have similar hysteresis losses. This is due to the strain induced crystallization of VMQ. Elongation modifies the conformation of the chains allowing the formation of crystals at or below the crystallization temperature.

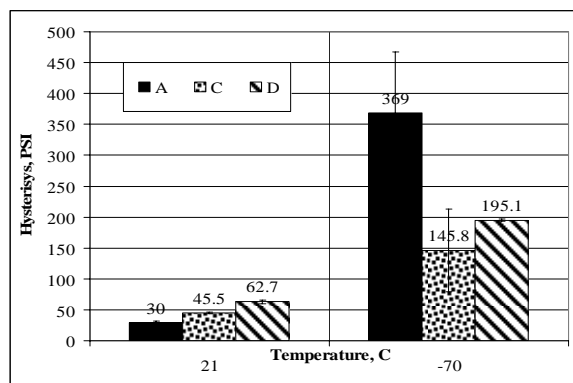


Figure 2 – Hysteresis loss of fusible tape formulations A, C, and D at 21°C and -70°C.

The crystallization exotherms of fusible tape formulations A – D are shown in Figure 3. The crystallization exotherm is a measure of the amount of energy released during crystallization. The enthalpy of crystallization decreases linearly with increasing content of PVMQ (Figure 4). The crystallization temperature, assigned at the peak of crystallization, varies little with VMQ/PVMQ ratio (Table 2).

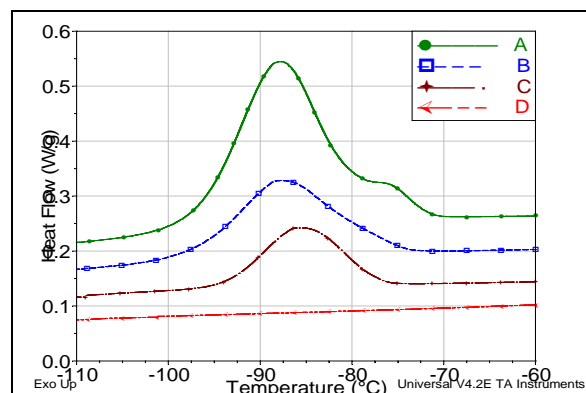


Figure 3 – DSC thermogram of fusible tape formulations A – D showing the associated crystallization exotherm.

Formulation	T _c	ΔH _c
	°C	J/g
A	-88.0	15.8
B	-88.1	7.8
C	-85.9	4.8
D	none	none

Table 2 – Crystallization temperature and enthalpy of crystallization for fusible tape formulations A - D.

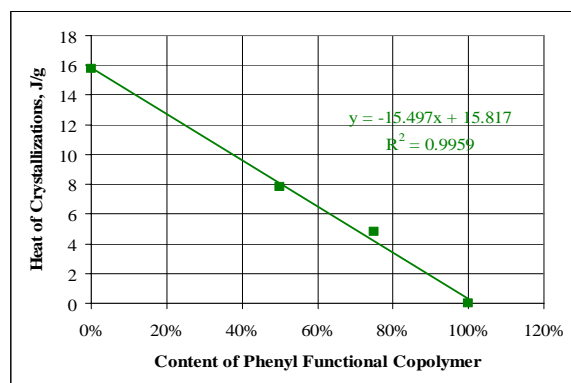


Figure 4 – Effect of phenyl functional copolymer on enthalpy of fusion.

The melt endotherms of fusible tape formulations A – D are shown in Figure 5. The melt endotherm is a measure of the amount of energy absorbed during melting. The enthalpy of fusion decreases linearly with increasing content of PVMQ (Figure 6). The melt temperature, assigned at the peak of melting, varies little regardless of VMQ/PVMQ ratio (Table 3).

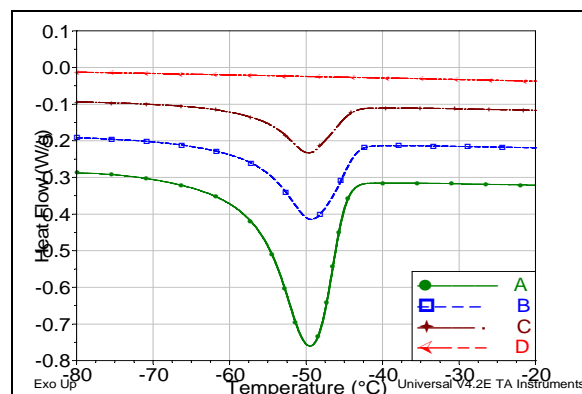


Figure 5 – DSC thermograms of fusible tape formulations A – D showing associated melting endotherms.

Formulation	T _M	ΔH _f
	°C	J/g
A	-49.5	17.1
B	-49.4	8.6
C	-49.7	4.8
D	none	none

Table 3 – Melt temperature and enthalpy of fusion of fusible tape formulations A - D.

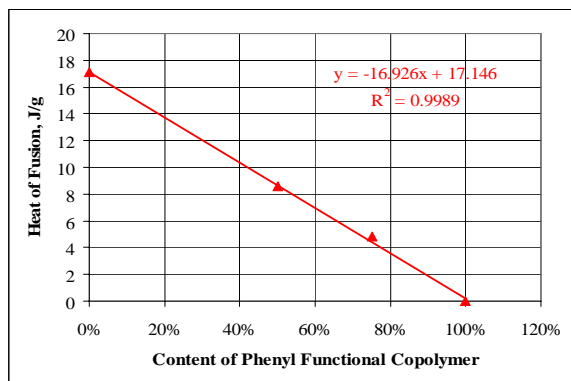


Figure 6 – Effect of phenyl functional copolymer on enthalpy of fusion.

The glass transition temperatures of silicone fusible tape formulations A - D are shown in Figure 7. The glass transition temperature is the temperature when the amorphous regions of the polymer shift from a glassy state to a rubbery state. The change in specific heat of the specimens, measured as the step change in the baseline at the glass transition temperature, increases linearly with increasing content of PVMQ (Figure 8). This is because only the amorphous, not the crystalline, regions of the polymer participate in the glass transition. As the amount of crystallinity decreases, the change in specific heat at the glass transition temperature increases. Fusible tape formulation A shows little shift in the baseline at the glass transition temperature indicating it is highly crystalline. However, the change is still visible, indicating the polymer is not completely crystallized and that amorphous regions still exist well below the crystallization temperature. The glass transition temperature increases with increasing content of PVMQ, but the increase in temperature is nonlinear.

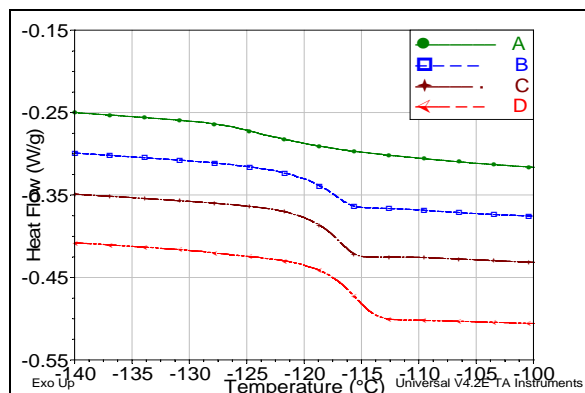


Figure 7 – DSC thermograms of silicone fusible tape formulations A - D showing associated glass transition.

Formulation	T _G	Step Change
	°C	W/g
A	-124.1	0.033
B	-117.4	0.053
C	-116.9	0.063
D	-115.4	0.071

Table 4 – Glass transition temperature of fusible tape formulations A - D.

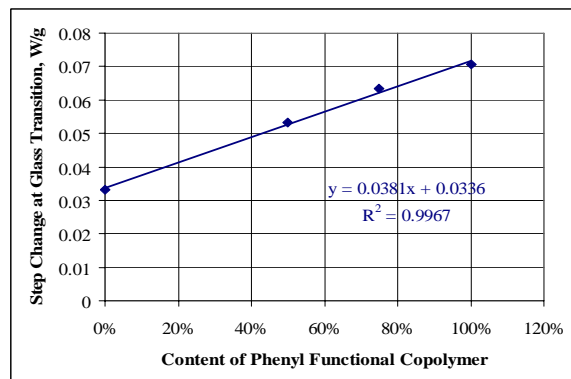


Figure 8 – Effect of phenyl functional copolymer content on the step change at glass transition temperature.

The isothermal crystallization thermograms of formulations A, C, and D produced by modulated differential scanning calorimetry (MDSC) are shown in Figures 9, 10 and 11, respectively. The heat flow signal is the sum of the reversing heat flow signal and the non-reversing heat flow signal and is what is normally displayed by typical DSC. Formulation A develops a second glass transition temperature at (-78°C) seen in the reversing heat flow signal. The second glass transition is accompanied by enthalpic relaxation seen in the non-reversing heat flow signal. These two transitions combine in the heat flow signal to resemble a weak melt that without the resolution of MDSC would likely be misinterpreted. The melt endotherm remains constant for a 1 minute and 60 minute isothermal hold in the crystallization range indicating crystallization occurs rapidly. The same occurrence is seen in formulation C with approximately the same position and intensity of the second glass transition temperature. Formulation D shows no sign of either the second glass transition temperature or enthalpic relaxation. This suggests that the presence of a second glass transition temperature and enthalpic relaxation is caused by VMQ alone. Also absent from Formulation D is a melt endotherm which indicates the absence of crystallinity even after a 60 minute isothermal hold in the temperature range of crystallization.

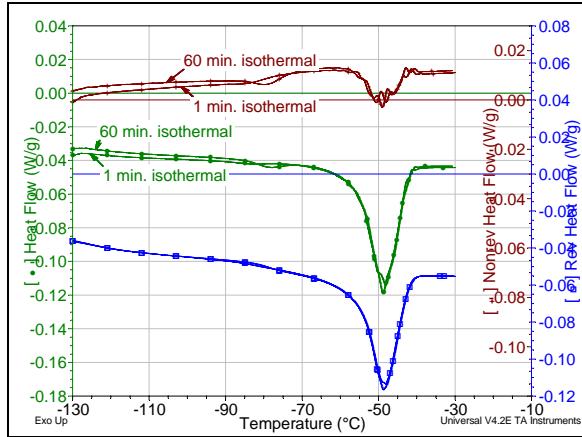


Figure 9 – Isothermal crystallization of fusible tape formulation A by modulated DSC. Sample held isothermally at -87°C for 1 and 60 minutes.

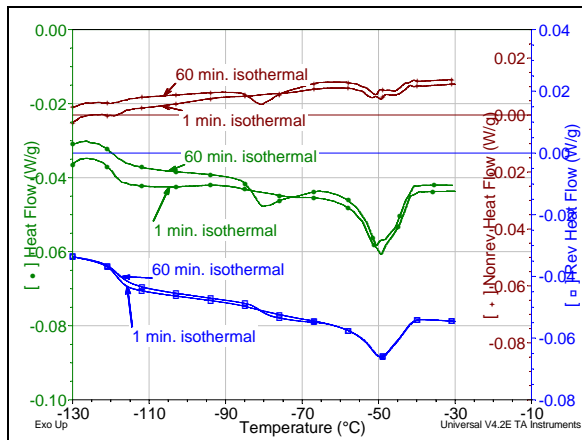


Figure 10 – Isothermal crystallization of fusible tape formulation C by modulated DSC. Sample held isothermally at -87°C for 1 and 60 minutes.

D. Fragiadakis et al. reports on two and three phase models of polymer networks, including MQ, with silica nano-particles. The two phase model indicates the presence of an interfacial phase and bulk phase of the polymer in which the interfacial phase is bound to the silica nano-particles and is responsible for the presence of a second glass transition temperature. The three phase model indicates a strongly bound phase that is immobile, a weakly bound interfacial phase that is responsible for the second glass transition temperature, and a bulk phase. [6]. The MDSC data generated in this study supports the presence of at least two phases of VMQ in which the bulk phase gives the expected glass transition temperature and a second phase produces another glass transition temperature near -80°C . Fusible tape formulation D, which contains only PVMQ, does not show the second glass transition temperature. Steric hindrance from phenyl functionality is responsible

for eliminating crystallization and formation of the interfacial layer. The second glass transition temperature observed in fusible tape formulations A and C does not appear without an isothermal hold in the crystallization range. This indicates the second phase forms slowly and only after sufficient energy has been removed from the polymer network.

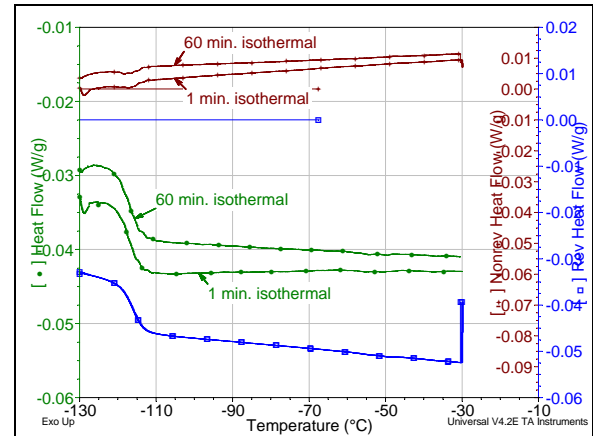


Figure 11 – Isothermal crystallization of fusible tape formulation D by modulated DSC. Sample held isothermally at -87°C for 1 and 60 minutes.

Conclusion

Silicone rubber fusible tape based on PVMQ exhibit improved hysteresis loss and more stable ultimate tensile strength and elongation than tapes based on VMQ at temperatures below -66°C . The improved stability of PVMQ based tapes is due to the inhibition of crystallization which preserves the polymer's amorphous structure and desirable elastomeric properties.

Silicone rubber fusible tapes containing VMQ produce a second glass transition temperature near -80°C when held isothermally for 60 minutes at -87°C . The glass transition temperature is the result of an interfacial layer of VMQ on the silica nano-particle surface. Fusible tape based on PVMQ produce only a single glass transition temperature. It is surmised that steric hindrance from phenyl functional pendant groups inhibits the formation of the interfacial layer in a mechanism similar to the inhibition of crystallization.

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