

Polymeric Phase Change Composites for Thermal Energy Storage

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ABSTRACT: This article describes a group of thermal energy storage (TES) composites that combine TES and structural functionality. The composites are encapsulations of low melt temperature phase change materials (PCM) such as paraffin waxes in polymer matrices. Room temperature cured bisphenol-A epoxy and styrene-ethylene-butylene-styrene (SEBS) polymers are chosen as matrix materials because of their excellent chemical and mechanical properties. The polymeric network structure in the composite encapsulates the PCMs, which transform from the solid to the liquid phase. The PCMs provide the energy storage function via

the solid-liquid latent heat effect. The resulting composite exhibits dry-phase transition in the sense that fluid motion of the PCM, when in the liquid phase, is inhibited by the structure of the polymer matrix. The polymer matrix is formulated to provide structural functionality. The latent heat, thermal conductivity and contact conductance, and structural moduli of composites having various PCM-to-matrix volume fractions are measured. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1240–1251, 2004

Key words: thermal properties; composites; phase behavior

INTRODUCTION

Many electronic devices are variable power devices requiring thermal control. As a consequence, conventional coolers must be designed for peak power operation or an active control system must be incorporated into the cooler to accommodate variations in heat loading. Incorporation of a thermal energy storage (TES) mechanism into the device will allow for a smaller, less power consuming and more reliable cooling system that is sized for some intermediate heat load. Heat is then stored in the TES system during periods of high power operation. It is subsequently released from the system during periods of reduced power operation. Phase change materials (PCM) formulated to undergo phase transition at key temperatures can provide this load-leveling capability via the latent heat effect.¹

Polymeric encapsulants provide an opportunity to utilize phase change materials within a unique composite structure. A variety of polymer matrices are available with a large range of chemical and mechanical properties. There are also many options for processing the polymer materials. These include injection

molding for thermoplastics and reaction injection molding for thermosets. A full range of mechanical properties can be achieved by modifying the structure of the polymer matrices. Thermoset polymers are particularly useful for this application because they can be used to encapsulate phase change materials at room temperature, so that the low transition temperature PCMs can stay in the solid phase during composite processing.

In many applications, such as military electronics where electronic packaging is very compact, TES systems should add no mass (or volume) to existing systems. Materials having multiple functionality can be used to meet this constraint. For example, TES composites that combine the heat storage function with a structural function can be formulated. These composites can be incorporated into the system as structural elements (frame members, enclosure skins, shock dampers, or acoustical control materials, etc.), while at the same time they are part of the temperature control system. Furthermore, hybrid TES coolers must have steady operating performance that is at least equal to existing systems, while at the same time they provide for improved reliability. This requirement can be met by incorporating desirable thermal and mechanical characteristics into the TES composite.

TES was employed in a variety of temperature stabilization applications, including thermal control of electronics. However, the requirement for a structurally simple, low unit cost, and easy-to-volume-manufacture device precludes many potential solutions.

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Typically, three methods are used for heat storage: reversible thermochemical heat storage, sensible heat storage, and latent heat storage. These methods differ in the amount of heat that can be stored per unit weight or volume of the storage medium, and in the time–temperature history of the medium during the heat storage process.

This research investigates the use of latent heat storage for thermal energy storage applications. By using this method, thermal energy is stored by means of a reversible change of state, or phase change of the storage medium. As the amounts of energy involved in these changes of state are usually large, this results in lower mass and/or volume required, which is often important in real applications. Also, in practice, latent heat storage systems make use of some sensible heat capacity in the system, so this contribution must be considered.

Solid–liquid PCMs are often used for heat storage applications. Examples include water, salt hydrates, paraffins, certain hydrocarbons, and metal alloys. Leoni and Amon² use paraffin PCM to control the operating temperature of wearable electronics. Systems utilizing PCMs that undergo solid–liquid transition present liquid expansion and containment problems, and, their performance when the PCM is in the liquid phase could be sensitive to system orientation or *g*-loading.

Certain molecular crystals undergo solid-state crystal transformations that absorb sufficient heat; they may be used for practical heat storage applications.^{3,4} An advantage of these solid–solid phase transformations is that, because of the absence of the liquid phase, there is no concern about liquid leakage. Unfortunately, these solid–solid PCMs have two disadvantages. First, the thermal conductivities of these materials are low for both solid phases. The second problem is that some of these materials have high vapor pressure and must be encapsulated for practical applications.

Bauer and Wirtz⁵ describe a TES composite that incorporates pentaglycerine (PG) as the PCM. A plate-like, thermally conductive sandwich structure is used. The structure has aluminum plates as skin and an aluminum foam core impregnated with PG. The effect of the aluminum foam metal fraction on effective thermal conductivity of the sandwich structure is investigated. The composite is suitable for use in electronics packaging.

Wirtz et al.⁶ also investigated the thermal response of a hybrid cooler, which is charged with PG/neopentaglycol (NPG) dry solid–solid PCM. They formulated the mathematical model that simulates the performance of the storage unit and tested the prototype heat sink that incorporates heat storage by using this dry PCM.

Zheng and Wirtz⁷ developed a semiempirical thermal response model for a hybrid TES heat sink. PG, NPG, and their solid solutions are used as solid–solid PCMs. The thermal response of a plate-type fin configuration is investigated. The design of a plate-type TES unit is optimized to minimize the temperature difference between the base temperature and the transition temperature of the PCM. Two figures of merit for the hybrid TES unit are developed.⁸ The study shows that the volumetric figure of merit and the temperature control figure of merit are related to the performance specification of the storage unit and its physical design.

Dry TES composites are encapsulations of materials that undergo either solid–solid phase transition, or they are composites that encapsulate a solid–liquid PCM in such a way that the liquid phase characteristic is not apparent. Colvin and Mulligan⁹ experimented with slurries of microencapsulated solid–liquid PCMs as a high-performance heat transfer liquid, and Fossett et al.¹⁰ experimented with avionics cold plates filled with these encapsulations. These are very attractive material systems because, similar to the solid–solid PCMs, packaging difficulties associated with liquids and vapors are mitigated so that very simple cooler design concepts can be implemented.

Immobilization of paraffin was accomplished by using a variety of approaches including encapsulation in graphite foams and other materials.^{11,12}

Yamaguchi¹³ describes the invention of a heat sink for effectively conducting and dissipating the heat of an electronic component. The invention comprises a heat dissipation plate formed by an aluminum plate (or other metal such as copper) and a phase change member made of a mixture of paraffin and epoxy resin that has alumina as thermal conductivity enhancement. In the patent, other potential polymer matrices such as styrene–ethylene–butylene–styrene (SEBS), styrene–isoprene–styrene (SIS), and styrene–ethylene–propylene–styrene (SEPS) are claimed.

Xiao et al.^{14,15} investigate composites based on paraffin and styrene–butadiene–styrene (SBS) block copolymer. These are described as shape-stabilized PCMs. The composites are prepared by mixing paraffin and SBS at 150°C by using a two-roll mixer. The paraffin used is a technical-grade paraffin with a melt temperature of 56–58°. The results also show that the composite can retain shape even when the paraffin is in the liquid state, and no paraffin leakage is observed during the thermal performance testing.

Inaba and Tu¹⁶ investigate another shape-stabilized paraffin system. In this case, paraffin and high-density polyethylene (HDPE) are mixed at high temperature. The resulting composite consists of 74 wt % paraffin and 26 wt % HDPE. The composite keeps its shape when the paraffin is in the liquid state. The thermo-

TABLE I
Approximate Property of Various PCMs

Material type	Transition	Approp. temp. range (°C)	Density (g/cm ³)	Latent heat (J/cm ³)	Latent heat (J/g)	Conductivity (W/m K)
Paraffin (Eicosane, etc.)	S-L (dry)	-12-71	0.75-0.88	128-197	145-260	~ 0.2
Metallics	S-L (dry)	30-125†	6-10	200-800	20-80	10-50
Polyalcohols (PG/NPG)	S-S (dry)	24-89	~ 1.1	144-212	140-200	0.17-0.22
Nonparaffin Organics	S-L (wet)	-13-187	0.85-1.54	131-438	80-280	~ 0.2
Salt hydrates	S-L (wet)	28-137	1.5-2.2	270-650	120-300	0.2-0.5

physical properties of the composite such as density, heat capacity, and latent heat are measured.

Wirtz et al.¹⁷ utilized a sandwich structure of a TES storage unit that incorporates paraffin/SEBS composite. Metal plates (copper or aluminum) can be used as a heat spreader to enhance the thermal performance of the unit. The utilization of thin layers of PCM/polymer composite in metallic substrates provides excellent heat transfer in these low thermal conductivity materials.

These thermoplastic polymer/phase change material composites provide relatively large storage capacity. Because of the encapsulation of the PCM when it is in the liquid phase, liquid phase characteristic is not apparent at elevated temperatures. Furthermore, the operation of a dry system is passive and inherently reliable. The solid-liquid PCM can be encapsulated so that thermal performance is independent of g-loading or orientation.

This work focuses on immobilizing paraffin waxes to form dry TES composites. The polymer matrices used are room-temperature cured bisphenol-A epoxy and SEBS polymers. The PCM used offer some significant advantages over other PCMs, as follows:

1. Paraffins have large mass-based latent heats (~ 250 J/g) and varied phase change temperatures. This gives the flexibility to choose proper PCMs for different applications.
2. Transition temperatures can be selected by choosing different systems.
3. Unlike some non-hydrocarbon-based PCMs (i.e., hydrated salts), the material formulations of the paraffins are stable. Phase separation after repeated cycling across the solid-liquid transition does not occur.
4. Unlike some high vapor pressure solid-solid phase transition materials such as polyalcohols, the vapor pressure of paraffin waxes is very low.
5. When they are microencapsulated, the heat transfer due to convection when the PCM is in the liquid phase is negligible. Conduction dominates heat transfer so that the composite acts like a solid. As a consequence, performance is reliable and g-load is insensitive.

6. These materials are produced in substantial quantities by the chemical process industry and thus they are readily available and inexpensive.

Table I summarizes the thermophysical properties of various PCMs that could be used in thermal management applications. Transition of the paraffins spans the temperature range of applications for thermal management of electronics (which is normally 40-80°C).

In this article, we describe procedures for formulating novel TES composites that imbed paraffin waxes in polymer to provide containment of the liquid melt, and control the mechanical properties of the composite. Steady-state and transient methods for measuring the thermal conductivity are described. Measurements of latent heat, transition temperature, thermal conductivity, bond thermal resistance, elastic, and loss modulus as a function of temperature are reported.

EXPERIMENTAL

Phase change materials

Two paraffin mixtures are used as phase change materials. The first paraffin mixture (IGI 422, Pourret Inc.) is used as the organic phase change material. It has a melt temperature range of 44-58°C and a specific gravity of 0.8. The other paraffin mixture (BW-422, Blend Waxes Inc., Oshkosh, WI) used has a melt temperature range of 50-60°C.

Paraffin particles are made by an emulsification method.¹⁸ The surfactant alkylaryl polyether alcohol (Triton X-100, Fisher) is dissolved in deionized water at 80°C; then, the molten paraffin liquid at 80°C is mixed with water by using a mechanical mixer. Small droplets are formed with the aid of the surfactant at high temperature. The amount of surfactant used is 3 wt % of the paraffin liquid, and paraffin is about 30 wt % of the total mixture. Mixing takes place for 10 min at 80°C. Cold deionized water (5°C) is then blended while mixing and the paraffin liquid droplets are solidified. The solid particles are suspended in the mixture because of the presence of the surfactant and mixing. After the mixture is cooled down to room temperature, it is filtered by using size 2 filter paper;

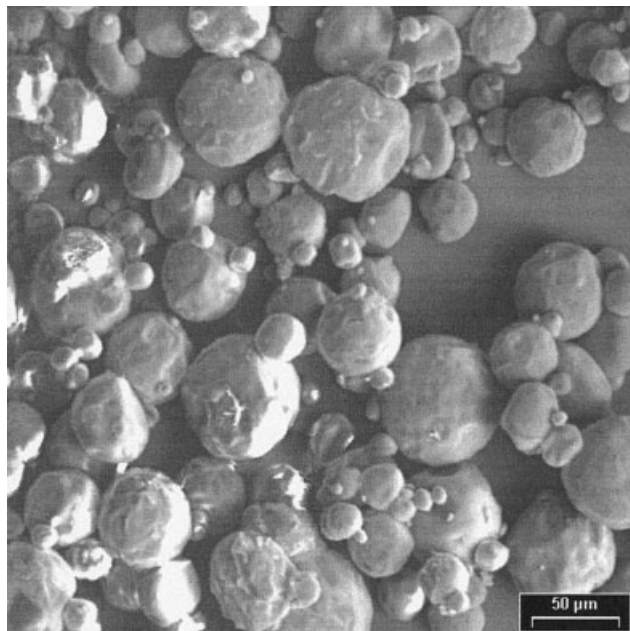


Figure 1 SEM image of paraffin particles produced by the emulsification method.

the filter paper size is $0.5 \mu\text{m}$. Paraffin particles are collected and dried in air for 12 h before being used to make composites. The particle size distribution is measured by using a laser diffraction method (Microtrac Inc., particle size distribution analyzer, X-100). Scanning electron microscopy (SEM) of the paraffin particles are shown in Figure 1. The SEM shows that the particles are spherical and exhibit rough surfaces.

Particle size plays an important role in the composite properties. The finer the particles, the more particle-polymer contact area. This leads to better mechanical and thermal properties. In this work, the paraffin particle size distribution is obtained by using a size distribution analyzer. The paraffin particles are dispersed in water and a laser diffraction method is used to measure the distribution of the particle sizes. The results are presented in Figure 2, which is a cumulative particle size distribution. Most paraffin particles have diameters from ~ 10 to $\sim 100 \mu\text{m}$.

Matrix materials

One thermoset and one thermoplastic are evaluated. The thermoset is a room temperature cured epoxy. The epoxy polymer is prepared from the diglycidyl ether of bisphenol-A epoxy (DGEBA; DER 736, $M_w = \sim 400$ and DER 324, $M_w = \sim 700$, functionality = 3.4, Dow Chemical) and a mixture of *m*-xylene diamine and isophorone diamine as curing agents (EPI-CURE 3370, Shell Chemical). The three following epoxy systems are used: $\sim 700 M_w$ DGEBA, $\sim 400 M_w$ DGEBA, and 50 wt % $\sim 700 M_w$ DGEBA + 50 wt %

$\sim 400 M_w$ DGEBA. The specific gravity of the epoxy is 1.2 for $\sim 700 M_w$ DGEBA and 1.0 for $\sim 400 M_w$ DGEBA. The equivalent weights are 175–205 and the functionalities are 2.0 for both. The material properties are listed in Table II.

One thermoplastic SEBS block copolymer (Kraton G1657M, Kraton Inc., 2–3 million molecular weight) is also used as the polymer matrix in a paraffin/SEBS composite and a SEBS coating is applied to the paraffin/SEBS composite. The SEBS copolymer is a linear triblock polymer with a styrene content of $\sim 13\%$.

Composite preparation procedure

For epoxy, polymer/PCM composites are made by thoroughly mixing the PCM particles with polymer at room temperature. The composition of the composite is 80 wt % paraffin/20 wt % epoxy. The composition of the epoxy system is stoichiometric. The mixture is then cast into the space between two aluminum plates by using a U-shaped Teflon mold. The sample is then cured at room temperature for 24 h. The SEBS/paraffin composite fabrication method is different because it is a thermoplastic polymer. Solid paraffin is placed in a three-necked flask with a stirrer rod. It is then heated to 300°C while stirring at 150 rpm in a nitrogen environment. The stainless stirrer used is $1.9 \times 7.5 \text{ cm}$. SEBS and fillers (such as silica) are then added into the molten paraffin. The paraffin, polymer, and fillers are mixed for 45 min. The final mixture, which is a homogeneous blend of paraffin, polymer, and fillers, is then poured into a Teflon-treated aluminum mold and allowed to cool to room temperature.

SEBS is also used to coat the composite. The polymer is dissolved in toluene (50 wt % SEBS) at room temperature. The paraffin/SEBS sample is dipped into the SEBS/toluene solution and withdrawn after 5 s.

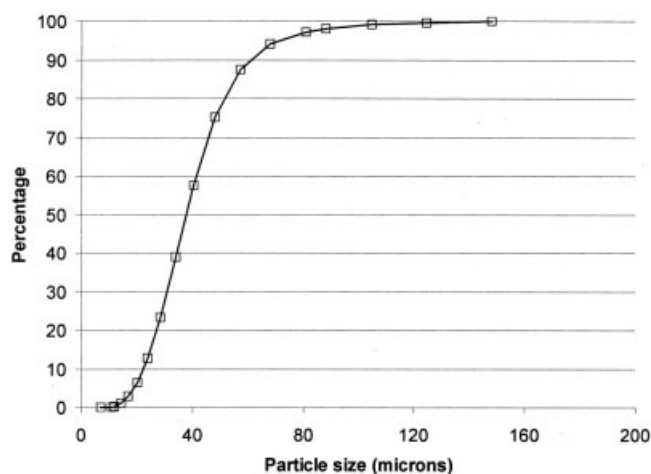


Figure 2 Paraffin particle size distribution from emulsification method.

TABLE II
Chemical Properties of Polymer Matrices

Matrix materials	Chemical name	Curing agent	Specific gravity	Molecular weight	Functionality	Equivalent weight
DER 324 epoxy	DGEBA	EPI-CURE 3370	1.2	~ 700	3.4	175–205
DER 736 epoxy	DGEBA	EPI-CURE 3370	1.0	~ 400	3.4	175–205
50% DER 324/50% DER 736 epoxy	C ₅ H ₁₂ O ₂	1.06	1.14	~ 550	3.4	175–205

After the toluene is removed by air-drying, a thin SEBS coating, approximately 100 μm thick, is left on the surface of the composite. The SEBS coating has good adhesion to the SEBS/paraffin composite. The SEBS coating apparently interpenetrates into the SEBS in the core because of SEBS diffusion in the toluene solvent. This results in a continuous bond of SEBS across the coating into the core material.

Instrumentation

Differential scanning calorimetry (DSC, Perkin–Elmer Pyris 1) is used to measure the latent heat and melt temperature of the composite materials. The temperature accuracy is $\pm 0.1^\circ\text{C}$, and heat flow repeatability is $\pm 0.2 \mu\text{W}$. A small quantity of sample (usually from 5 to 10 mg) is sealed in a small aluminum pan. The sample and reference pans are heated at $5^\circ\text{C}/\text{min}$ and the net heat flow is measured. Thermal transitions including melt temperatures and glass transitions are identified by using DSC.

Dynamic mechanical analysis (DMA, Perkin–Elmer 7e) is used for measurement of storage and loss moduli (using sinusoidal deformation) as a function of temperature. The displacement repeatability is $\pm 50 \text{ nm}$, and force repeatability is $\pm 0.003\text{N}$. Measurements are done by using a three-point bending accessory.

The thermal diffusivity of SEBS/paraffin composites are measured by using a transient heat transfer approach. The instrumentation for the transient method is shown in Figure 3.

A sample core ($\sim 2 \text{ cm}$ thick) is cast between two aluminum plates (0.16 cm thick). Two thermocouples are imbedded in the aluminum plates. One of them is imbedded in the aluminum plate with the heater. The other one is imbedded in the other aluminum plate to confirm that the temperature of that aluminum plate remains constant. This boundary condition is required by the semi-infinite slab model. A third thermocouple is imbedded in the core about 1 cm from the aluminum plates. A foil heater is glued to one of the aluminum plates to provide the heat input. The sandwich structure is insulated by polystyrene rigid foam to prevent heat loss to the surroundings. For testing when paraffin in solid state, the sample is equilibrated

at room temperature ($\sim 25^\circ\text{C}$). Xu's algorithm is used to calculate the thermal diffusivity of the samples.¹⁹

RESULTS AND DISCUSSION

The polymer matrix plays an important role in the PCM/polymer composite. Because small PCM particles are used in the composite, the polymer provides the primary reinforcement of the composite. The polymer matrices used should not react with the PCMs, be thermally stable in the working temperature range, have sufficient strength to encapsulate the PCMs (in both the solid and the liquid phase), and incorporate structural functionality into the composites.

Latent heat/melt temperature

The melting temperatures and latent heats of the paraffin and their polymer matrix composites are measured by using DSC. The DSC thermogram of paraffin and the paraffin/polymer composite are presented in Figures 3 and 4.

In Figure 4, the melt temperature of the paraffin (IGI 422)/ $\sim 700 M_w$ DGEBA sample is measured by calculating the onset temperature of the peaks. The completion of the transition is determined from the trailing edge of the curve. A heating rate of $5^\circ\text{C}/\text{min}$ is used in this work. Figure 4 shows that paraffin and its polymer composite have two major transition temperatures, one at $\sim 45 \pm 0.5^\circ\text{C}$ and a second at $\sim 58 \pm 0.5^\circ\text{C}$. The broad melt peaks of the paraffin may indicate that the paraffin mixture has a broad molecular range.

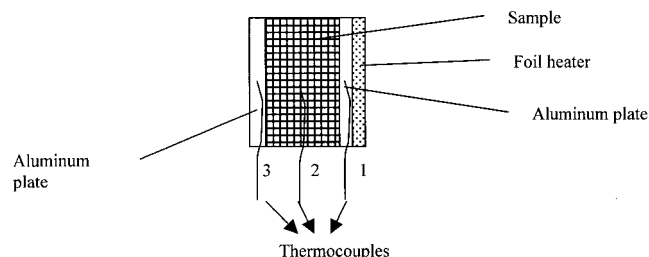


Figure 3 Sample structure for transient thermal diffusivity measurement.

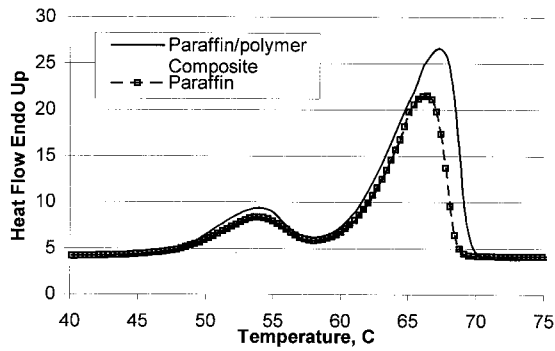


Figure 4 DSC heat flow measurement of pure paraffin and paraffin/epoxy composite, 85% paraffin.

The latent heat of the transition can be calculated from the area of the heat flow peak. The area of the peak is proportional to the mass of the sample. Integration under the heat flow curve and division by the mass of the sample gives the latent heat. The paraffin mixture has an overall latent heat of 252 J/g and a composite, which is about 75 wt % paraffin, has a latent heat of 189 J/g, which is 75% of the latent heat of the pure paraffin. This indicates that there is no chemical reaction between the paraffin and the polymer matrix. The two peaks represent the two pure substances in the paraffin mixture; the peak with a transition temperature of 58°C has a much larger area than the smaller peak, which has a transition temperature of 45°C. This indicates that the majority of the paraffin mixture is made up of the higher temperature paraffin, whose transition is the major transition of the paraffin mixture.

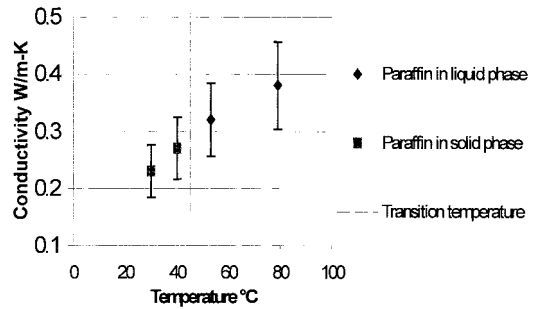


Figure 6 Thermal conductivity of paraffin/epoxy composite, 85 wt % paraffin.

The DSC result of paraffin (BW-422) is presented in Figure 5. A heating rate of 5°C/min is used. Figure 5 shows that the paraffin has two major transition temperatures, one at $\sim 44 \pm 1^\circ\text{C}$ and a second at $\sim 55 \pm 1^\circ\text{C}$. The paraffin has an overall latent heat of $\sim 194 \pm 5 \text{ J/g}$.

Thermal conductivity

Thermal conductivity measurements are done on the polymer matrix and polymer/PCM composites by using steady-state and transient methods. The results are presented in Figure 6 for paraffin/thermoset polymer composites.

The thermal conductivity of the epoxy/paraffin composite is shown in Figure 5. The conductivity of the composite is $0.23 \pm 19\% \text{ W/m-K}$ at room temperature and increases with temperature. A 3- σ error analysis is done by Monte Carlo simulation. The in-

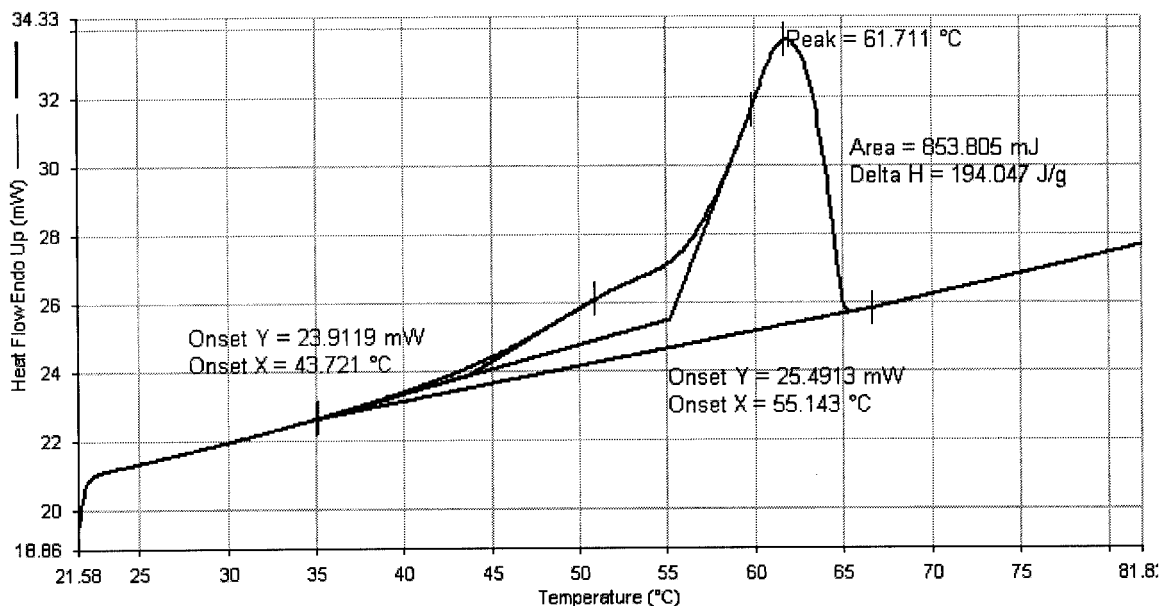


Figure 5 DSC thermogram for paraffin (BW 422).

TABLE III
Thermal Diffusivities of Various PCM and PCM/Polymer Composites

Sample	α , m ² /s solid state, 25–45°C	K, W/m-K, solid state, 25–45°C	α , m ² /s liquid state, 65–83°C	K, W/m-K, liquid state, 65–83°C
Paraffin	1.17 E-07 (\pm 21%)	0.22		0.22[20]
80% Paraffin/SEBS	1.13 E-07 (\pm 21%)	0.20	1.36 E-07 (\pm 21%)	0.25
50% Paraffin/SEBS	1.08 E-07 (\pm 21%)	0.19	1.22 E-07 (\pm 21%)	0.22

strument accuracies, which are provided by the manufacturers, are used in these calculations.

The thermal conductivity of the composite slightly increases with temperature. The highest conductivities are observed when the sample temperature is higher than the paraffin melt temperature (\sim 45°C in this case) and the paraffin particles are in the liquid phase. The rate of change of the thermal conductivity with temperature is less when the paraffin is in the liquid phase than when the paraffin is in the solid phase.

Thermal diffusivities of paraffin, 50 wt % paraffin/50 wt % SEBS, and 80 wt % paraffin/20 wt % SEBS are measured. In thermal diffusivity measurement, because the transient method is used, there is a temperature gradient in the sample. The sample temperature is averaged for thermal diffusivity calculations. For solid-state measurements, the temperature is \sim 35°C and for liquid measurements, and the temperature is \sim 75°C. The thermal conductivity of the samples are calculated from the thermal diffusivity, density, and heat capacity of the material. The results are given in Table III.

Literature values show that the thermal conductivity of the liquid paraffin is lower than solid paraffin.²⁰ O'Connor and Weber report that, for a paraffin con-

sisting of 99% hexatriacontane (C₃₆H₇₄, which has a melt temperature of 72°C), the thermal conductivity is 0.28 W/m-K when the paraffin is in the solid state (no temperature reported). The thermal conductivity is 0.22 W/m-K when the paraffin is in the liquid state (no temperature reported). They also report that the paraffin has a volume expansion of 12.4% from the solid to the liquid state. For a SEBS polymer with a ethylene butylene to styrene ratio of 71 : 29, Agari et al.²¹ report that the thermal conductivity is 0.28 W/m-K at $50 \pm 3^\circ\text{C}$.

Dynamic mechanical testing

The storage and loss moduli of the composites, epoxy matrix, SEBS, and paraffin are measured by a DMA three-point bending method. The results are shown in Figures 7-14.

Figure 7 shows the storage (elastic) modulus of the paraffin, the \sim 700 M_w DGEBA epoxy, and the paraffin/epoxy composite. The heating rate is 5°C/min. As shown in Figure 7, all of the moduli decrease with increasing temperature. \sim 700 M_w DGEBA epoxy has the highest storage modulus, 883 mPa at 0°C, and decreases with temperature. This sharp decrease in

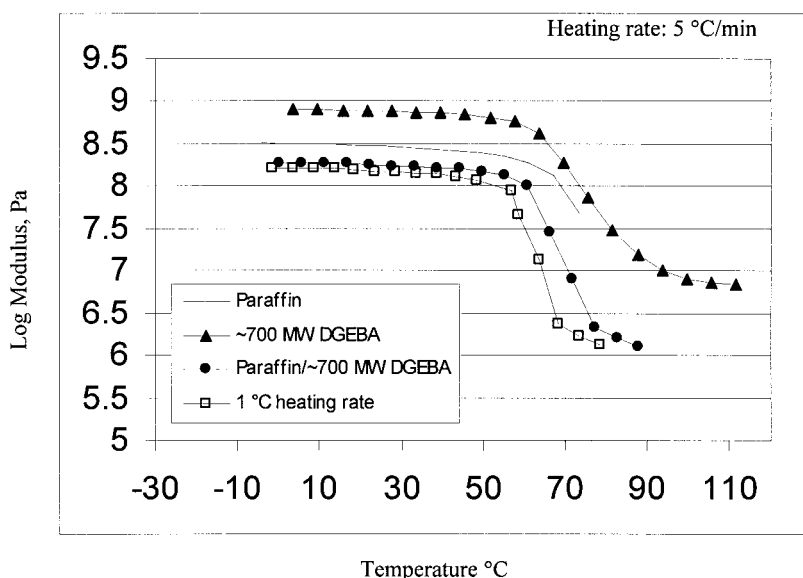


Figure 7 Storage moduli of \sim 700 M_w DGEBA, paraffin, and paraffin/ \sim 700 M_w DGEBA composite.

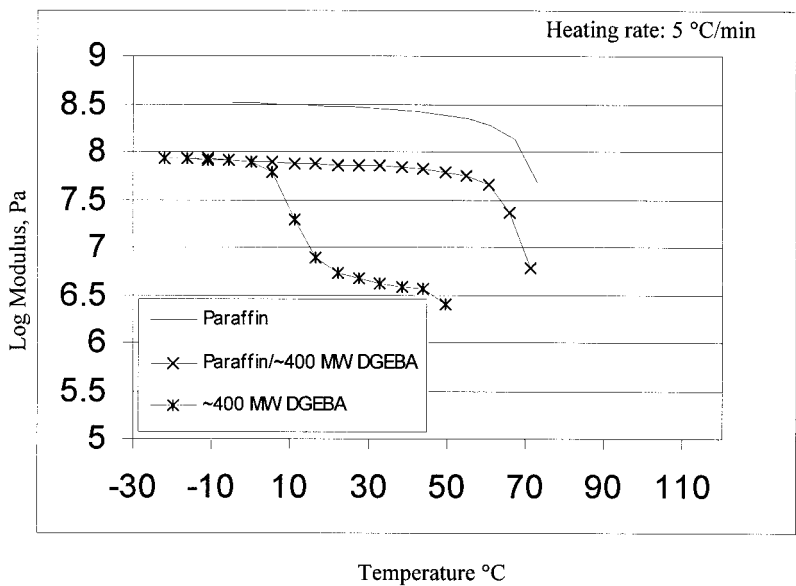


Figure 8 Storage moduli of $\sim 400 M_w$ DGEBA, paraffin, and paraffin/ $\sim 400 M_w$ DGEBA composite.

storage modulus represents the glass transition temperature (T_g) of the epoxy polymer, which is slightly below 60°C . Paraffin has the next highest storage modulus. The paraffin storage modulus decreases sharply after the paraffin phase transition, at 58°C . The paraffin/ $\sim 700 M_w$ DGEBA composite has the lowest storage modulus. It is believed that the low storage modulus of this composite may be due to poor wetting of the paraffin particles by the epoxy matrix. In the case of the $\sim 700 M_w$ DGEBA/paraffin composite, it is believed that the composite properties are inferior to what might be expected from a law of mixtures determination because the mechanical properties are dom-

inated by the poor wetting at the interface. Figure 8 shows the storage moduli of the paraffin, $\sim 400 M_w$ DGEBA epoxy and the paraffin/epoxy composite. The $\sim 400 M_w$ DGEBA epoxy has much lower modulus than $\sim 700 M_w$ DGEBA epoxy discussed in Figure 9. The storage modulus of the epoxy is $\sim 92 \text{ mPa}$ at -20°C . The storage modulus decreases sharply at $T_g \sim 8^\circ\text{C}$ for this polymer. The paraffin/epoxy $\sim 400 M_w$ DGEBA composite has storage modulus values intermediate between the values of paraffin and the polymer. Because 80 wt % of the composite is paraffin, this component dominates the properties of the composite. The storage modulus of the composite decreases dra-

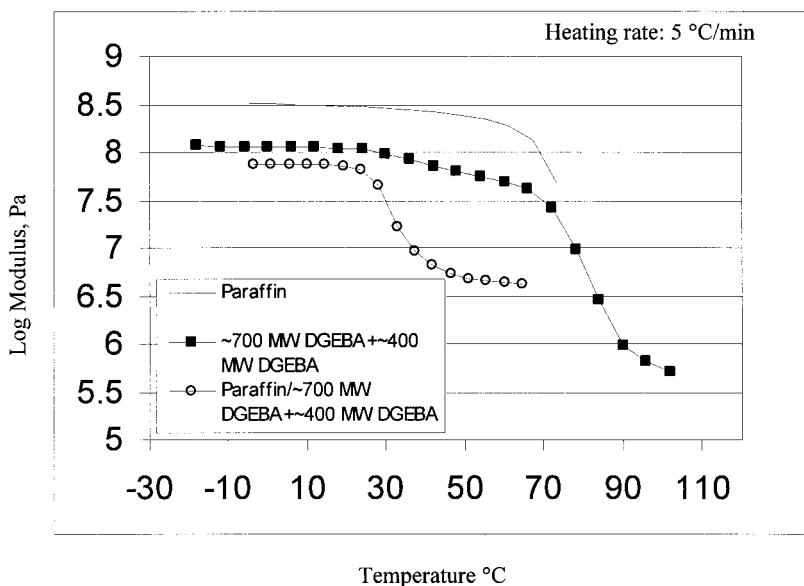


Figure 9 Storage moduli of $\sim 400 M_w + \sim 700 M_w$ DGEBA, and paraffin/ $\sim 400 M_w + \sim 700 M_w$ DGEBA composite.

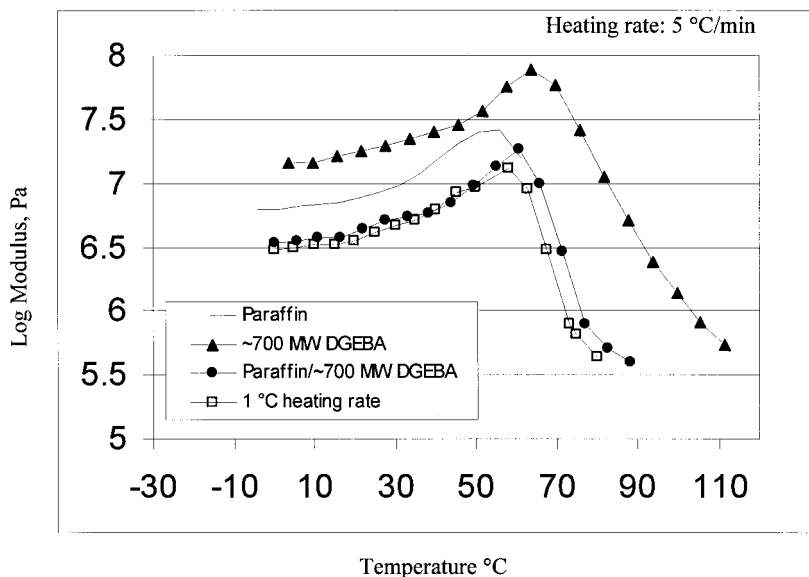


Figure 10 Loss moduli of $\sim 700 M_w$ DGEBA, paraffin, and paraffin/ $\sim 700 M_w$ DGEBA composite.

matically when the paraffin undergoes a solid-liquid phase transition.

Figure 9 shows the storage moduli for the paraffin, mixtures of 50 wt % $\sim 700 M_w$ DGEBA and 50 wt % $\sim 400 M_w$ DGEBA and the paraffin/ $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA composite. A mixture of the two polymer matrices are investigated here to demonstrate that polymeric/thermal energy storage composites can be developed with controllable mechanical properties. The storage modulus of $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA, which is about 82 mPa, is very close to the storage modulus of $\sim 400 M_w$ DGEBA at low temperatures because the mechanical properties of the softer polymer dominate. The storage modulus of the paraffin/ $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA composite has two peaks. The first one is $\sim 32^\circ\text{C}$, which is due to the storage modulus decrease of the $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA at the same temperature. The second peak is $\sim 60^\circ\text{C}$, which is related to the phase transition of the paraffin.

Figure 10 shows the loss moduli (damping modulus) for paraffin, $\sim 700 M_w$ DGEBA epoxy, and paraffin/epoxy composite. The peaks of the loss moduli represent the maximum mechanical energy absorbing potential of the material. The peak of the loss modulus occurs at the T_g of the amorphous polymer. $\sim 700 M_w$ DGEBA has a peak value of 181 mPa at 55°C . For paraffin, the loss modulus reaches its maximum at 56°C due to the phase transition. The loss modulus of the paraffin/ $\sim 700 M_w$ DGEBA epoxy composite has a peak at $\sim 57^\circ\text{C}$. In this case, the T_g of the $\sim 700 M_w$ DGEBA is coincidentally nearly the same as paraffin phase transition temperature.

Figure 11 shows the loss moduli for paraffin, $\sim 400 M_w$ DGEBA epoxy, and the paraffin/epoxy composite.

It shows that $\sim 400 M_w$ DGEBA has a T_g at $\sim 8^\circ\text{C}$: the loss modulus at the peak is about 7.5 mPa. The loss modulus curve for paraffin/ $\sim 400 M_w$ DGEBA epoxy composite shows a small peak near the glass transition temperature of the $\sim 400 M_w$ DGEBA epoxy (8°C), but the peak at 57°C is very clear and represents the phase transition effect of the paraffin.

Figure 12 shows the loss moduli for the paraffin, $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA epoxy, and the paraffin/epoxy composite. The peak loss modulus of the $\sim 700 M_w$ DGEBA + $\sim 400 M_w$ DGEBA epoxy is about 24 mPa and the T_g of the system, at $\sim 32^\circ\text{C}$, is between those of $\sim 700 M_w$ DGEBA and $\sim 400 M_w$ DGEBA epoxies. This epoxy mixture obeys the rule of mixture, which gives the ability to tailor the T_g of the polymer by changing the ratio of the two components. The loss modulus of the paraffin/ $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA epoxy composite has peaks that are caused by both paraffin and $\sim 400 M_w$ + $\sim 700 M_w$ DGEBA. There are two peaks on the loss modulus curve: the first one is at around 32°C , which represents the glass transition of the epoxy polymer. The second peak is around 57°C and corresponds to the phase transition of the paraffin. Even though it is quite well known that the paraffin does not completely wet the epoxy, these mechanical results and the previous thermal conductivity results demonstrate that the interaction between these components is sufficient to provide the adequate performance shown in Figures 6–12. However, to provide improved compatibility over the paraffin/epoxy system, another system based on thermoplastic SEBS/paraffin was chosen for investigation.

Figure 13 shows the storage moduli of SEBS, paraffin, and paraffin/SEBS composite. As shown in Figure 13, all of the moduli decrease with an increase in the

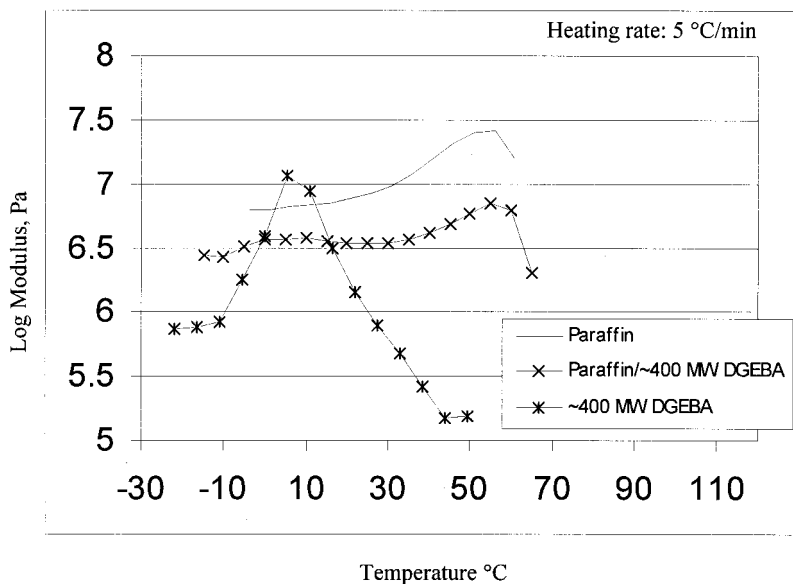


Figure 11 Loss moduli of ~ 400 M_w DGEBA, paraffin, and paraffin/~ 400 M_w DGEBA composite.

temperature. Paraffin has the highest modulus of 475 mPa around 0°C. Its storage modulus decreases sharply after the paraffin phase transition, around 5°C. The SEBS has the lowest storage modulus because of its rubbery nature. It starts from 5.62 mPa and decreases with the temperature. The sharp decrease in storage modulus around 50°C is caused by the soft segments of ethylene and butylene blocks of SEBS polymer. The paraffin/SEBS composite has storage modulus between paraffin and SEBS. Because 80 wt % of the composite is paraffin, this component dominates the properties of the composite. From the figure, we can see that the storage modulus of the composite

decreases dramatically when the paraffin undergoes a solid-liquid phase transition around 55°C. After the phase transition, the sample becomes very soft and eventually breaks at the bending force.

The loss moduli results of paraffin, SEBS, and paraffin/SEBS composite are shown in Figure 14. As shown in the figure, SEBS has the lowest loss modulus. Paraffin has the highest loss modulus and paraffin/SEBS has the value in between. The peak of the loss modulus normally occurs at the T_g of the amorphous polymer. In SEBS case, the peak value of 1.18 mPa at 50°C represents the movements of the polystyrene rigid segments. For paraffin, the loss modulus

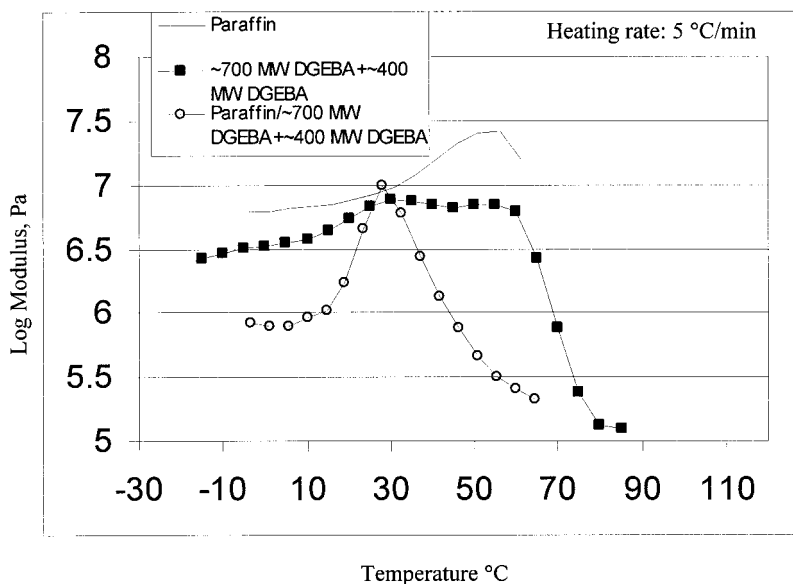


Figure 12 Loss moduli of ~ 400 M_w + ~ 700 M_w DGEBA, paraffin, and paraffin/~ 400 M_w + ~ 700 M_w DGEBA composite.

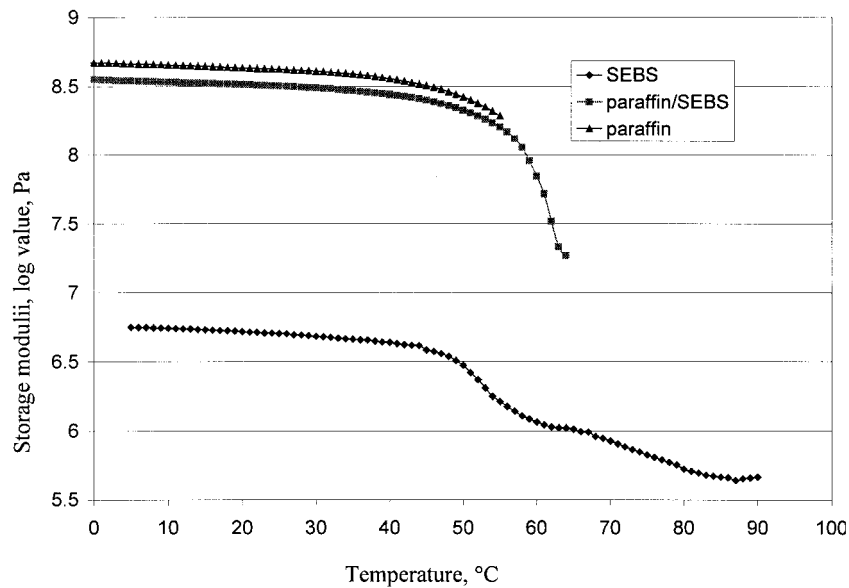


Figure 13 Storage moduli of paraffin, SEBS matrix, and 80 wt % paraffin/SEBS composite.

reaches its maximum at 5°C because of the phase transition. The loss modulus of the paraffin/SEBS composite has a peak at ~55°C, which also represents the paraffin phase transition. Because 80% of the composite is made of paraffin, the influence of the SEBS peak at 50°C is covered by the paraffin phase transition. The mechanical behavior of the composite is a combination of both paraffin and SEBS. In this case, the composite behavior is between the two components.

The DMA data show that the mechanical properties of the composite can be tailored by using different

polymer systems. It gives the flexibility of controlling mechanical properties for different applications.

CONCLUSION

Polymeric thermal energy storage composites incorporating phase change materials are developed. Low melt temperature paraffin is investigated as the phase change material. Paraffin particles are encapsulated by using epoxy matrices. The particle size distribution, thermal conductivity, contact resistance R'' , thermal diffusivity, and latent heat of the composites are mea-

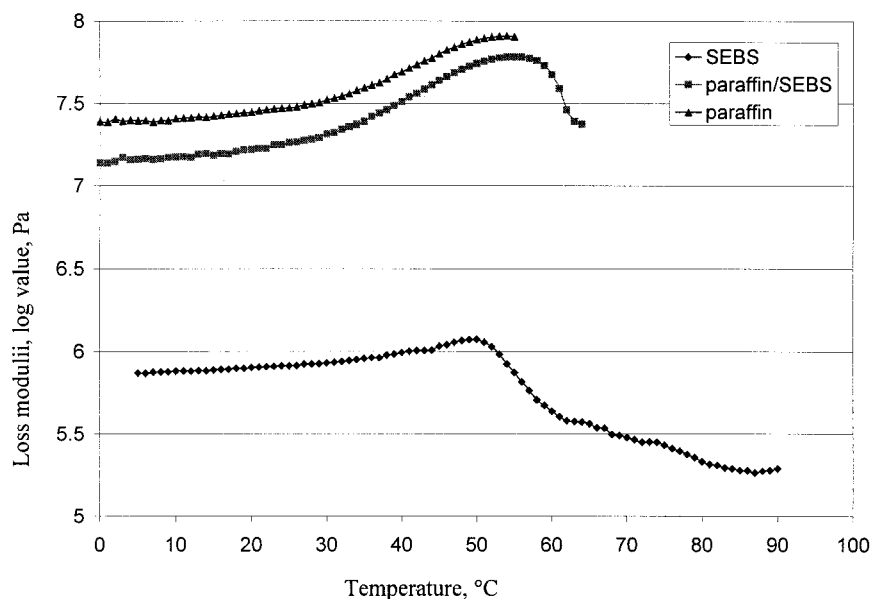


Figure 14 Loss moduli of paraffin, SEBS matrix, and 80 wt % paraffin/SEBS composite.

sured. The thermal conductivity of the composites increases when the phase change material is a liquid, partly because of better wetting of the epoxy by the liquid paraffin. Additionally, volume expansion of the paraffin liquid in the composite increases conductivity of the composite. The epoxy conductivity increases with temperature. DMA is used to measure storage and loss moduli of the paraffin, polymers, and composites. Three different epoxy systems and a thermoplastic SEBS/paraffin system with different glass transition temperatures are investigated. The dynamic mechanical properties of these systems are measured. The results demonstrate that, in the case of paraffin/epoxy, the interaction between these components is sufficient to provide adequate thermal and mechanical performance. The thermoplastic SEBS/paraffin system demonstrates excellent thermal and mechanical performance.

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