

# Differential Scanning Thermal Analysis of Shape-Memory Polymers, Polymer Blends and Composites



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**Abstract** Calorimetry is the primary technique for measuring the thermal properties of materials. From calorimetric methods, it is possible to perform a correlation between temperature, structure, and the physicochemical properties of the materials. The differential scanning calorimeter (DSC) is one of the most common methods used to determine the thermal properties in polymeric materials. To determine the thermal properties of thermally activated polymeric materials is fundamental for the development of the programming cycle of these materials. This chapter presents a brief discussion about the application of the DSC in determining the thermal transitions of the materials and its correlation with the structure and memory effect.

## 1 Differential Thermal Analysis of Shape-Memory Polymers

Shape-memory polymers (SMP) are materials that can recover an original shape with a specific stimulus after programming steps. The shape-memory process is intrinsically related to a specific stimulus applied to the material (light, heat, electric field, magnetic field, pH, enzymes, ions, etc.) [1–3]. In this way, when a shape-memory polymer is developed, the behavior as a function of a specific stimulus must be studied to determine the future working conditions of this material.

Nowadays, most of the shape-memory polymers developed are based on thermal stimulus (thermally activated memory effect). The thermal transitions temperatures (melting temperature, glass transition temperature, for example) of specific segments in the polymer chain are the start parameters to the development and programming of the shape-memory cycle [4].

In this way, the polymer chain structural organization must be considered to study the shape-memory effects on polymers. The shape-memory programming process is

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**Fig. 1** Schematic representation of the hard and soft segments in shape-memory polymers [9]

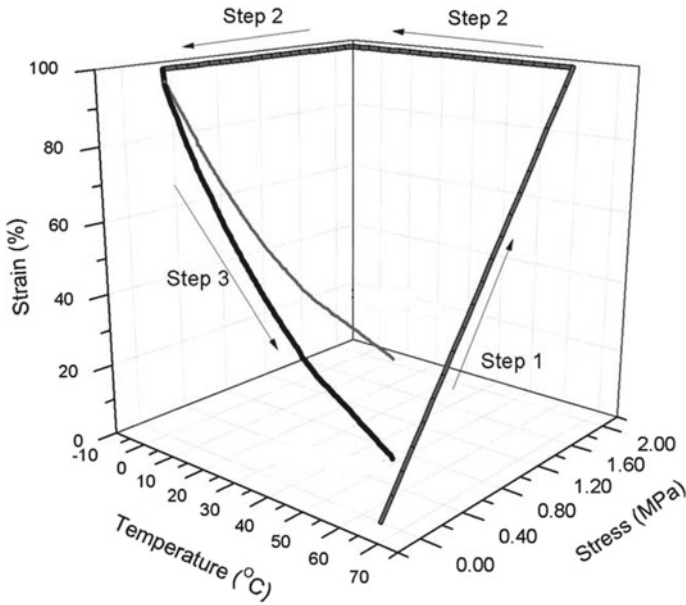
performed from structures responsible for the “permanent shape” and the “temporary shape” generally denoted as “hard domains/hard segments” and “soft domains/soft segments” with different thermal transitions (Fig. 1). These structures determine the initial thermal parameters in the development of the polymer. The hard domains are generally formed by regions with high cross-linking density, entanglement between the polymer chains and groups, or chemical functions that hinder the mobility of the chain. These domains are responsible for the permanent shape and have normally the higher thermal transition temperatures. By the other side, the soft domains are formed by chemical groups with high molecular mobility and the structures build during the mechanical deformation [5]. These domains are responsible for the temporary shape. The soft domains are rigid below the temperature of transition, when heated above this temperature they turn flexible and can be deformed when subjected to mechanical stress. The shape can be maintained during the cooling process if the deformation is maintained. The polymer restores the original shape when heated again above the transition temperature of soft domains [6–8]. The material returns to the original shape due to structural tension stored in the hard segments.

Liu et al. [7] stated that the mechanisms of memory are based on the intrinsic elasticity of the polymer networks. This model is based on the structural crystallinity of the polymer. Shape-memory polymers are constituted of covalent or physical cross-links. They are flexible when subjected to high stresses at temperatures above the glass transition temperature ( $T_g$ , amorphous case) or the melt temperature ( $T_m$ , crystalline case) [3, 7].

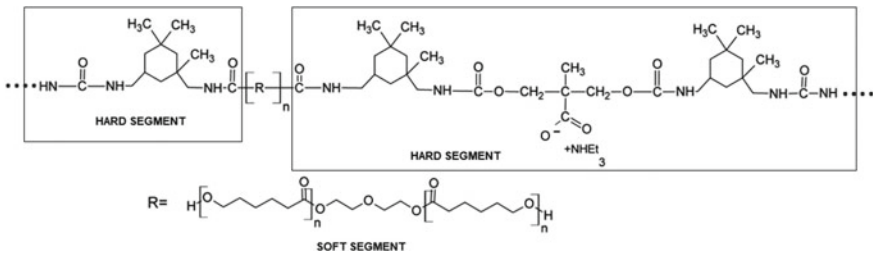
At temperatures higher than the thermal transition temperatures, the polymer networks exhibit superelasticity. In these conditions, the chain segments between the bonding points are able to freely deform and can be twisted randomly, via rotations over the bonds, maintaining a maximum entropy and minimum internal energy [7].

Macroscopically, the shape-memory effect on polymers can be graphically described in the form of the temperature  $\times$  stress  $\times$  strain measurement (Fig. 2). Initially, polymer is heated above the transition temperature of the soft segments. The material is then deformed from the application of stress (step 1). Subsequently, the applied stress is maintained and the material is cooled at temperatures below the thermal transition of the soft segments (step 2). After cooling, the stress is withdrawn. At this stage, the deformation is frozen. Finally, the material is reheated and returns the original shape (step 3).

Shape-memory polyurethanes (SMPU), by the example, are structurally formed by block copolymers with alternating segments having different properties called “segmented polyurethanes” (Fig. 3) [10, 11]. These polymers are formed by differ-



**Fig. 2** Shape-memory effect in polymers: temperature × stress × strain [10]. Reproduced with permission



**Fig. 3** Structure of an SMPU repeat unit [10]. Reproduced with permission

ent alternating polymeric monomers linked by covalent bonds and polymer chains bonded by reversible secondary bonds. Such bonds are weak and may include hydrogen bonds and ionic bonds [9]. Usually, SMPU are formed of two phases: one permanent and one reversible. The permanent shape consists of hard segments that can be formed via hydrogen bonding and crystallization below the melting temperature. The reversible phase consists of soft segments and is mainly responsible for the memory effect and to the temporary shape [12].

The segments can be manipulated to have different transition temperatures to build a shape-memory polymer thermally activated. The memory effect can be controlled via the molar mass of the soft segment that affects directly the thermal transition of this segment and the molar ratio of the rigid and soft segments [13]. In polyurethanes, the

rigid segments are formed of diisocyanates and chain extenders, and are responsible for the permanent shape. The soft segments are formed by polyols and are responsible for the temporary shape (reversible phase). Normally, this transition is associated with the glass transition temperature or other transition of the soft segment. In this type of polymer, it is possible to change the shape-memory properties by modifying the thermal transitions. This process is carried out by manipulating the composition of the polymer by the ratio of the rigid and soft segments to obtain different glass transition temperatures ( $-30\text{ }^{\circ}\text{C}$  to  $70\text{ }^{\circ}\text{C}$ ) [13, 14].

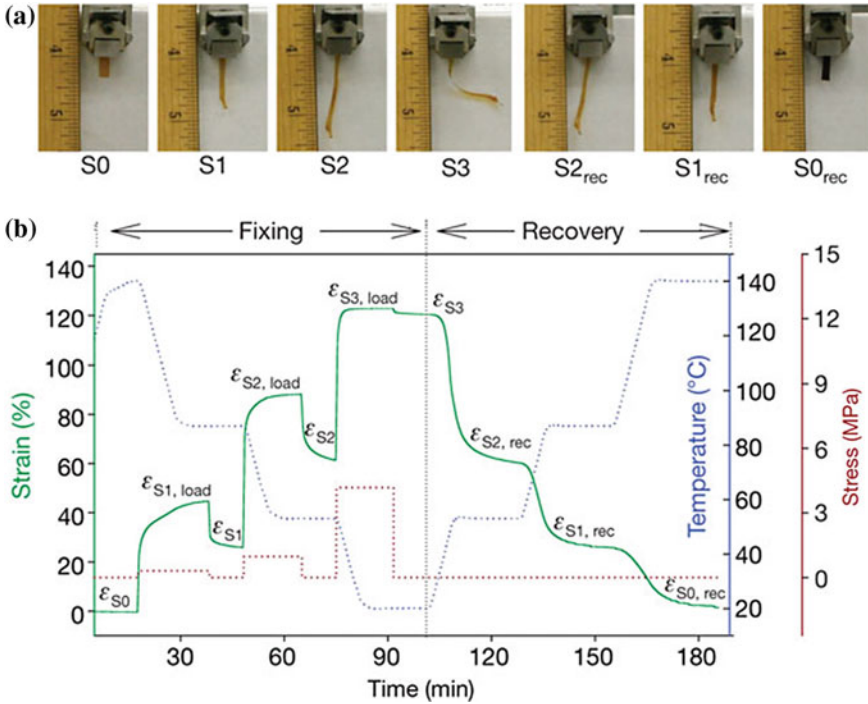
Typically, the shape-shifting activity of memory polymers is identified by a one-way behavior, in which the material has a permanent initial shape, can be deformed and fixed in a temporary shape, and recovers the permanent shape through a stimulus [15].

Some polymers have multiple memory effects, i.e., there is more than one temperature at which temporary shapes can be programmed, allowing these polymers to memorize many shapes that are produced during the cooling of the material and restored during the heating process [15]. The property of polymers to memorize many shapes comes from the ability to stretch the chains during heating and fix them during cooling [16, 17]. The maximum number of temporary shapes that a polymer can memorize correlates directly with the number of discrete reversible phase transitions (shape-memory transitions) [2, 18]. Xie [16], for example, developed a polymer with quadruple shape-memory (Fig. 4a, b). This effect is produced by introducing an additional reversible phase transition. However, synthesizing a polymer with more than two distinct and tightly bound reversible phases is extremely difficult [16, 18].

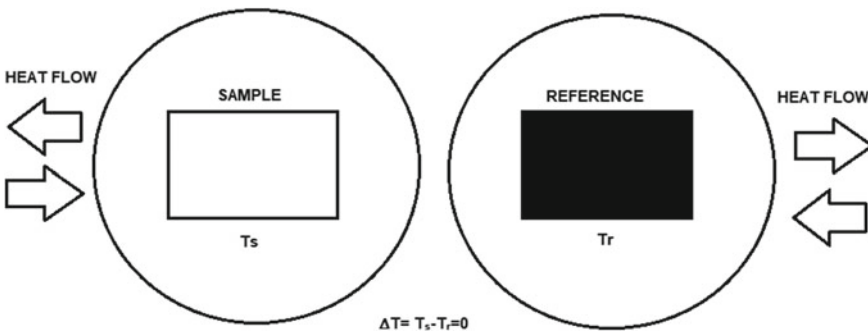
The determination of the thermal transitions in shape-memory materials is essential to the development of the shape programming process. The main method for measuring the thermal properties of materials is calorimetry. Calorimetrically, it is possible to establish a correlation between the physicochemical properties of the substances and the temperature. It is also the main method for direct determination of the enthalpy associated with the process of interest [19]. The most employed calorimetric technique is the differential scanning calorimeter (DSC). This technique measures the change in thermal properties as a function of temperature along with the time (heat flow). The thermal transitions and parameters detected in DSC (melting temperature, crystallization temperature, glass transition temperature, crystallization enthalpy, melting enthalpy, etc.) are associated with alteration in the microstructure of the polymeric material.

The use of DSC has many advantages, such as the low cost of the test, use of small amounts of sample, control of the time test and precision in the results. However, DSC is a destructive calorimetric method. During measurement on the DSC, the sample is degraded and cannot be recovered.

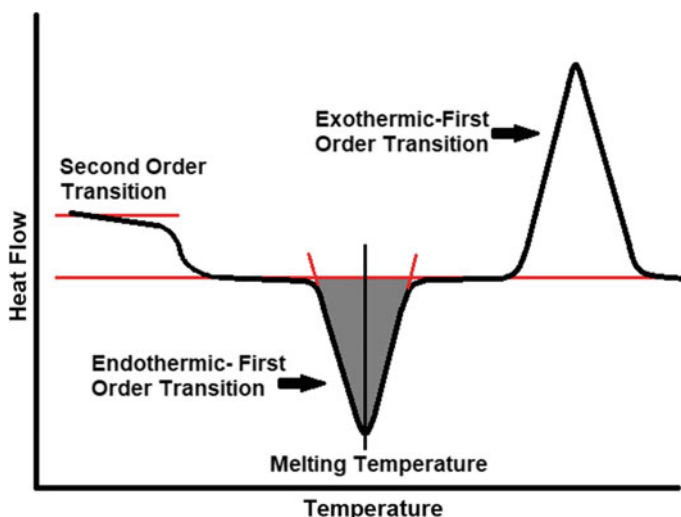
DSC analysis is performed using the sample and a reference material. The reference material is inert (does not undergo thermal transitions or structural modifications during the analysis), usually alumina ( $\text{Al}_2\text{O}_3$ ) or platinum (Pt). During the test, the sample temperature ( $T_s$ ) and the temperature of the reference material are maintained equal (Fig. 5). The energy difference to keep the sample and the reference at the same temperature are quantified to determine the thermal transitions in the sample.



**Fig. 4** Quadruple-shape-memory properties of perfluorosulphonic acid ionomer (PFSA): **a** Visual demonstration. S0: permanent shape; S1: first temporary shape ( $T_{d1}$ : 140 °C); S2: second temporary shape ( $T_{d2}$ : 107 °C); S3: third temporary shape ( $T_{d3}$ : 68 °C); S2<sub>rec</sub>: recovered second temporary shape ( $T_{r1}$ : 68 °C); S1<sub>rec</sub>: recovered first temporary shape ( $T_{r2}$ : 107 °C); S0<sub>rec</sub>: recovered permanent shape ( $T_{r3}$ : 140 °C). **b** Quantitative thermal mechanical cycle ( $T_{d1} = T_{r3} = 140$  °C,  $T_{d2} = T_{r2} = 90$  °C,  $T_{d3} = T_{r1} = 53$  °C). Shape fixity,  $R_f$ , (S0 → S1): 58.7%,  $R_f$ (S1 → S2): 57.1%,  $R_f$ (S2 → S3): 96.1%, shape recovery,  $R_r$ (S3 → S2): 100.0%,  $R_r$ (S2 → S1): 99.6%,  $R_r$ (S1 → S0): 93.0% [16]. Reproduced with permission



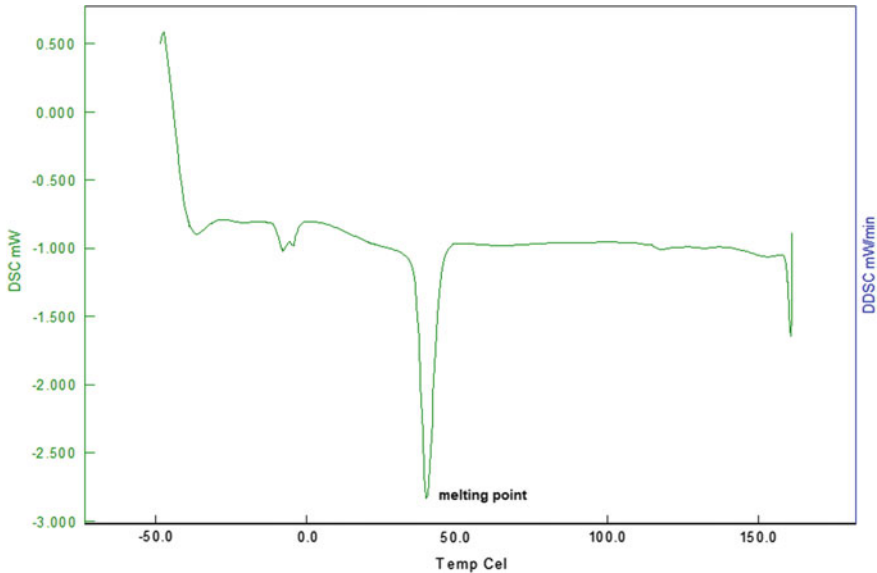
**Fig. 5** Schematic representation of the DSC



**Fig. 6** DSC thermal transitions of first and second order

Many thermal events can be quantified from the energy used to maintain the same temperatures between the materials (reference and sample). These thermal events are usually transitions of second and first order (Fig. 6). First-order transitions can absorb energy (melting, loss of mass, desorption, or reactions of reduction, etc.) giving rise to endothermic peaks or releasing energy (crystallization, polymerization reactions, cure, oxidation, oxidative degradation, adsorption, etc.) giving rise to exothermic peaks. By another side, the second-order transitions do not modify the enthalpy and do not give origin to events endothermic or exothermic. The second-order transitions (glass transition and relaxations of thermal stresses of the polymer chain, for example) only provoke alterations in calorific capacity alternating the position of the baseline.

Shape-memory polymers may be amorphous or semicrystalline materials. Amorphous polymers showed a disordered structure throughout the length of the polymer chain. The absence of organization in the polymer structure results in the absence of marked thermal events in the DSC readings. By other side, semicrystalline polymers have partially ordered regions (short-range organization) accompanied by disordered structures in the chain extension. During the heating process, the crystalline segments absorb thermal energy and melt. The melting process is responsible for the origin of the endothermic peaks (Fig. 6). The melting event can occur at a given temperature resulting in high amplitude peaks when the material is highly crystalline or in a range of temperatures in the material that have a large size distribution of the crystalline regions in polymer chains. In the endothermic melting event, the region correspondent to central peak showed in the curves is associated with the melting point. Conversely, the cooling process, responsible for the formation of crystals, gives origin to exothermic peaks (opposite to the previous ones). Figure 7 shows the first heating obtained from shape-memory polyurethane samples synthesized in aqueous

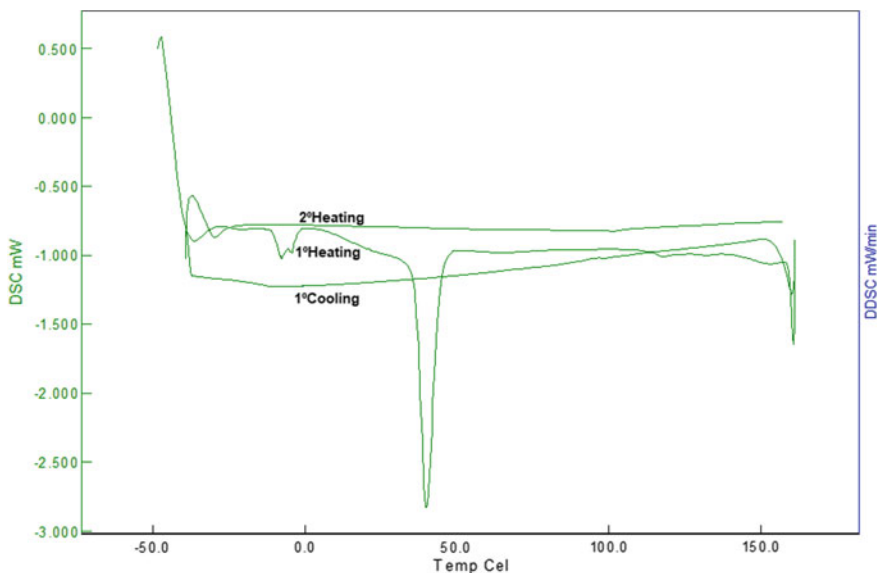


**Fig. 7** DSC assay performed with shape-memory polyurethane sample

dispersion. The heating behavior is typical of semicrystalline materials. This material has in its structure polycaprolactone diol (PCL) which are crystalline at temperatures below 40 °C (melting point) showing an endothermic event near to this temperature [10].

The experimental parameters can be modified considering the result to be obtained. Some procedures can be performed to get more accurate results. Typically, the DSC assay is performed using a complete heating and cooling thermal cycle to determine the major thermal transitions related to heating and cooling. However, for the readings relating to the crystallization process to be respected, it is necessary that the cooling rate allows crystal formation and rearrangement of the polymer chains. The relationship between temperature and time variation (heat flow) is extremely important to understand the kinetics of crystallization. Figure 8 shows a DSC assay performed with shape-memory polyurethane samples from a complete cycle (heating and cooling) followed by a heating step. Note that the heating process has an endothermic peak related to the melting of the soft domains. For the cooling, we would expect the appearance of an exothermic peak related to the crystallization process; however, the same is not detected. This phenomenon occurs due to the heat flux applied. When the applied rate is high, the segments that have undergone fusion cannot organize during the cooling process to form crystals.

The endothermic peak related to the melting process of the crystalline segments, besides allowing the determination of the melting temperature of these segments, is an important tool to study the degree of crystallization of the polymer. The calculation of the area belonging to the exothermic peak is a measure of the melting enthalpy



**Fig. 8** DSC assay with shape-memory polyurethanes: the samples were submitted to a complete cycle of heating and cooling followed by second heating

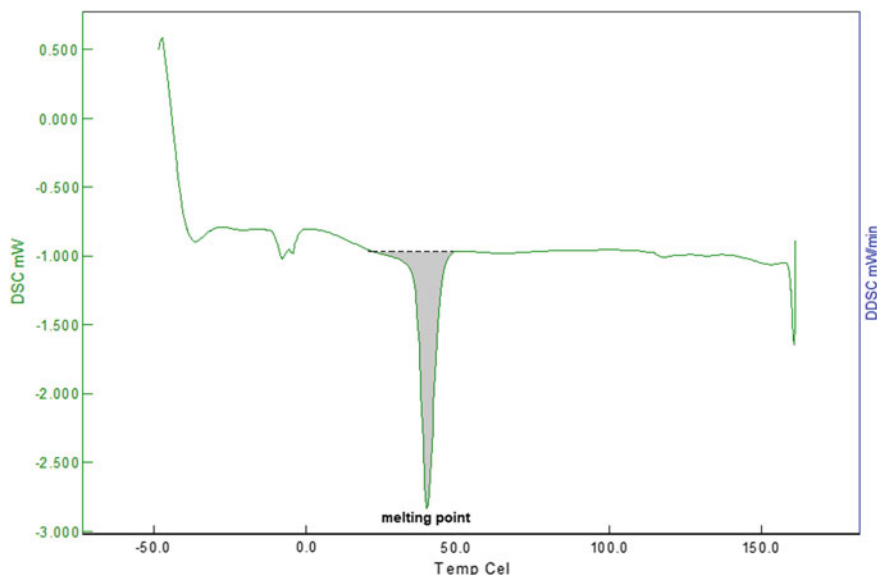
of the material (Fig. 9). By this process, we can determine the energy used to melt the crystalline segments of the material. The higher the enthalpy value obtained, the more crystalline the polymer is; in this way, it is possible to estimate the degree of crystallinity present in the polymer structure. The same process can be applied in the exothermic peaks of the cooling, considering in this case that the calculated enthalpy and the respective degree of crystallinity determine the proportion of crystallized segments during the cooling. The difference of the areas between the endothermic peak of the melting process and the exothermic peak of the crystallization process can help to determine the ideal heat flow rate for the experiment.

## 2 Blends

Polymers blends are a physical mixture of two or more homopolymers or copolymers [1, 20]. The polymers are combined to produce a new material with desirable from the combination of known polymers.

Thermal analysis is an important tool to aid in the development of polymer blends. The amorphous polymeric molecule exhibits a glassy state at low temperatures where the molecular motion is frozen. The molecular motion of the polymeric start with the increase of temperature in the glass transition temperature ( $T_g$ ) [20]. The glass transition temperature ( $T_g$ ) is a relevant thermal criterion for the blends miscibility



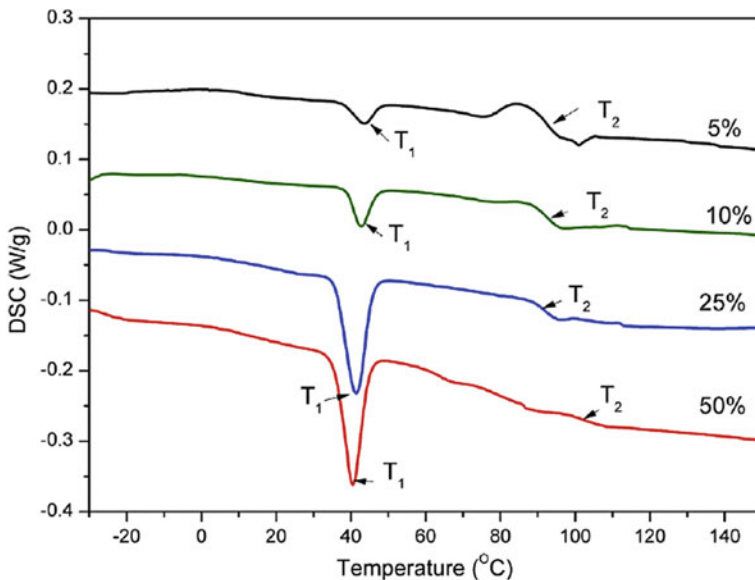


**Fig. 9** DSC enthalpy: the enthalpy of melting/crystallization is determined from the area relative to the endothermic/exothermic peak

evaluation [6]. Following this criterion, the blend is considered to be “miscible” if it exhibits only a single  $T_g$  lying in a temperature range intermediate to the  $T_g$  of the original components of the blend. The condition for the application of this criterion is that there is a difference of at least 20 °C between the  $T_g$  of the components of the phases of the polymer mixture. When a blend exhibits two or more  $T_g$  corresponding to the different phases displaced relative to the  $T_g$  of the pure components is considered to be “partially miscible.” In this case, each phase consists of a miscible mixture containing different compositions. Finally, “immiscible mixtures” exhibit the same glass transition temperatures of pure raw materials.

The melting temperature of the crystallization and the melting enthalpy may also be employed to study the miscibility of the components of the phases of the blend [21]. The information about the polymeric structure and its correlation to the physical and thermal properties could be provided in the melting temperature.

The following figure (Fig. 10), for example, shows the DSC (first heating) curves of polystyrene and the shape-memory polyurethane (PS/SMPU) blends produced by thermomechanical mixing [21]. Note that the curves show two thermal transitions correlated with the melt temperature of the soft segments (approximately 45 °C) of the SMPU and the glass transition temperature of the polystyrene phase (approximately 90 °C) [10]. Note that the glass transition temperature of the polystyrene was slightly reduced when the SMPU concentration was increased. At the same time, the enthalpy of fusion becomes higher. Modifications in the parameters occur because the interaction between the PS and SMPU chains in the mixing interfaces restricts

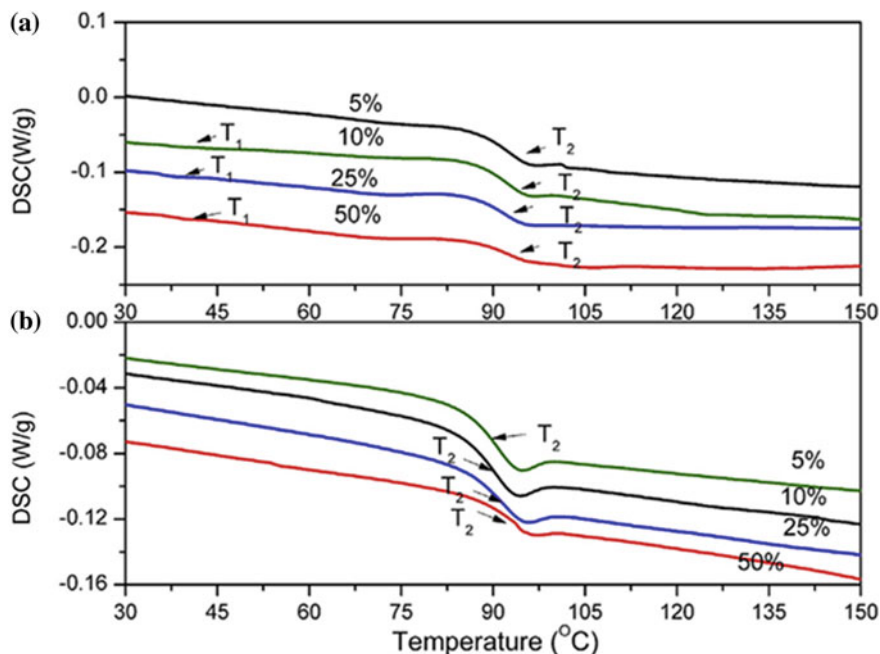


**Fig. 10** DSC curves of the non-compatible blends (Polystyrene—PS/shape-memory polyurethane—SMPU). The curves show blends of composition of 5% wt% (5%PU/95%PS), 10% wt% (10%PU/90%PS), 25% wt% (25%PU/75%PS), and 50% wt% (50%PU/50%PS). Reproduced with permission [21]

the crystallization in the SMPU phases and contributes to the reduction of the glass transition temperature of the PS.

The addition of compatibilizer is an alternative to increase the dispersion and adhesion between the phases of a blend formed by immiscible polymers. The compatibilizers are usually blocked or graft copolymers, which act at the interface, reducing interfacial tension [22]. According to Bellin et al. [18], compatibilizers act as emulsifiers by reducing phase interfacial energy and domain size. According to Araújo et al. [23], another alternative is to generate this copolymer in situ during the preparation of the mixture through grafting reactions using functionalized polymers. In this case, the compatibilizing copolymer would migrate to the interfacial region of the dispersed phase, increasing interfacial adhesion and reducing the size of the dispersed phase [24]. When the compatibilization process is effective, it can modify the thermal transitions in the material, causing a reduction of the melting temperature of the crystallized phases.

The glass transition temperature and the melt temperature may be used as a parameter for studying the miscibility of the blends with the addition of compatibilizer. Figure 11 shows the effect of the addition of compatibilizer (maleic polystyrene anhydride) on the thermal transitions of the blends of shape-memory polyurethane and polystyrene. In Fig. 11a, the compatibilization was performed using a pre-compatible shape-memory polyurethane (shape-memory polyurethane exerted



**Fig. 11** DSC curves of the compatibilized blends (Polystyrene/Shape-Memory Polyurethane/Polystyrene co-anhydride maleic). The curves show blends of composition of 5% wt% (5%PU/95%PS), 10% wt% (10%PU/90%PS), 25% wt% (25%PU/75%PS), and 50% wt% (50%PU/50%PS): **a** the compatibilization was performed using a pre-compatibilized shape-memory polyurethane; **b** the compatibilizer was added during the thermomechanical cycle. Reproduced with permission [21]

with maleic polystyrene anhydride) blended with polystyrene. In Fig. 11b, the compatibilizer was added during the thermomechanical cycle (thermomechanical mixture of polystyrene/shape-memory polyurethane/maleic polystyrene anhydride). Note that the melt transition is reduced (temperature close to 40 °C). This reduction occurred because the degrees of phase mixing in these systems restrict the crystallization of soft segments. The presence of PS units in the SMPU and SMA chains hinders the crystallization of the soft segments [25].

According to Song and Liao [25], the study of heat capacity differential,  $dC_p/dT$ , with temperature signal is an important resource to study the miscibility between two components of a blend. This is because the differential is sensitive to change the components of blend [26].

The analysis is performed from the study of derivative ( $dC_p/dT$ ) as a function of temperature. For a fully miscible blend of two-component polymers, the differential as a function of temperature is a single Gaussian curve. For a mixture of fully immiscible two-component polymers, it is a two-separate Gaussian. For partially miscible two-component polymer blends, the signal is a sum of multiple Gaussian [25, 26].

### 3 Composites

Composites are materials constructed of two or more components with different physical or chemical properties. These components are combined to produce a material having different properties than the individual components. There is no chemical interaction. The individual components remain separate and distinct within the final structure. The materials are combined for the purpose of obtaining better properties than the source materials for specific technological applications.

The studies of the thermal transitions of the materials' constituents of the composite are fundamental to obtain materials with satisfactory properties. Many works showed the importance of the thermal characterization for the development and the study of composites materials. The parameters are strictly related to the structure. The principal parameters are melting point, glass transition temperature, and heat capacity.

Song and Liao [25], by example, has been developed modulated differential scanning calorimetric (MDSC) method combining transmission electron microscopy (TEM) for characterizing the morphology of composite latex particles. The polymer composites' properties are strictly related to the degree of crystallization, crystalline structure, and morphology [27].

The possibilities of thermal analysis applications for composite materials depend on the composition and number of materials used to produce them. However, the basic principles used in the analysis of a constituent phase can be used to analyze the properties of the materials. Thermal transitions are used to determine composite morphology. Melting transitions, for example, are employed to study the degree of crystallization of the phases of the composite material and possible structural changes in the polymers after the production of the composite material. From this transition, the properties directly related to the crystallization of the polymers can be determined. Basically, the same thermal parameters (melting point, glass transition, melting enthalpy, melting crystallization, etc.) can be used to determine or predict the properties of a composite material. The changes existing in these parameters before and after the production of the composite material are taken as reference for study in the structural changes and in the degree of interaction between the constituent phases of the composite material.

### 4 Conclusion

The characterization of material properties during the design steps is essential for cost and time reduction. The characterization of a material during development allows to partially predict the behavior during its useful life.

Considering this point of view, DSC is an essential tool for the development and characterization of shape-memory polymers, polymer blends, and composites. This is because the thermal transitions from the constituent structures of the polymer

chain determine the behavior of these materials. In shape-memory polymers, thermal transitions are responsible for determining how programming processes can occur. The glass transition and the melt temperature are intrinsically associated with the mobility of the polymer, structural, and morphological characteristics. High thermal transition temperatures are generally associated with high molar mass, crystallinity, and high entanglement.

On the other hand, in composites and mixtures, the thermal transitions are an important parameter to study the affinity between the constituents of the polymer phases, interfacial adhesion, and degree of mixtures between the constituents of the polymers forming a blend or composite.

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