Improving low temperature properties in a silicone elastomer

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Elastomers based on silicone polymers, MQ and VMQ, are widely used in industrial, aerospace and medical applications where, among other attributes, they retain their performance characteristics under both very low and very high temperature conditions. One challenge to using these materials at low temperatures is a change in the mechanical properties at about -40°C. At this temperature the modulus of a typical silicone elastomer increases significantly.

It has been shown that this increase in modulus is because of alignment of the dimethylsiloxane molecules in a quasi-crystalline fashion. In their efforts to overcome this mechanical property limitation, scientists at General Electric, Dow Corning and others developed a bulkier sidechain would help prevent this crystallization from occurring. Much as the presence of salt lowers the temperature conditions. One challenge to using these materials at low temperatures is a change in the mechanical properties at about -40°C. At this temperature the modulus of a typical silicone elastomer increases significantly.

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For practical considerations, a series of commercial vinyl terminal VMQ product samples from the Andisil SF line were evaluated. Andisil phenyl methylvinyl polymers consist of copolymers of dimethyl siloxane and diphenylmethylsiloxane (Fig. 1). They may be variously vinyl terminal, vinyl pendant or both depending on the specific need of the application. These are synthesized using a re-equilibration process resulting in the final desired MW and phenyl content. These materials are available in a variety of degrees of substitution of the phenyl content. The phenyl concentration of the commercial products ranges from about 3 Mol percent up to about 42 Mol percent. A range of viscosities from about 1000 cSt up to about 10,000 cSt are commercially available. Preliminary work was performed assessing the compatibility of these polymers with dimethyl polymer. The 29 percent and 42 percent phenyl substituted polymer blended with dimethyl polymer appeared hazy and nearly opaque suggested a highly incompatible two phase mixture which would make it difficult to co-cure the polymers. Four diphenyl containing vinyl terminal copolymers were selected. These are synthesized from the second instance different viscosity ranges were chosen, representing a higher and lower molecular weight. Molecular weight is not routinely measured as part of the quality acceptance testing. It is important to point out that the viscosity does increase with increasing phenyl content and so can only approximately represent the molecular weight of the polymer. A phenyl substitution level of 1 percent and 3 percent was selected for evaluation in an example base, J244. Andisil SF 1421, SF 1721, SF 2430 and SF 9530 diphenyl dimethyl vinyl polymers were selected for evaluation. The target phenyl level is the percent of diphenyl in the final base composition. The phenyl mol percent is the amount of phenyl in the vinyl diphényl dimethyl copolymer, and the approximate viscosity represents a measure of the molecular weight of the phenyl copolymer. Therefore all of the non-vinyl specific peroxide was not practical at 3 percent loading level (Table 1). It was also decided that an intermediate 2 percent phenyl level would not be evaluated.

Evaluation of the effect of cure mechanisms on compound

To evaluate the effect of the phenyl methylvinyl copolymers and low temperature performance, it was necessary to prepare a silicone rubber base incorporating these polymers. A commercial base known as J244 was selected as a starting point. This extrusion base is intended for use in low temperature-seals. J244 contains PVMQ to maintain good sealing properties at temperatures as low as -86°C. J244 is manufactured in-house at Jamak Fabrication for internal use. J244 is a proprietary base used for the formulation. These are synthesized by ACE Products and Consulting using advanced methods such as differential scanning calorimetry.

This study concludes that this approach can also be extended to other vinyl containing functional materials for modification of VMQ base. In this particular development project, the functional requirements of the elastomer were met while lowering the cost and improving the mechanical properties.

In order to ensure complete reaction of all vinyl groups, including in the copolymer additive a blend of vinyl specific and non-vinyl specific cure systems were evaluated. These included both a blend of vinyl specific and non-vinyl specific peroxides as well as an addition cure phenyl catalyzed cure system. The selected base can be described as a blend of vinyl-terminated polydimethylsiloxane gum and vinyl and phenyl-containing polydimethylsiloxane (phenyl silicone) fluid hot mixed with fumed silica, T-2430, and a coupling agent for in-situ treatment of the filler. This base is then blended with conventional VMQ base to create a final compound for extrusion.

A second experimental design was performed using the blended peroxide system. In this compound mechanical properties and heat aging data are highlighted below. Utilizing a peroxide cure system incorporating a vinyl-specific peroxide was key to unlocking the potential of this project by forming a true co-polymer between the PDMS gum and phenyl silicone. The dimethyl siloxane and the copolymer diphenyl dimethyl siloxane are connected by cross-links at the terminal vinyl groups.

Up to this point the commercially produced Andisil SF 9530 CV have been used as the starting material for the selection of a high temperature base manufacturing process and the efficiency of the batch storage stability. Silicones, a new product was created—Andisil SF 6030—which did not undergo the high vacuum evaporation stripping process needed to achieve a “controlled volatility” CV designation. The most recent commercial production of phenyl base and compound for internal use at Jamak has been based on Andisil SF 6030.

Based on the success of the vinyl specific evaluation, the platinum catalyzed addition cure was evaluated. All compounds incorporating the diphenyl dimethyl copolymer pass the 80°C low temperature flexibility test with the platinum catalyzed version exhibiting the best mechanical properties.

Conclusions

There are a number of benefits to using a relatively low molecular weight vinyl functional copolymer as a way to modify the properties of VMQ base. In this particular development project, the functional requirements of the elastomer were met while lowering the cost and improving the mechanical properties.

Use of a copolymer containing a high percentage of pendant vinyl groups such as Andisil VDMQ-1000 may be more conducive to provide additional toughness and improve mechanical characteristics, to take the place of a high vinyl VMQ gum.

References


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