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INVESTIGATION OF LATENT HEAT-THERMAL ENERGY STORAGE MATERIALS. I. THERMOANALYTICAL EVALUATION OF MODIFIED POLYETHYLENE

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ABSTRACT

Differential scanning calorimetry is used to evaluate polyethylene for latent heat-thermal energy storage. Polyethylene is a suitable material from the points of view of latent heat, behavior of melting and crystallization, and material cost. The thermal stability is satisfactory when it is used in a closed system with heat transfer media, such as silicone oil, alkyldiphenyl, alkyldiphenylethane, Caloria HT and ethylene glycol, which shield polyethylene from air. Surface-crosslinking by ion bombardment prevents polyethylene from mutual adhesion and it retains its form after melting. Surface-crosslinked polyethylene with silicone oil or ethylene glycol is the most promising, while the heat transfer media, such as alkyldiphenyl, alkyldiphenylethane and Caloria HT, which dissolve polyethylene, decrease the melting point, but have little effect on the latent heat and sharp DSC peaks of melting and crystallization. Thus, the composite of polyethylene with these media can also be used at an adjusted and desirable operating temperature.

INTRODUCTION

Thermal energy storage is an essential technique for thermal energy utilization. For example, it is indispensable for solar thermal electric power generation and solar air-conditioning to overcome intermittence of sunshine [1,2]. It is also an important technique for utilizing heat exhausted from industrial processes, such as electric power stations, for urban utility [3]. Furthermore, reflecting the recent situation that electric load change is becoming sharper year by year, thermal energy storage becomes an alternative for load levelling and load management [2] to increase the working ratio of electric generators among other alternatives such as pumped hydro, secondary batteries, fly wheels and superconducting magnets.

For thermal energy storage, there are four alternatives: sensible heat utilization, latent heat utilization, utilization of reversible chemical reaction heat, and utilization of heat of dilution. Sensible heat utilization has been applied in practical processes, such as refractory furnaces, but the storage density is low and the temperature of the released heat decreases during the release, so that the obtained heat is of low quality. In reaction utilization, solid reactions involving the gas phase are generally applied because of controllable reversibility, but this limits the power density and the response to load to its kinetics and heat transfer in the powder. The thermal energy storage in highly concentrated solutions is suitable for transportation and long-term storage, but the temperature of the stored heat is limited because aqueous solutions are usually used. In the latent heat-thermal energy storage, the released heat is almost at a constant temperature so that it is of high quality and the energy is densely stored. However, it depends primarily on the characteristics of the materials; the temperature and latent heat of transition or fusion define the operating temperature and the energy density. Therefore, the development of latent heat-thermal energy storage is predominantly dependent on exploration, screening and modification of the materials storing the thermal energy in their latent heat.

As described below, from a preliminary screening, polyethylene is seen to be one of the promising materials. For the experimental evaluation, differential scanning calorimetry (DSC) was applied to polyethylene, and modification was also made for improving its characteristics. The results are reported in this paper.

EXPERIMENTAL

Apparatus

Two types of power-compensation DSC (Rigaku Denki Co. Ltd.) were used: one with an outer heater maintaining the temperature around the sample and reference materials to improve the precision of the measurement of temperature and latent heat, and the other without an outer heater for rapid heating and cooling. Some modifications were made to the former to improve the precision of the temperature measurement, i.e., a reverse bias voltage was fed from a DC voltage standard (Yokogawa Electric Works Ltd., type 2853) against the temperature output signal. The sample container was a 5 mm diameter aluminum pan. After loading the sample, the container was sealed, with the sealing endurable up to an inner pressure of 2 atm. The DSC measurement was made in a flow of nitrogen at 2.5°C min^{-1}.

To improve the polyethylene, plasma bombardment on the surface of the polyethylene pellets was carried out for 30 min with plasma CVD equipment (Kokusai Electric Co., Ltd.) in an argon atmosphere of about 0.25 Torr under an anode voltage of 1.5—2.5 kV and an anode current of 0.25 A. To observe the thermal stability and compatibility of the materials, the samples, in either a sealed or open DSC container, were aged in an oven (Toyo Seiki Sesaku-sho, Ltd.) in which hot air was circulated to maintain a uniform temperature.

Materials

High-density (0.96) Yukalon HD-EX 40 polyethylene, kindly supplied by Mitsubishi Petrochemical Co. Ltd., was used. The pellets were used as received, without further treatment. In order to examine the possibility of direct contact with heat transfer medium, silicone oil (Shin-etsu Chemical

Co., Ltd. KF-54), alkyldiphenyl (Nippon Steel Chemical Co., Ltd. Therm S 600), alkyldiphenylethane (Nippon Oil Co., Ltd. Hitherm PS-5), Caloria HT-43 (Exxon Corp.) and ethylene glycol (Kishida Chemical Co., Ltd.) were used to observe the compatibility.

RESULTS AND DISCUSSION

Screening of materials

The materials were first screened from the points of view of temperature of transition or fusion, latent heat and material cost. The results are reported elsewhere [4,5], and therefore only a brief description is given here.

Some important performances of the latent heat-thermal energy storage system are primarily dependent on the characteristics of the heat storage materials, and other performances are dependent on the design of the system as well as the materials. Figure 1 shows the relations between the performance of the thermal energy storage system and the characteristics of the materials. The solid lines represent relations in which the performances are strictly limited by the characteristics connected with the solid lines, and the limit cannot be overcome by changing the design of the system. For instance the energy density of the system cannot by any means be increased beyond the limit of the latent heat of the materials, and the operating temperature of the system is defined by the temperature of transition or fusion.

On the other hand, the broken lines express relations where the performances can be improved by the design of the system, even if the characteristics of the materials are poor. Examples are the response to load and the power density. These performances are dependent not only on the thermal conductivity of the materials but also on the surface area for the heat transfer between the storage material and the heat transfer medium.

The screening method is derived taking account of the relations shown in Fig. 1. Because they limit the performances, the characteristics connected with the solid lines were investigated first. Among them, data concerning the

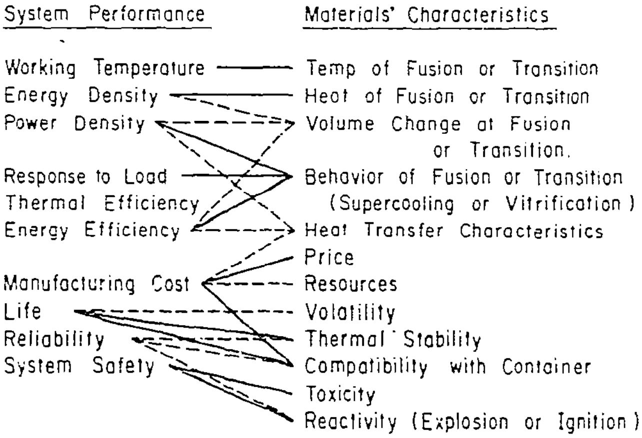

Fig. 1. Relations between the performance of the thermal energy storage system and the characteristics of the materials.

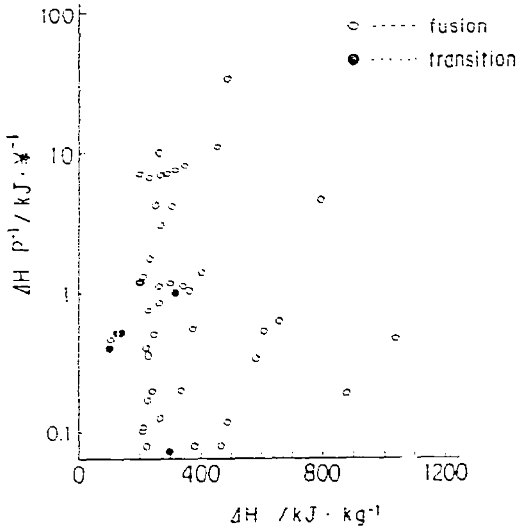

Fig. 2. Plots of reciprocal price of material vs. latent heat.

temperatures of transition and fusion and latent heat had already been comprehensively evaluated, e.g. in ref. 6. About 3000 of these evaluated thermodynamic data were listed in the order of temperature [7] and promising fusions and transitions with large latent heats were selected in the temperature range 100—1000°C by criteria of 200 kJ kg^{-1} for fusion and 100 kJ kg^{-1} for transition. They were also roughly screened for toxicity, availability (or resources), compatibility with the container, and chemical reactivity. Commercial prices of the materials as industrial products were then investigated, and finally, inexpensive materials with large latent heats were selected.

In Fig. 2, the reciprocal prices of the materials thus selected are plotted vs. the heat of fusion or transition, ΔH. The reciprocal price, $\Delta H/P$, on the ordinate is the heat storable with materials purchased for 1 yen (the unit of

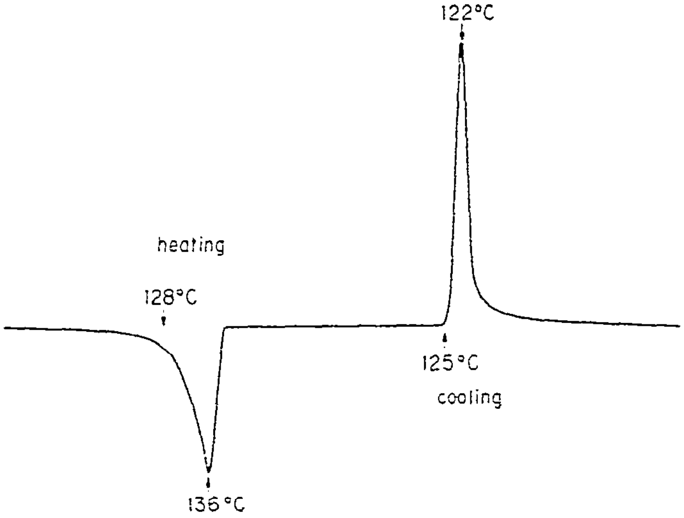

Fig. 3. DSC curves of melting and crystallization of original polyethylene.

Japanese currency). These plots express potential applicability of the latent heat-thermal energy storage, and the reciprocal price of 1 kJ/yen is quite a reasonable criterion for the thermal energy storage. Polyethylene is indicated with a double circle in Fig. 2, and it is clearly seen that it is one of the most promising materials, since only a few other materials are found in the temperature range around the melting temperature of polyethylene, and the temperature range is very important for solar energy utilization as well as exhausted heat utilization.

Modification of polyethylene

As described above, polyethylene is one of the promising materials from the points of view of latent heat and material cost. However, because of low thermal conductivity, the heat transfer within polyethylene is undesirably low. Although the heat transfer in molten salts is sufficient by natural convection [8], the heat transfer within polyethylene, even in the melt, is poor due to high melt-viscosity. In order to overcome this drawback of the low heat transfer, the forms of polyethylene should be fine, e.g. thin plates, slender cylinders or small spheres, to increase the surface area for the heat transfer between polyethylene and surrounding heat transfer medium.

One way of maintaining the fine form of polyethylene in storage-and-release cycles or melting-and-crystallizing cycles is to place the material in small capsules, but the cost of the capsules is high. One alternative is partial crosslinking of polyethylene by means of chemical crosslinking agents or electron beams [9], and encapsulation with a silicone coupling agent is also proposed [9]. However, the former has the drawback of decreasing its crystallinity and latent heat, and the latter is expensive. The authors have made an attempt at surface-crosslinking by an ion plasma [10].

In order to examine the effect of the surface-crosslinking, comparison of the DSC curves between the original material and the surface-crosslinked polyethylene was made. Typical DSC curves of melting and crystallization of the original polyethylene sample are reproduced in Fig. 3. As is seen, there is little supercooling and the heat is released reversibly: these characteristics are suitable for thermal energy storage. The heat of fusion was also measured (given in Table 1) and is higher than the criterion for the latent heat of 200 kJ kg^{-1} mentioned above.

Similar curves were obtained for the polyethylene crosslinked by ion bombardment, and the reversibility is also good. Little decrease in the heat of fusion due to the surface-crosslinking was observed, as is seen in Table 1. It is inferred from the fact that the crosslinking occurs only in the surface layer of the polyethylene, presumably because the collision cross-section of the argon ion is remarkably larger than that of the electron.

Thermal stability and compatibility of polyethylenes

One of the drawbacks of organic materials is their thermal degradation, especially thermo-oxidative degradation. Moreover, the purpose of the surface-crosslinking is direct contact between the polyethylene and the heat

TABLE 1

Effect of surface-crosslinking, heat transfer media and aging on melting temperature [a], crystallizing temperature [a] and heat of fusion

(a) Untreated polyethylene							
Heat transfer medium	None		Silicone		Alkyldiphenyl		
Aging time at 150°C (h)	0	500	0	500	0	500	
Heat of fusion (J g^{-1})	226	211	233	220	232	232	
Melting temp. (°C)	128	131	128	128	106	108	
Crystallizing temp. (°C)	125	128	124	125	109	110	
(b) Surface-crosslinked polyethylene							
Heat transfer medium	None	Silicone		Alkyl-diphenyl		Alkyldi-phenylethane	
Aging time at 150°C (h)	0	0	600	0	600	0	600
Heat of fusion (J g^{-1})	221	228	225	233	195	239	221
Melting temp. (°C)	126	127	127	112	107	112	111
Crystallizing temp. (°C)	124	123	123	110	109	110	111
Heat transfer medium	Ethylene glycol		Caloria HT				
Aging time at 150°C (h)	0	600	0	600			
Heat of fusion (J g^{-1})	225	207	219	212			
Melting temp. (°C)	128	128	115	116			
Crystallizing temp. (°C)	123	123	112	114			

[a] The temperatures are the extrapolated onset temperatures.

transfer media. For these reasons, the thermal stability and the compatibility with the heat transfer media were examined. The polyethylenes, both the surface-crosslinked and the untreated, were packed in sealed DSC pans with or without the heat transfer media and kept in an oven which was maintained at 150°C. As a control, the thermal degradation of the untreated polyethylene was also observed in an open DSC pan under the same conditions. DSC measurements were made intermittently for these samples.

Some DSC curves thus obtained are reproduced in Fig. 4. As is seen, the peak of the untreated polyethylene in the open pan decreases remarkably, and therefore it is clear that the molten polyethylene degrades very rapidly in air. For the surface-crosslinked polyethylene, similar, but somewhat retarded degradation is observed in the open pan. On the other hand, little change is observed in the peak of the surface-crosslinked polyethylene packed with the silicone oil in the sealed pan, and also the original polyethylene is scarcely degraded, as is seen in Table 1. Thus, the degradation of the polyethylenes does not proceed in the absence of air, and the silicone oil may also play a role of shielding polyethylene from air. It is also elucidated that the compatibility of the polyethylene with the silicone oil is very good. The latent heat, melting temperature and crystallizing temperature are listed in Table 1. It was also observed that the form of the surface-crosslinked polyethylene was retained after keeping it in the silicone oil for 500 h at 150°C. Similar results were also obtained for ethylene glycol as a heat transfer medium. The fact that the form of the surface-crosslinked polyethylene does not change after melting was also reported by Hansen and

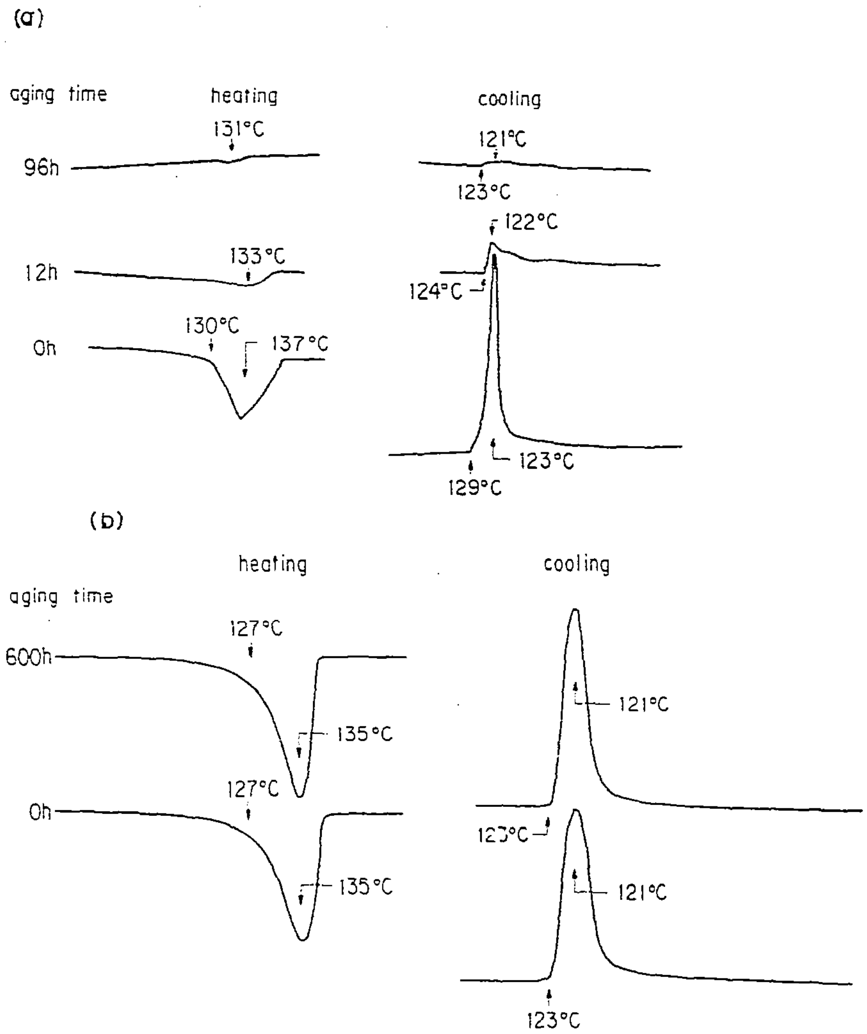

Fig. 4. Effect of aging on (a) original polyethylene in an open pan, and (b) surface-cross-linked polyethylene immersed in silicone oil in a sealed pan.

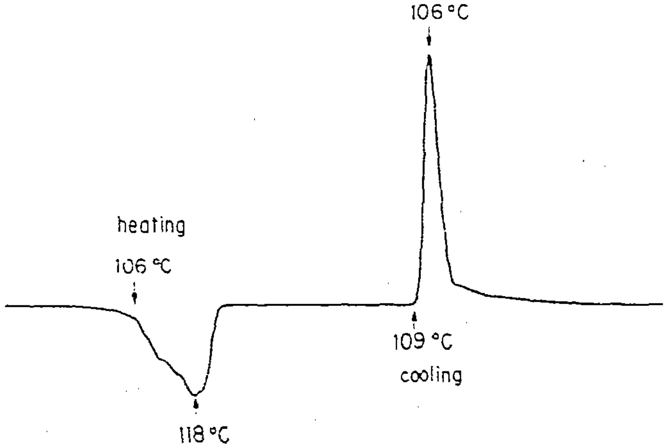

Fig. 5. DSC curves of melting and crystallization of polyethylenes immersed in alkyldiphenyl.

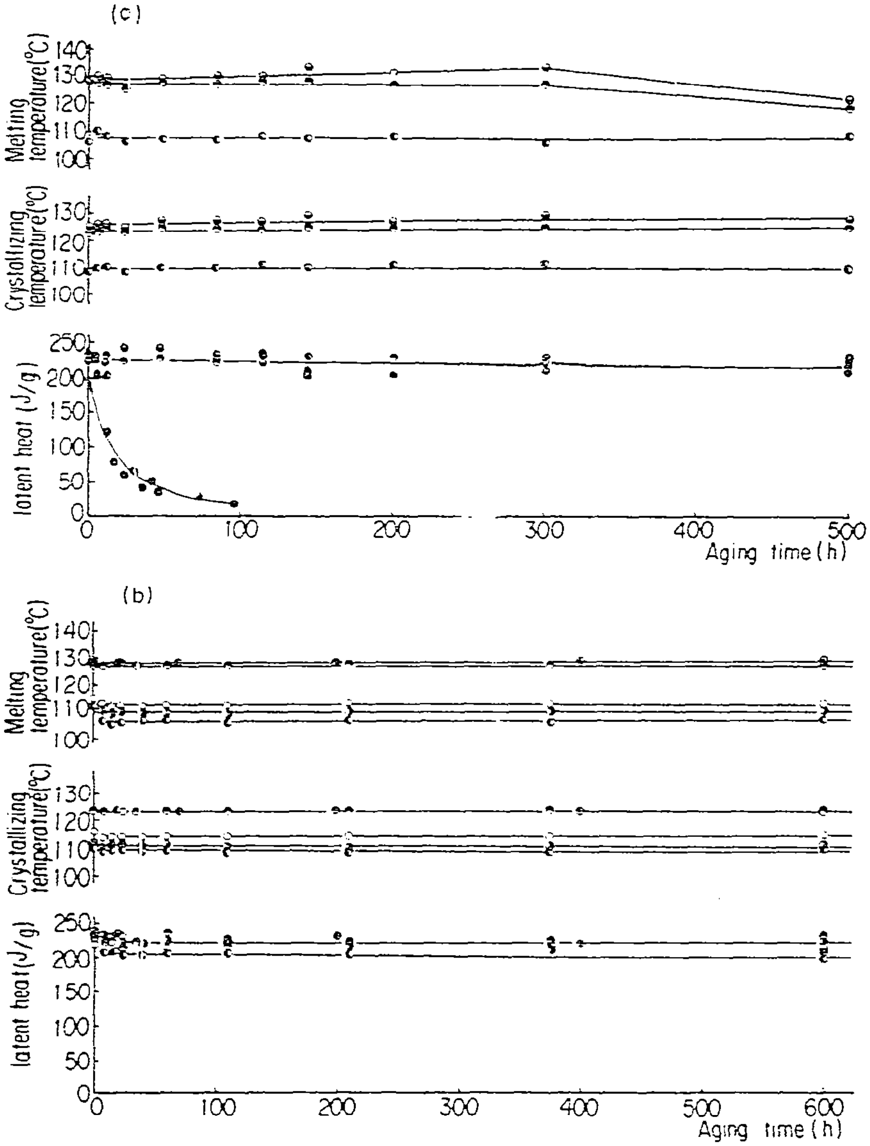

Fig. 6. Changes in melting temperature, crystallizing temperature and latent heat during aging of (a) original polyethylene and (b) surface-crosslinked polyethylene. ⊖, Polyethylene wihout heat transfer medium; ◓, polyethylene with silicone oil; ◐, polyethylene with alkyldiphenyl; ◑, polyethylene with alkyldiphenylethane; ○, polyethylene with Caloria HT; ⊖, polyethylene with ethylene glycol; ◉, polyethylene without heat transfer medium. All but the last sample were aged in a sealed pan.

Schonhorn [10]. In the case of the untreated polyethylene immersed in the silicone oil, the melting temperature, crystallizing temperature, latent heat and DSC peak did not change as in the case of the surface-crosslinked polyethylene, but the forms changed entirely and the sample formed a lump due to mutual adhesion.

For the other heat transfer media, i.e., alkyldiphenyl, alkyldiphenylethane and Caloria HT, different phenomena were observed for both the polyethylenes. Although sharp and reversible DSC peaks were observed, the melting and crystallizing temperatures were lower by 15—20°C than those of the original polyethylene, but the latent heats are almost the same for both the untreated polyethylene and the surface-crosslinked polyethylene, as shown in Table 1. Typical DSC curves are reproduced in Fig. 5. Both the polyethylenes were immersed in these media in test tubes and kept at 150°C for a while. After cooling to room temperature, the media above the polyethylene lump became a white opaque liquid. By observing the liquid with a polarizing microscope, spherulites were found. From this, it is clear that both the polyethylenes are swollen and dissolved in these media and that the phenomenon leads to the lower melting and crystallizing temperatures. However, the melting-and-crystallizing behavior is quite suitable for latent heat-thermal energy storage. Finally, the changes in the melting temperature, crystallizing temperature and latent heat are shown in Table 1 and Fig. 6.

From the results described above, the following conclusions can be drawn. Polyethylene surface-crosslinked by ion bombardment is a useful material for latent heat-thermal energy storage. Its optimum application is with non-solvent type heat transfer media, such as silicone oil and ethylene glycol, and this enables direct contact of the polyethylene with the medium to improve its heat transfer characteristics. The use of polyethylene with heat transfer media which dissolve it is another application of the material, and it may be possible to adjust the operating temperature of the thermal energy storage system, if a suitable medium is used, but this application needs capsules for the composite of polyethylene and the heat transfer medium.

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