

Thermal and Mechanical Behavior of Unsaturated Polyesters Filled with Phase Change Material

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ABSTRACT: Samples of commercial unsaturated polyester (UPE) resin, filled with phase-changeable fillers (PCMs), were prepared, and the thermal and mechanical properties of the cured samples were examined. Fillers chosen were paraffin and Wood's metal. Samples were prepared by making dispersions of these fillers in liquid unsaturated polyester followed by curing with methyl ethyl ketone peroxide (MEKP) and conaphtanate and rigid thermoset samples filled with PCM particles were obtained. The thermal and mechanical behaviors of such a filled composite around the melting points of fillers are very interesting. Effects of varying proportions of PCM on mechanical and thermal properties of final products were examined. The samples show thermal melting behavior without undergoing a change in physical state. Decreases in the maximum working temperature from 75 to 53°C for metal-filled samples and from 75 to 43°C for paraffin-filled samples were observed by using dynamic mechanical thermal analysis. Differential scanning

calorimetry indicated that heat absorption of paraffin samples were higher than that of metal-filled samples. For paraffin-filled samples, heats of fusion were 3.44 cal/g for 10% filled sample and 6.35 cal/g for 20% filled sample. For Wood's metal-filled samples, heats of fusion were 1.18 cal/g for 10% metal-filled sample and 1.54 cal/g for 20% metal-filled sample. Surface hardness was tested with Shoremeter D. Surface hardness of metal-filled composites varied from 86 to 34 shore D at 21°C and 80.6 to 35 shore D at 80°C. For paraffin-filled samples, surface hardness changed from 86 to 42 shore D at 21°C and from 80.6 to 13 shore D. Morphology of the samples was determined by scanning electron microscopy, of the crack surfaces. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 832–838, 2006

Key words: unsaturated polyesters; phase change materials; fillers; thermal properties; mechanical properties

INTRODUCTION

Unsaturated polyesters, also called polyester resins, are based on macromolecules with a polyester backbone in which both a saturated acid, such as phthalic or isophthalic, and an unsaturated acid, such as maleic or fumaric acid, are condensed with a dihydric alcohols. The degree of crosslinking can be controlled through the concentration of unsaturated acids.¹ The length of crosslinks can be controlled to some degree by concentration and type of crosslinking reactive diluents employed. Rigidity can be introduced by the use of aromatic acids or glycols, and a high degree of crosslinking.

Unsaturated polyesters are one of the most widely used liquid molding resins in the world. Many inert solids are added to polyesters to improve mechanical properties and decrease cost. These materials, called fillers or reinforcers, are inert and infusible inorganic materials such as calcite, alumina, clays, mica, or fi-

berglass.² Composites manufactured in this manner are important in automotive, boat, infrastructure, and sporting goods industries.

In this work, we introduce the concept of meltable i.e., phase-changeable fillers. When a substance is used to store and release latent-heat reversibly in a phase transition, they are called "phase change materials" (PCMs).^{3–7} PCMs have found some application as heat storage media where their high-heat of fusion is used. Application of PCMs in solar heating,⁸ emergency heating, heat-transfer fluids,^{9–11} and cooling fluids for metal grinding,¹² food storage, etc are well known. When such materials are used in a finely divided form as filler in a high-melting plastic, new materials with interesting properties are produced. If the filler is load bearing, such materials should show abrupt and reversible changes in modulus around the melting point of filler. This property could allow the production of intelligent plastics. When the filler melts, the corresponding heat of fusion is absorbed at the melting point of the filler. Reversing this process allows this heat to be emitted by the sample. This property would allow the production of plastic parts that show melting behavior in a thermal sense (i.e., heat absorption) without exhibiting melting behavior externally. To examine the feasibility of such PCM-filled plastics, we

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undertook a study of finely divided paraffin and Wood's metal-filled thermoset unsaturated polyesters. We planned to examine both the mechanical and the thermal behavior of such samples around the melting point of the filler.

EXPERIMENTAL

Materials

Unsaturated polyester, including 42% styrene as reactive diluent, with a brand name of CE 92 N8 was obtained from Cam Elyaf A.S. (Istanbul, Turkey). Methyl ethyl ketone peroxide used as initiator and cobalt naphthanate used as an accelerator were obtained from Akzo-Nobel (Chicago, IL, USA). Wood's metal was obtained from Mallinckrodt Chemical Works (St. Louis, MO, USA), and paraffin was obtained from Harleco (West Chester, PA, USA). Stearic acid was obtained from Fisher Scientific (Fair Lawn, NJ, USA).

Apparatus

Dynamic mechanical thermal analyses (DMTA) of the samples were performed using a Polymer Laboratories Dynamic Mechanical Analyzer. Samples having dimensions about $100 \times 150 \times 2 \text{ mm}^3$ were scanned at a frequency of 1 Hz and heating rate of $5^\circ\text{C}/\text{min}$. Thermal behaviors of all samples were examined by differential scanning calorimeter (DSC) from Rheometric Scientific. Heating rate was $5^\circ\text{C}/\text{min}$. Electron micrographs of the samples were obtained on a Philips scanning electron microscope (SEM). Finally, surface hardness of the samples was determined by using Shoremeter D, from Zwick.

Preparation of paraffin sols

Two different methods were used to prepare paraffin wax dispersions in UPE. In the first method, molten paraffin-surfactant mixture was added to liquid UPE with high-shear stirring, and the mixture was cooled under stirring. Many surfactants such as Cu (II) stearate, polyethylene glycol 300 monooleate, oleic and stearic acids, pine oil, and hexadecyl trimethyl ammonium chloride were used. In the second method, molten paraffin and sodium stearate were added to water with high-shear stirring, and the mixture was cooled under stirring to give paraffin dispersion. The solid phase was filtered and dried, and the resulting powdered paraffin was mixed with UPE under high-shear stirring. The second method gave more stable dispersions than the first method.

In a typical procedure, 10 g of paraffin was added to 250-mL of water at 80°C , and 3 g of surface active agent was added. This mixture was stirred at high-

shear rate and cooled to room temperature. The suspended paraffin particles were filtered and dried. 2.1 g of dried paraffin powder was mixed with 40 g of UPE (for 5% dispersion) and stirred at a high-shear rate.

Preparation of Wood's metal sols

Wood's metal consisting of 50% Bi, 25% Pb, 12.5% Sn, and 12.5% Cd with a melting point 68°C and density of $9.67 \text{ g}/\text{cm}^3$ was mechanically ground by a powered grinder. Metal dust was sieved on No. 230 sieve to give a maximum particle size of $60 \mu\text{m}$. For 5% metal sol, 0.25 g of metal powder was taken and mixed with 4.75 g of UPE. This sol was very unstable because of the high density of the Wood's metal and had to be stirred continuously during cure.

Curing of samples

For all sols and emulsion, 0.5% Co Naphtanate and 1% of MEKP (based on UPE) were used. The mixture was stirred and allowed to gel and cure in a mold. All samples were cured under atmospheric conditions and at room temperature. None of fillers used interfered with the cure chemistry of UPE.

RESULTS AND DISCUSSIONS

Dynamic mechanical thermal analysis

If the filler is a load-bearing component, the overall mechanical properties of the filled sample should show a change around the melting points of fillers. Therefore, mechanical properties of material under static loading at room temperature may not fully represent its performance. Hence, the cured samples were investigated by dynamic mechanical testing at different temperatures.

Samples were scanned at maximum strain of 0.01% at the frequency of 1 Hz and heating rate $5^\circ\text{C}/\text{min}$. Dynamic moduli (E') values were recorded in a temperature range from 25 to 120°C . Figures 3 and 4 give

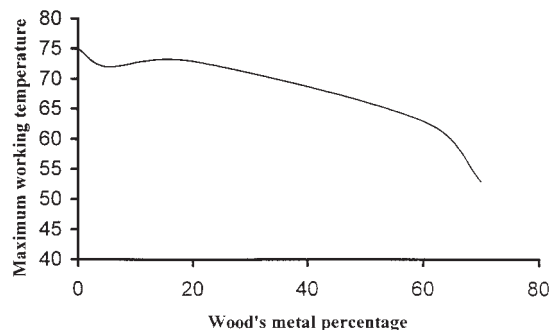


Figure 1 Maximum working temperature of some metal-filled samples.

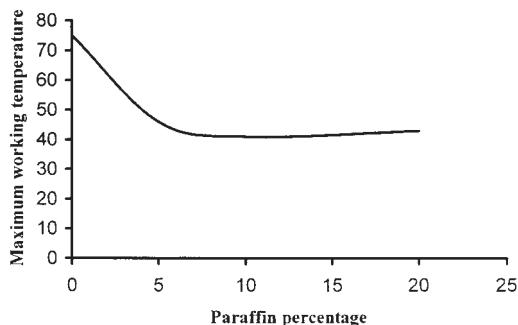


Figure 2 Maximum working temperatures paraffin-filled samples.

the plots of dynamic mechanical data of the cured samples.

For Wood's metal-filled samples with up to 40% filler, there is no apparent decrease in storage modulus (E') at the melting point of the filler. At the filler concentration above 50%, however, there is a dramatic decrease in storage modulus around 68°C, the melting point of the filler. Storage modulus of a filled sample correlates well with volume fraction of the filler. The density of Wood's metal is 9.67 g/cm³, and the weight percentages translate to very low-volume fractions (e.g., a 30% (w/w) correlates to 5% (v/v)). At these low-volume fractions, the material is insensitive to the phase change of the filler. However, as the volume fraction approaches 15% (v/v), the effect of the phase

change of the filler becomes measurable. In these samples, we demonstrated that the Wood's metal and paraffin are load-bearing, and that the mechanical properties of the sample show a marked change at the melting point of the filler.

Maximum working temperature is defined as the temperature at which a material shows 10% loss of its modulus at room temperature. It is a measure of the highest working temperature of a given material. DMTA curves can be used to determine the maximum working temperature. The maximum working temperature data for the filled samples are given in Figures 1 and 2. For Wood's metal-filled samples, no change is observed in maximum working temperature up to 60% (w/w) (15% v/v) filler content. Above this value, there is a sharp decrease in maximum working temperature.

For paraffin-filler, concentration as low as 5% leads to a reduction of maximum working temperature from 75 to 46°C. It is possible that the partial solubility of sodium stearate, surface active agent used in UPE, may have an effect on the matrix mechanical properties, and the reduction in maximum working temperature is due to the matrix as well as the phase change of the filler.

For paraffin-filled polyester samples, a decrease in storage modulus is observed with increasing paraffin content, as shown in Figure 4. Even at 5% paraffin, room temperature modulus of the sample is lower

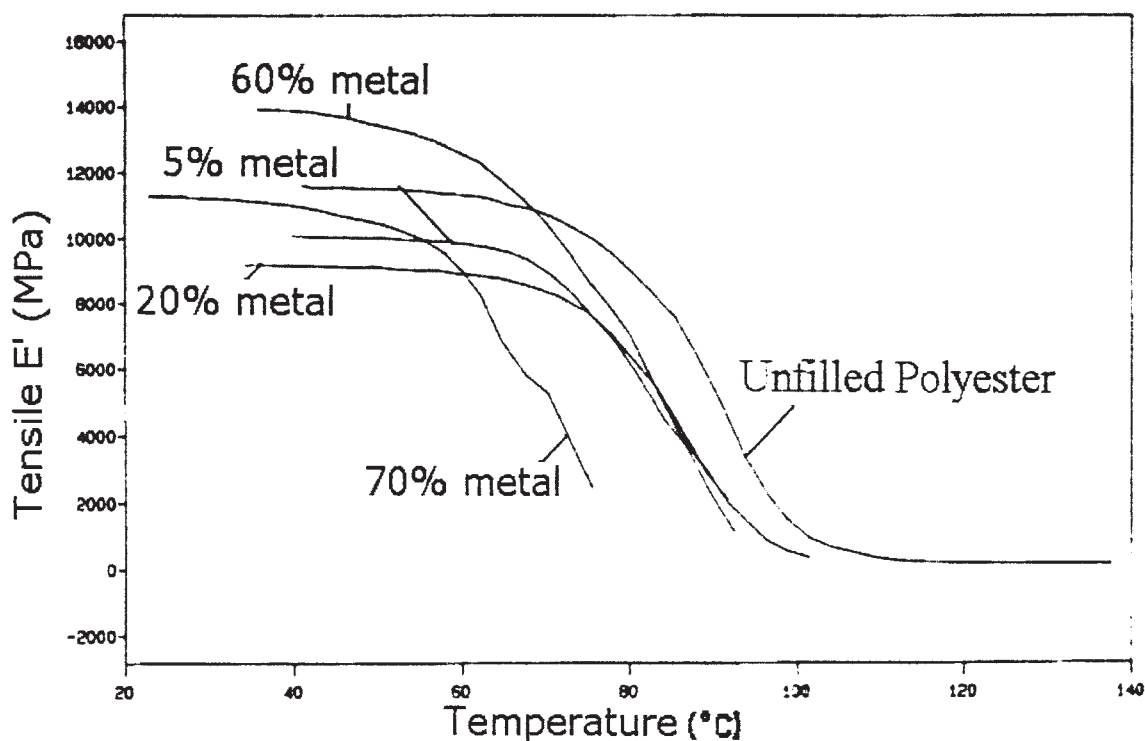


Figure 3 E' curves of Wood's metal-filled polyester samples.

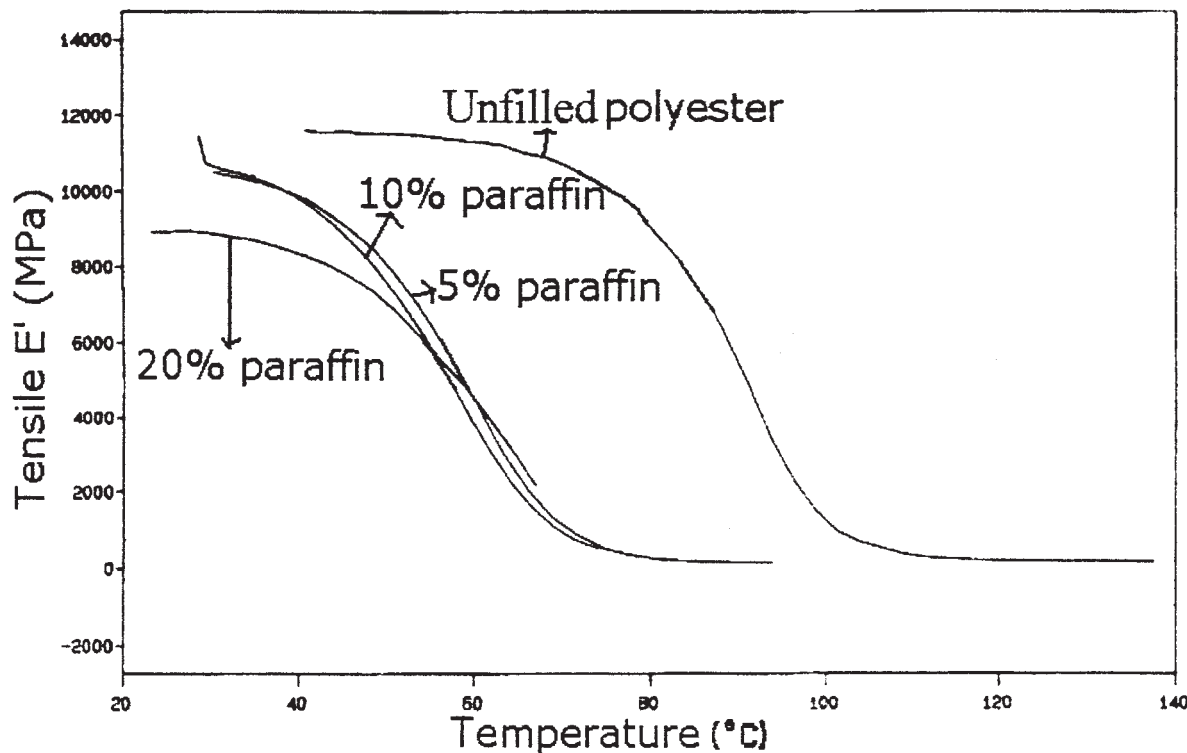


Figure 4 E' curves of paraffin-filled polyester samples.

than that of neat polyester. Modulus of the sample is also lower than that of pure polyester at the maximum working temperature. Relatively small increases in the amount of paraffin causes very observable changes in E' values. Dynamic moduli of the samples, containing different percentage of paraffin, decreases rapidly with increasing paraffin content. From 5 to 10% filled samples, there are small changes, and at 20%, a large change is observed, as shown in Figure 4. Also, maximum working temperature of the samples decreased with increasing paraffin content (Fig. 2). The density of paraffin (0.8 g/cm^3) is close to the density of UPE ($1.1\text{--}1.2 \text{ g/cm}^3$), and so the weight ratio of paraffin is nearly the same as its volume ratio. Thus, mechanical changes correlate well with weight fraction of paraffin in the sample.

For paraffin and Wood's metal samples, storage modulus (E') decreases around the melting point of the filler, which shows that the filler is bearing load in the sample. This observation leads us to believe that with further work, intelligent materials that show a marked and reversible change in modulus at a desired temperature can be manufactured by using different phase-changeable fillers.

DSC analysis

Paraffin and Wood's metal-filled polyester samples were tested by DSC from 25 to 120°C. Melting behav-

ior should be observed around melting point of filler, since at these temperatures, fillers change their phase and they absorb heat. Paraffin and Wood's metal have heat of fusion of 37.18 and 7.55 cal/g, respectively.

As expected, neat polyester did not exhibit any melting transition; therefore, melting transitions of any filler in the samples could be easily determined. Melting transitions in all samples filled with paraffin and Wood's metal can be observed in DSC graphs (Figs. 7 and 8). Samples exhibited well-defined melting transitions, and the area under the melting curve shows a progressive increase as the amount of the filler increases (Figs. 5–8). Melting transition was completed in a narrow temperature range ($69\text{--}74^\circ\text{C}$) in Wood's metal-filled samples. However, the melting transition of paraffin-filled samples was completed in

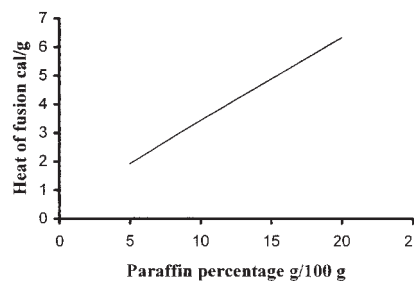


Figure 5 Heat of fusion of paraffin-filled samples.

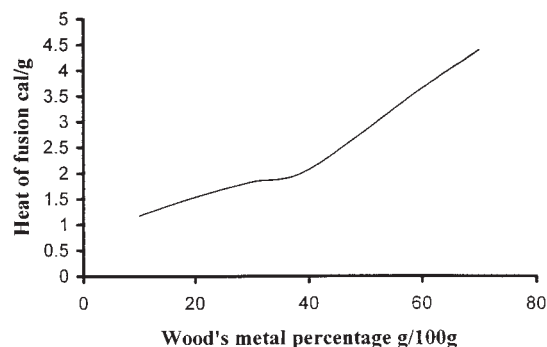


Figure 6 Heat of fusion of Wood's metal-filled polyester samples.

a broader temperature range than that of Wood's metal-filled samples, which indicates that paraffin includes different crystalline regions of different molecular weight aliphatic carbon chains. For paraffin-filled samples, melting transitions started at 40°C in DSC spectra that coincides with the start of modulus loss in the DMTA spectra.

This behavior of our samples is new and unique. At the melting point of the filler, material shows an endotherm, but it does not physically melt. To our knowledge, there is no such material produced or described before. With the correct choice of the filler, materials that absorb or emit heat at chosen temperature without physically melting can be produced. Materials that can absorb and release heat reversibly, but

still remain as a load-bearing solid during this process, becomes a possibility through our work

Surface hardness tests

Hardness tests involve the quantitative assessment of the resistance to penetration of material by an indenter. The test pieces were mechanically unstressed before the test and had a thickness of 3-mm. The results are summarized in Figures 9 and 10.

A minimum of five tests were performed at different points on a specimen, and reported value is an average of these values. Tests were done first at room temperature (~21°C), and then at 60°C for paraffin-filled samples, and at 80°C for Wood's metal-filled samples. The distance between the test points was ≥ 6 mm from each other and ≥ 12 mm from each edge of the sample.

Higher surface hardness values were observed on the metal-filled samples, while the paraffin-filled samples showed lower values. These results are compatible with DMTA results, since metal-filled polyesters show the highest E' values. As no surface-active agent was used for the metal-filled samples, no loss of mechanical properties was observed for the matrix. In paraffin-filled samples, the surface-active agents contribute some plasticization for the matrix, and a reduction of surface hardness is a consequence of this plasticization.

Finally, it can be concluded that above the phase-change temperature of the filler, marked decreases in

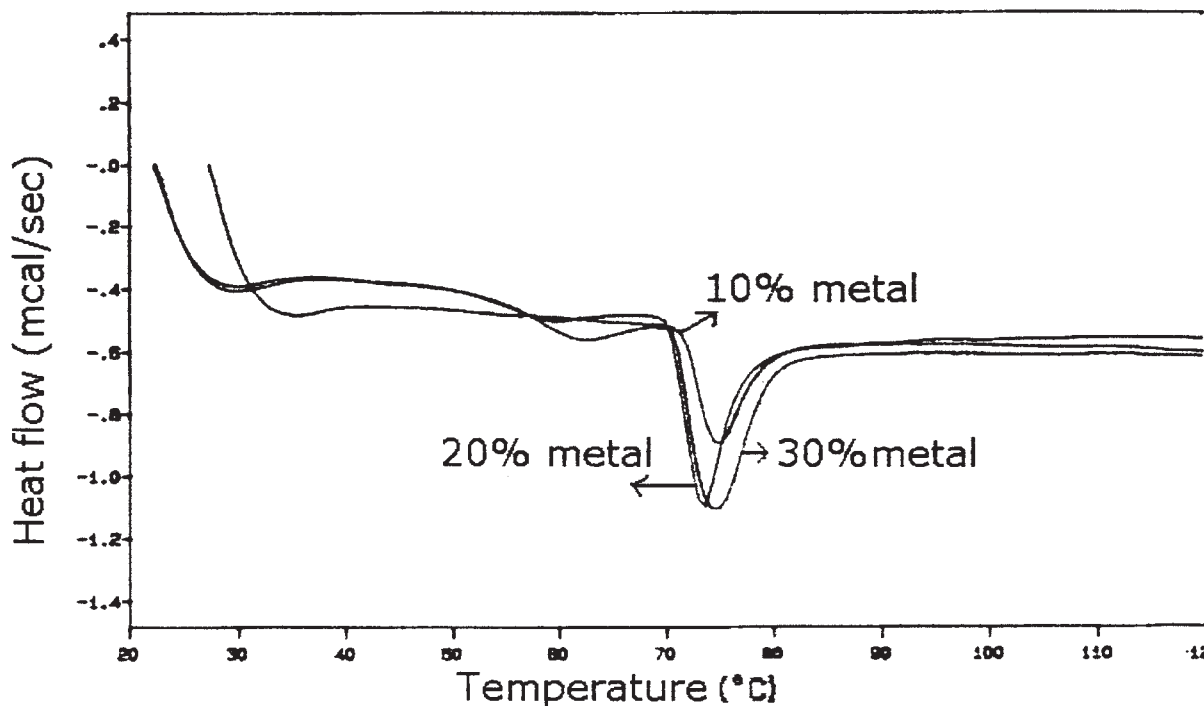


Figure 7 DSC curves of some of Wood's metal-filled samples.

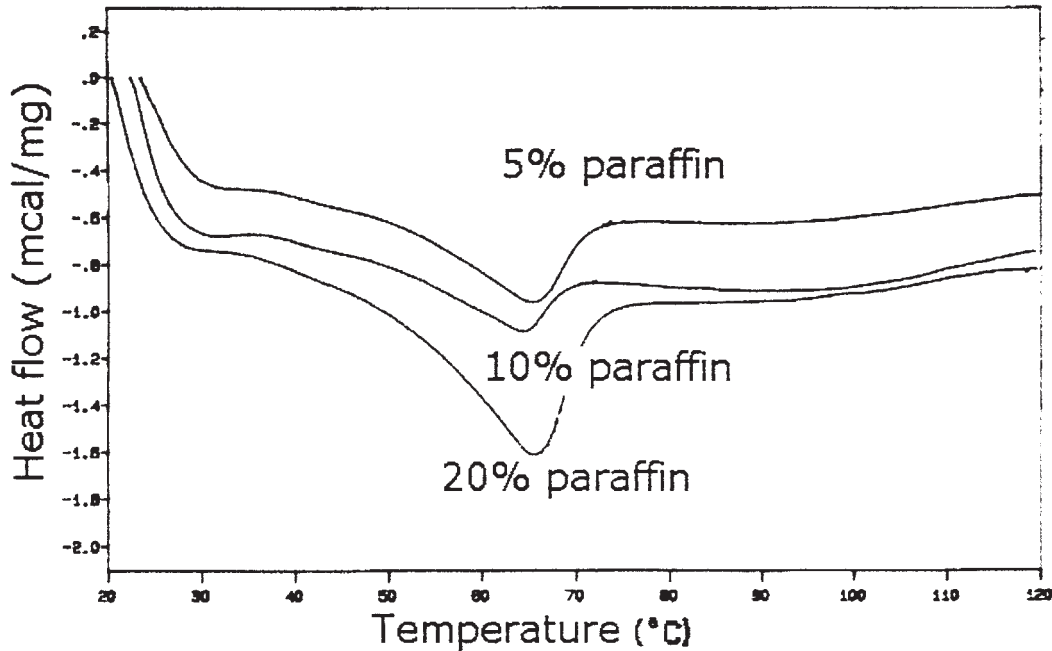


Figure 8 DSC curves of some paraffin-filled polyester samples.

the hardness were observed. For Wood's metal-filled samples, these decreases were observed only at high-metal percentage because of the high density of Wood's metal.

SEM analysis

The SEM images of the crack surface of 30% paraffin-filled sample at 173× magnification are shown in Figure 11. The shape of paraffin particles is almost spherical, and no agglomeration was observed. As the paraffin was emulsified in a molten state, the spherical shape, which minimizes surface area for a given volume, is the expected shape. Every paraffin particle is independent of the other, and a closed cell-like structure was observed. Some voids are also observed, and the surfaces of these voids are very smooth, which is an indication that there is no adhesion between paraffin particles and polyester matrix at the interface.

The crack surface of 30% of metal-filled sample at 170× magnification is shown Figure 11. The surface represents a typical polyester surface. As the volume fraction of the material is only 3%, only a few metal particles were observed. When these samples were made, the metal was mechanically ground to a fine powder, and the irregular and chip-like shape of the mechanically powdered metal is observed in the micrograph.

No attempt was made to increase interfacial adhesion strength by the use of coupling agents in these samples. SEM images, therefore, show no indication of adhesion between the metal particles and the polyester matrix.

CONCLUSIONS

Cured thermoset polyesters with fillers composed of PCMs were prepared. PCMs used in this study were

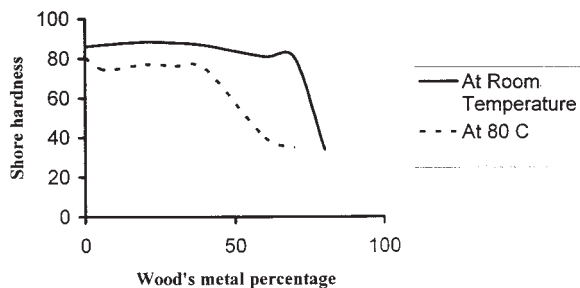


Figure 9 Shore hardness of Wood's metal-filled polyester samples.

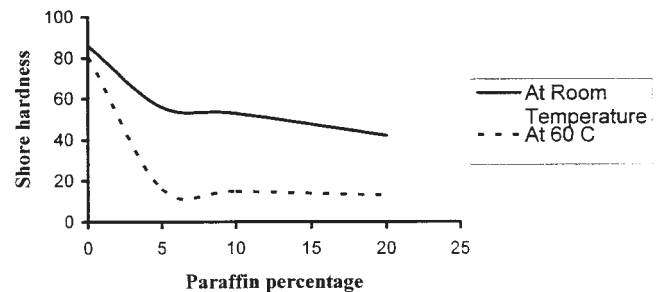


Figure 10 Shore hardness of paraffin-filled polyester samples.

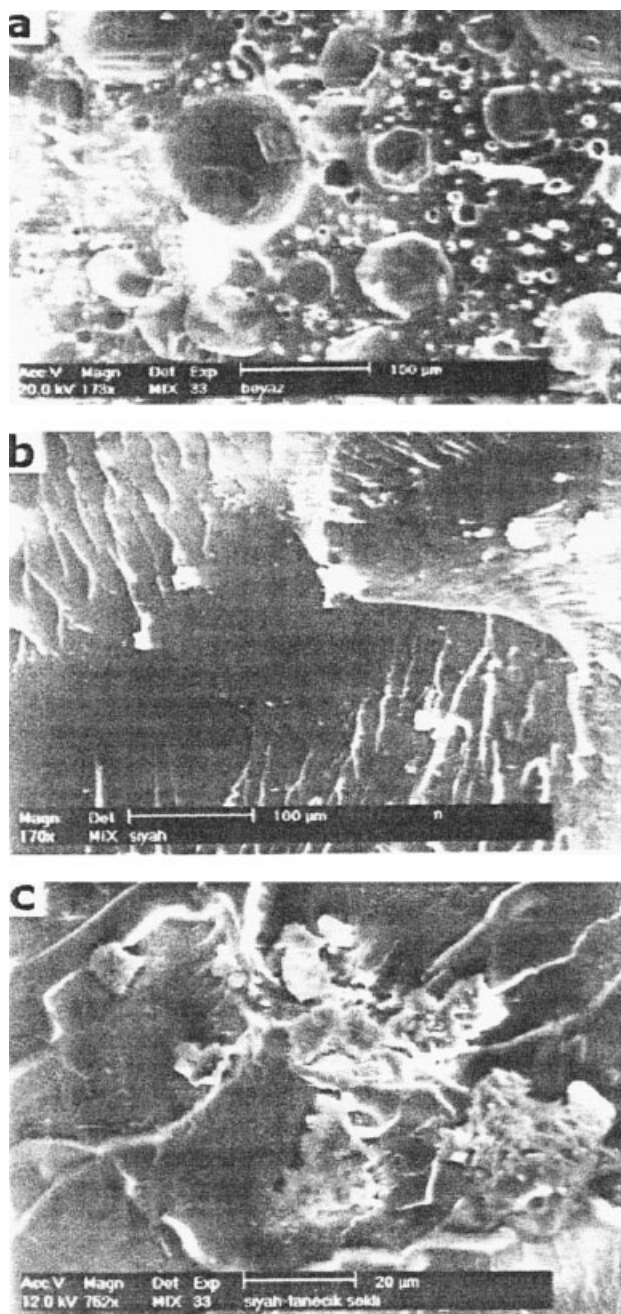


Figure 11 SEM images of (a) 30% of paraffin-filled polyester sample (magnification, 173 \times), (b) 30% Wood's metal-filled polyester sample (magnification, 170 \times), and (c) 30% Wood's metal-filled polyester sample (magnification, 762 \times).

paraffin and Wood's metal, uniformly and homogeneously dispersed in polyester matrix.

In all samples, unsaturated polyester is the continuous phase, and the fillers are the discrete phase. Up to 50% dispersions were prepared with paraffin. And, up to 80% dispersions were prepared with Wood's metal. For all emulsion and dispersions, viscosity of

the system before cure increased with the increasing amount of filler.

DMTA data of cured samples showed a reduction in glass-transition temperature (T_g) when compared with those of neat polyester. The mechanical properties of cured resins vary with PCM content. Wood's metal does not cause a sharp reduction in mechanical properties at low percentages. In paraffin and Wood's metal-filled samples, the filler is a load-bearing component. We observed a regular decrease in maximum working temperature with increasing filler content and a reduction in the modulus around the temperature of phase change of the filler in most of our samples. For paraffin-filled polyesters, even at 5% filler content, a sharp decrease in E' is observed. However, for Wood's metal-filled samples, these changes can be observed only at high-metal percentages. Maximum working temperatures of cured samples decrease with increasing filler amount and show abrupt changes around melting point of the fillers.

DSC examination shows that polyester does not show any melting transition. However, paraffin and Wood's metal-filled samples show melting transitions. Around the melting point of fillers, materials absorb heat. Paraffin and metal-filled samples show endotherms around the melting point of filler while the samples themselves show no indication of melting externally and retain their physical shape and most of their mechanical strength. We believe that with further work, intelligent materials that show a marked change in modulus at a desired temperature and that can store large amounts of heat without melting can be manufactured by using phase-changeable fillers.

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