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MDSC study of melting and glass transitions in elastomeric dental impression materials

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Abstract

A modulated differential scanning calorimetric (MDSC) study was performed to investigate melting and glass transitions in vinyl polysiloxane, polyether and polysulfide dental elastomeric impression materials. The MDSC analyses were performed from −150 to 200°C, using heating-only modulation conditions and sufficient modulations to define the transitions. The two vinyl polysiloxane materials had a single melting peak near −50°C, whereas the polyether material had two melting peaks near −20 and 50°C. The polysulfide material had a small apparent melting peak near 70°C and an endothermic peak near 190°C that requires further investigation. Apparent crystallization peaks were observed on the nonreversing heat flow curves for the vinyl polysiloxane materials. These two silicones had glass transitions near −125°C that were very weak because of their high filler content. The polyether material had a glass transition near −80°C, and the polysulfide material had a glass transition near −55°C. More research is needed to elucidate the nature of the melting peaks in these elastomers and the relationships between polymer structural transformations and clinically relevant properties.

Keywords: Thermal analysis; Modulated differential scanning calorimetry; Glass transition; Melting; Elastomer; Polysiloxane; Polyether; Polysulfide

1. Introduction

Vinyl polysiloxane, polyether and polysulfide elastomeric impression materials are used extensively in dentistry for the fabrication of accurate single-unit inlays or crowns, complex multi-unit metal–ceramic restorations, and fixed and removable partial dentures [1–3]. The general polymeric structures of these elastomers are described in detail in textbooks on dental materials [1–3]. Clinically relevant mechanical properties of these viscoelastic materials include rheological behavior prior to setting (polymerization), elasticity after setting (measured as strain in compression), extent of permanent deformation and recovery of anelastic (retarded elastic) deformation when the set impression is withdrawn (particularly past undercuts on teeth), and tear strength after setting, since relatively thin layers of material are used to obtain impressions. However, minimal information is currently available on fundamental relationships between the microstructures and the ultrastructures (at the

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submicron or nanometer level) of these elastomers and their mechanical properties.

Differential scanning calorimetric (DSC) and modulated differential scanning calorimetric (MDSC) analyses were previously performed on a silicone maxillofacial material [4], which has a structure similar to that of the vinyl polysiloxane impression materials. We have previously reported the use of MDSC to investigate the glass transitions and melting peaks for representative vinyl polysiloxane, polyether and polysulfide impression materials [5]. In that study, apparent crystallization peaks were observed on the nonreversing heat flow curves, suggesting that the modulation conditions had inadvertently resulted in some cooling of the polymer melt. An apparent crystallization peak was also previously observed on the nonreversing heat flow curve for the silicone maxillofacial elastomer, using similar modulation conditions [4]. The purpose of the present study was to employ different modulation conditions to obtain more accurate information about the glass transitions and melting peaks in the elastomeric impression materials, as part of our continuing investigation of the relationships between polymer structure and properties of these materials.

2. Experimental

The two vinyl polysiloxane impression materials studied were Examix-Light Body (GC America, Alsip, IL) and Reprosil-Light Body (LD Caulk, Milford, DE). The polyether and polysulfide impression materials selected were Impregum-Medium Body (ESPE America, Norristown, PA) and Coe-Flex Injection (Light Body) (GC America), respectively. The terms "Light Body" and "Medium Body" refer to the levels of viscosity provided by the manufacturers for various clinical applications [1–3].

The materials, initially in the form of separate base and catalyst pastes, were manipulated following manufacturer recommendations. Reprosil-Light Body and Examix-Light Body were mixed during delivery by syringes; Coe-Flex Injection (Light Body) was mixed by hand, and Impregum-Medium Body was automixed, using an apparatus provided by the manufacturer. Samples of uniform thickness (~0.5 mm) were obtained by compressing the mixed materials between glass microscope slides.

The MDSC analyses were conducted (Model 2910, TA Instruments, Wilmington, DE) over a temperature range from −150 to 200°C. The linear heating rate was 2°C/min, and two heating-only modulation conditions were used: (a) a period of 60 s with an amplitude of 0.318°C (from the TA manual), and (b) a period of 100 s with an amplitude of 0.50°C. Modulation condition (a) provided a smaller amplitude and should not induce any crystallization peaks on the nonreversing heat flow curve over the temperature range of a crystalline polymer melting peak. The larger amplitude with modulation condition (b) was employed to increase the sensitivity for detection of the weak glass transitions in the vinyl polysiloxane materials. All analyses were accomplished with the use of a helium purge gas. Baseline calibrations were carried out for the two modulation conditions, and temperature calibrations were performed using *n*-pentane, acetone, water and indium.

3. Results

Figs. 1 and 2 present MDSC plots for the vinyl polysiloxane impression material, Examix-Light Body, and both modulation conditions. A very weak glass transition occurs at approximately −125°C (barely evident in Figs. 1 and 2), and a strong melting peak occurs at approximately −50°C. Despite the use of modulation condition (a), an apparent crystallization peak can be seen on the nonreversing heat flow curve in Fig. 1. This apparent crystallization peak also can be seen on the nonreversing heat flow curve in Fig. 2, where modulation condition (b) was used. Very similar results were found for the other vinyl polysiloxane impression material, Reprosil-Light Body, where the glass transition and melting peak occurred at about the same temperatures as for Examix-Light Body. Fig. 3 shows the MDSC plot for Reprosil-Light Body and modulation condition (a).

Figs. 4 and 5 present MDSC plots for the polyether impression material, Impregum-Medium Body, and the two modulation conditions. There is a weak glass transition at about −80°C and melting peaks near −20 and 50°C. For modulation condition (b), there are apparent crystallization (exothermic) peaks on the nonreversing heat flow curve. However, only endothermic peaks that are not indicative of

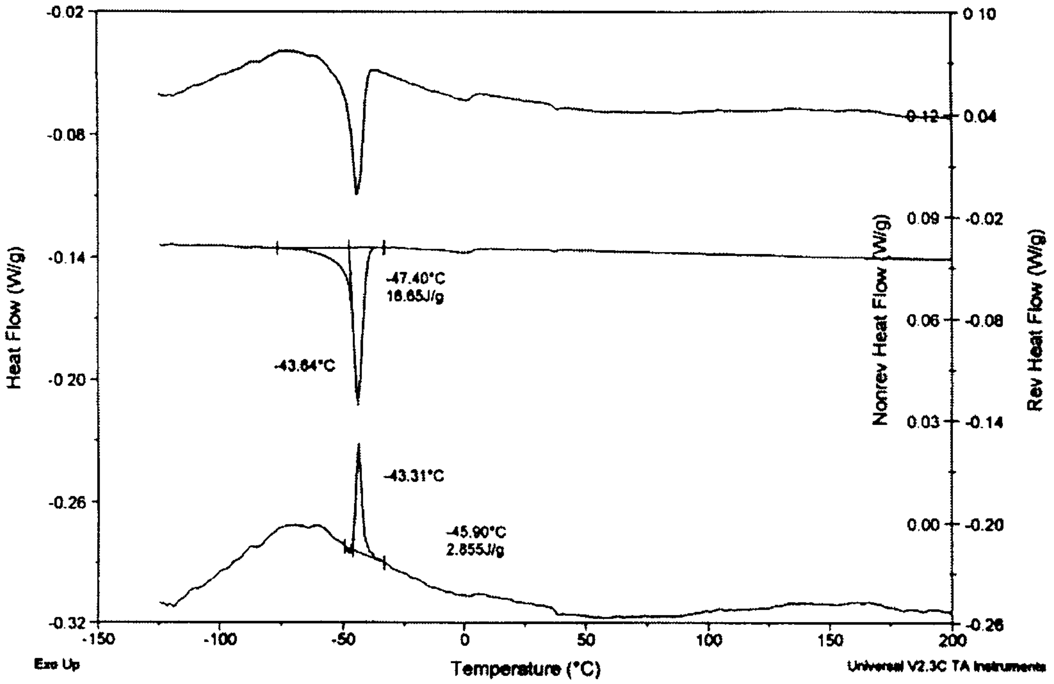

Fig. 1. MDSC plot for vinyl polysiloxane impression material, Examix-Light Body, and modulation condition (a). The positions of the total (top), reversing (center) and nonreversing (bottom) heat flow curves are the same in all figures.

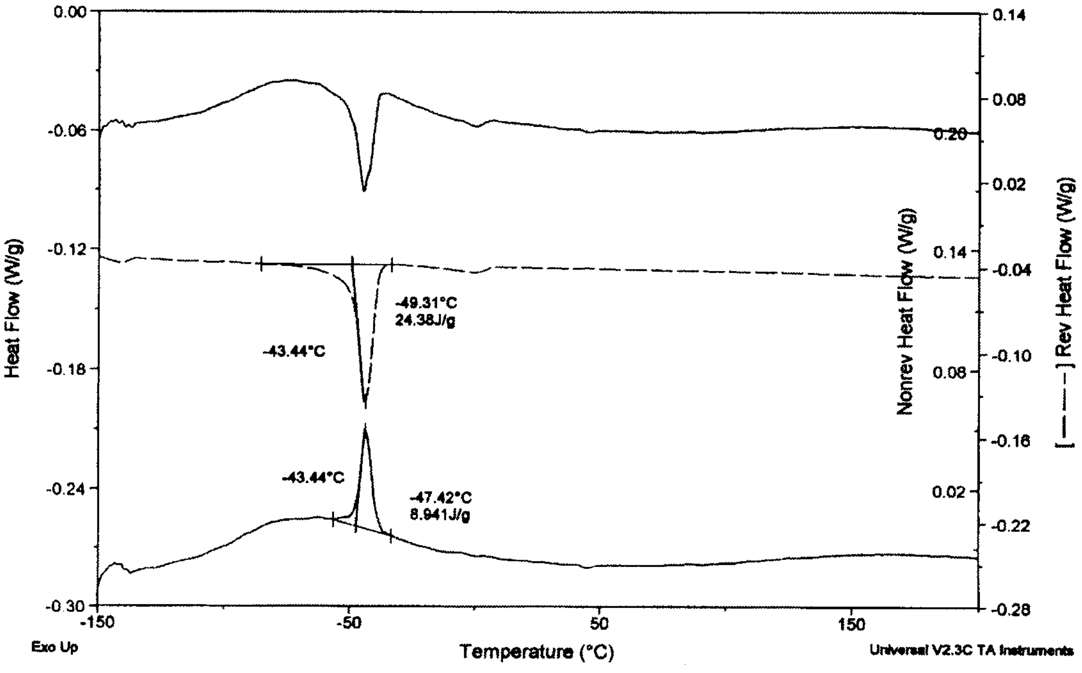

Fig. 2. MDSC plot for Examix-Light Body and modulation condition (b).

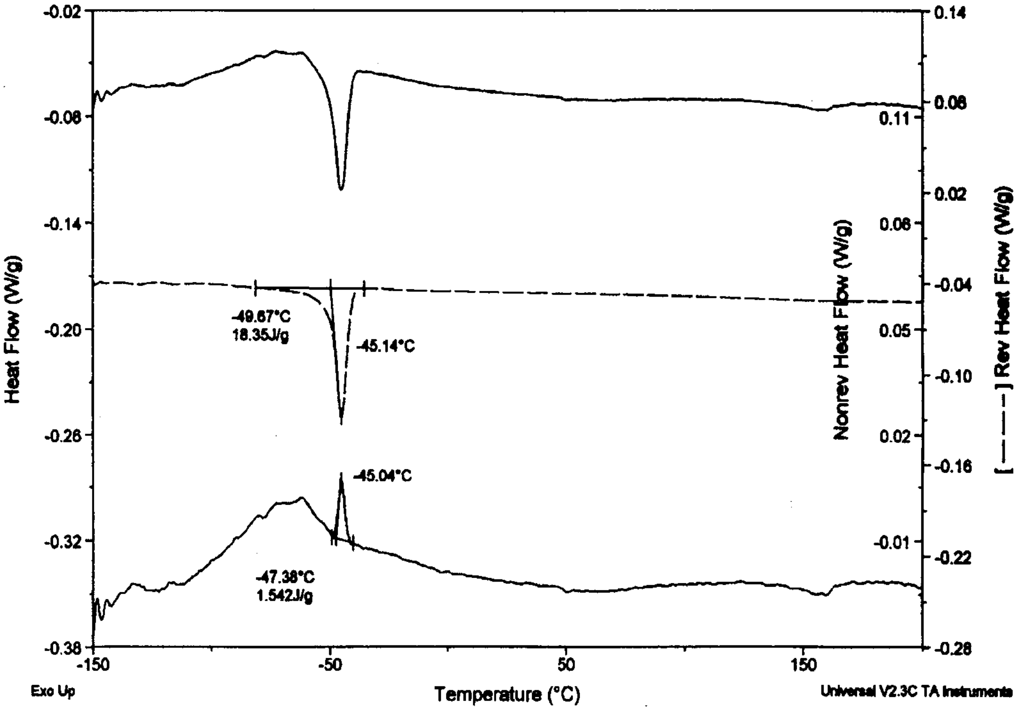

Fig. 3. MDSC plot for vinyl polysiloxane impression material, Reprosil-Light Body, and modulation condition (a).

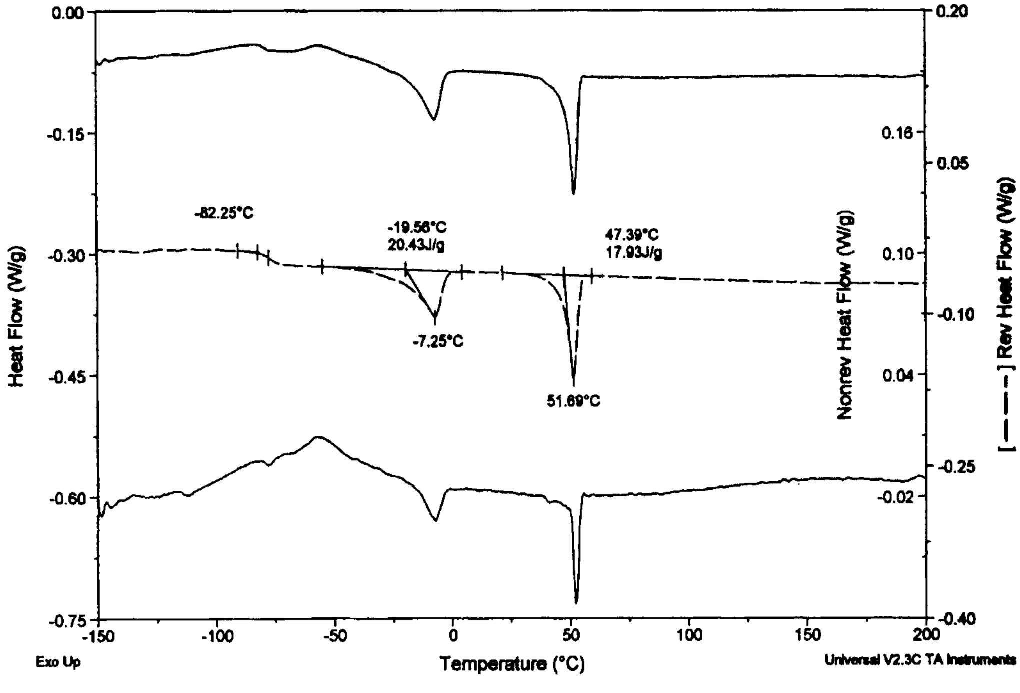

Fig. 4. MDSC plot for polyether impression material, Impregum Medium-Body, and modulation condition (a).

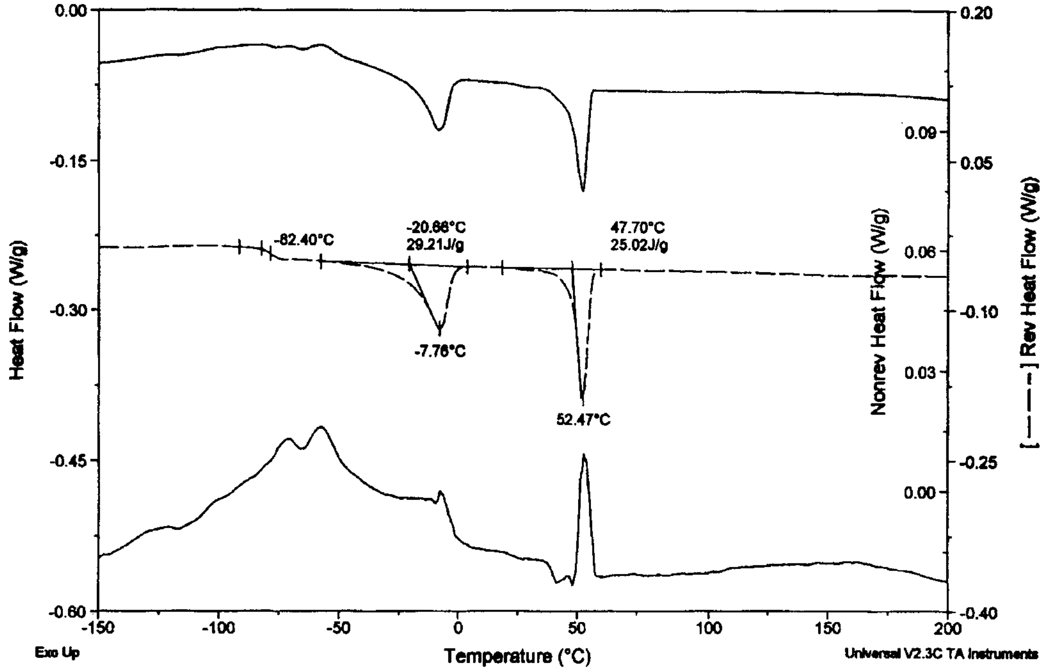

Fig. 5. MDSC plot for polyether impression material, Impregum Medium-Body, and modulation condition (b).

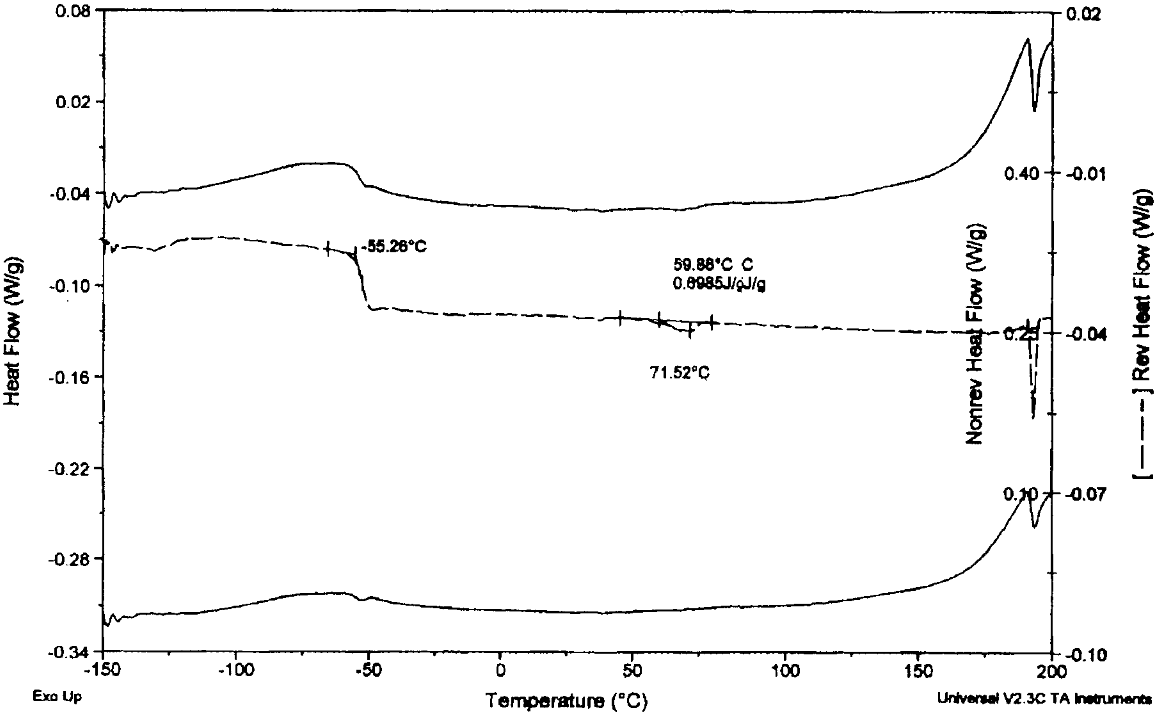

Fig. 6. MDSC plot for polysulfide impression material, Coe-Flex Injection (Light Body), and modulation condition (a).

crystallization are found on the nonreversing heat flow curve for modulation condition (a).

Fig. 6 shows an MDSC plot for the polysulfide impression material, Coe-Flex Injection (Light Body), and modulation condition (a). A similar MDSC plot was obtained with modulation condition (b). This material has a glass transition near −55°C and a small apparent melting peak near 70°C, without evidence of a crystallization peak on the nonreversing heat flow curve for either modulation condition. An exothermic peak near 190°C requires further study.

4. Discussion

The glass transitions and melting peaks in Figs. 1–6 are in excellent agreement with our previous study [5], where a different MDSC apparatus (TA Model 2920) and analysis conditions (linear heating rate of 5°C/min, modulation amplitude of 0.7°C and period of 60 s) were used. The temperatures for the glass transitions and melting peaks in the silicone materials are similar to those previously found for a silicone maxillofacial prosthetic material [4] and reported for other siloxane polymers [6].

With the modulation condition (a), apparent crystallization peaks still occurred on the nonreversing heat flow curves for the two vinyl polysiloxane materials (Figs. 1–3). These peaks were larger for modulation condition (b), where the larger amplitude and longer period might cause inadvertent cooling during the modulation cycle and allow greater time for formation of crystallites. For Examix-Light Body, the apparent crystallization peaks were smaller for specimens aged 24 and 48 h, compared to fresh specimens.

Figs. 4 and 5 show that the nature of the peaks on the nonreversing heat flow curves for the polyether depended dramatically upon the modulation conditions. For modulation condition (a) in Fig. 4, there were no exothermic peaks suggestive of crystallization during melting, whereas such exothermic peaks were observed for modulation condition (b) in Fig. 5. For the polysulfide, there was no crystallization peak associated with the small apparent melting peak for both modulation conditions; this can be seen in Fig. 6 for modulation condition (a).

X-ray diffraction and scanning electron microscopic investigations [7] have revealed that all four impression materials contain large amounts of crystalline fillers, with particles in the micron size range. These filler particles are added by the manufacturers to adjust the viscosity of the impression materials after mixing and the mechanical properties after polymerization. Silica was detected in the vinyl polysiloxane and polyether materials, and the polysulfide material contained lead dioxide. The large filler loading is assumed to account for the very weak glass transitions observed in the two vinyl polysiloxanes (Figs. 1–3), but detailed information about the extent of polymer matrix-filler bonding is proprietary with the manufacturers and is an important area for future research.

At the ultrastructural level and at very low temperatures, the vinyl polysiloxane impression materials contain crystallites in a relatively rigid amorphous matrix. This polymer matrix assumes a rubbery or flexible character in the two vinyl polysiloxane materials above the very low glass transition temperature of approximately −125°C. Localized melting of the crystallites subsequently occurs at approximately −50°C, although the macroscopic elastomer remains in the solid state. Thus the inability of X-ray diffraction analyses performed at room temperature to detect sharp peaks from these polymer crystallites [7] is expected. However, any crystalline phase with submicron particle sizes in the polymer matrix will not yield sharp (Bragg) X-ray diffraction peaks [8]. For the polyether impression material, Figs. 4 and 5 show that there are two different crystalline polymer phases in the amorphous polymer matrix; these two phases undergo melting at temperatures near −20 and 50°C.

The dramatically different MDSC results in Figs. 4 and 5 for the polyether impression material illustrate the strong dependence of the crystalline melting peaks on the nonreversing heat flow curve for the modulation conditions employed to study the melting peaks. For the modulation condition (a), no crystallization occurs, although an apparent strong crystallization peak is induced at the higher-temperature melting peak near 50°C for modulation condition (b).

With the polysulfide impression material (Fig. 6), no apparent crystallization peak was found on the nonreversing heat flow with the modulation condition (a) for the weak apparent melting peak near 70°C. However, in contrast to the results for the polyether impression material in Figs. 4 and 5, no crystallization peak was observed when modulation condition (b) was used as well.

For the two vinyl polysiloxane impression materials, Figs. 1 and 3 show that apparent crystallization peaks were nonetheless found on the nonreversing heat flow curve associated with the crystalline melting peak near −50°C, despite the use of modulation condition (a), which was not expected to induce crystallization. While further investigation of the melting process in these materials is needed, using other modulation conditions and experimental techniques, one explanation is that melting is followed by molecular reorganization to form more perfect crystals that subsequently undergo remelting. Additional factors for this process are the expected variation in the molecular weight (melting point) of the crystallites and the relatively rapid cooling that occurs during a portion of the modulation cycle.

The relevance of viscoelastic properties for impression materials has been recognized [9], and the vinyl polysiloxane impression materials have superior recovery from viscoelastic deformation in the mouth, compared to the polyether and polysulfide impression materials [1–3]. Additional research is required to determine fundamental relationships between polymer structure and clinical performance for these elastomers, and to elucidate possible roles of the crystalline melting peaks on the rheological behavior and other mechanical properties. The relationships of the apparent crystallization peaks on the nonreversing heat flow curves for the vinyl polysiloxane and polyether materials to the modulation conditions remain an important area for further study, along with the precise nature of the crystalline polymer melting peaks.

5. Conclusions

The representative products for the three major types of dental elastomeric impression materials analyzed in this study exhibit glass transitions and crystalline melting peaks. Very weak glass transitions near −125°C are found for the two vinyl polysiloxane elastomers and are influenced by the high percentages of filler particles in the polymer matrix. Much stronger glass transitions near −80 and −55°C, respectively, are found for the polyether and polysulfide impression materials, which also contain substantial amounts of filler particles. The nature of the filler-matrix bonding in all of these impression materials requires further study. Crystalline melting peaks near −50°C for the vinyl polysiloxanes, and near −20 and 50°C for the polyether, were much stronger than the glass transitions in these materials, whereas this was reversed for the polysulfide impression material which had a small apparent melting peak near 70°C. The experimental results showed that the crystalline melting peaks in these elastomers can be strongly affected by the modulation conditions chosen. Induced crystallization peaks on the nonreversing heat flow curves were absent for the polyether impression material, when a lower-amplitude, shorter-period modulation condition was employed. For the polysulfide material, no induced crystallization peak was associated with the small apparent melting peak near 70°C for either modulation condition. Apparent crystallization peaks persisted with the vinyl polysiloxane impression materials for the lower-amplitude, shorter-period modulation condition, suggesting that melting led to the formation of more perfect crystals which subsequently remelted. Additional factors that may affect this complex melting/crystallization process are variation in the crystallite molecular weight and sensitivity of the crystallization process to the more rapid cooling rate that occurs during a portion of the modulation cycle.

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