

Thermal-Energy Storage in Crosslinked Pellets of High-Density Polyethylene for Home Heating and Cooling via Off-Peak Electric Power Utilization

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Synopsis

Electron beam crosslinking of high-density polyethylene (HDPE) was studied to obtain pellets for phase-change thermal-energy storage that retain their original shape and form through repeated melt/freeze cycles, and thus "serve as their own container." Electron-beam voltage, amperage, atmosphere, pellet-bed depth, traverse rate, and total dose were varied to establish cost/effective conditions for adequate thermal form stability combined with highest retention of heat of fusion. The results of electron beam crosslinking are compared with chemical crosslinking in cost and effectiveness. Utility of the electron-beam crosslinked HDPE pellets in a low-cost, efficient pellet-bed heat exchanger was demonstrated. Potential applications discussed include thermal storage for home heating and cooling, industrial processing, and off-peak electric utilization for load leveling.

INTRODUCTION

In research sponsored by the Department of Energy, a polymeric phase-change material (PCM) for thermal-energy storage (TES) was developed that has all the basic properties required for home heating and cooling (via absorption air conditioning), and is nearly ready for commercial application. This TES material is lightly crosslinked pellets of high-density polyethylene (HDPE), which has a melting point of $\sim 271^{\circ}\text{F}$, which is in the center of the $248\text{--}284^{\circ}\text{F}$ range, which is most suited for efficient operation of absorption air-conditioning units. HDPE has a high initial heat of fusion (up to 100 Btu/lb), and melts and freezes congruently. The crosslinked HDPE pellets are "thermally form stable" (do not undergo melt flow when heated above the crystalline melting point) and, thus, require no separate packaging of the TES material. The crosslinking modification, via electron beam irradiation, is expected to add no more than \$0.01/lb to the cost of the starting pellets. The HDPE pellets are apparently unaffected by the usual heat transfer media, such as water and ethylene glycol and mixtures thereof. HDPE is a relatively low-cost material ($\sim \$0.52/\text{lb}$) that is produced commercially on a large scale in the United States ($>4 \times 10^9$ lb/year).

However, the 45–50 cal/g initial heat of fusion (ΔH_f) was obtained in commercial grades of HDPE developed for ordinary extrusion and injection-molding applications. It is, at least theoretically, possible to prepare a more linear polyethylene having a heat of fusion of >100 Btu/lb (~ 66 cal/g). With further research and development, it should be possible to, thereby, obtain a crosslinked pellet having 20–25% more thermal-energy storage capacity than the current commercial HDPE material at little or no increase in cost. This higher storage

capacity obviously increases the economic attractiveness of the HDPE-*TES* system, and should be investigated if supporting funds can be obtained from either government agencies or private industry.

The utility of HDPE, PCM in the form of a low-cost, efficient pellet-bed heat exchanger, has been adequately demonstrated in an insulated 60-gal (250-lb) pilot plant that has been cycled through more than 100 successive melt/freeze cycles without change in melting point or heat of fusion. Design and application testing of a larger unit such as would be required for 12 h storage in conjunction with off-peak electric power still also remains to be completed.

EXPERIMENTAL RESULTS AND DISCUSSION

The development of a cost-effective durable energy storage material is essential to widespread utilization of off-peak electric power for heating and cooling of buildings. High heat storage efficiency, low cost, retention of capacity with time and use, effectiveness around 255–300°F (125–150°C), nontoxicity, nonflammability, and noncorrosivity, and suitability for use with either liquid or gas heat exchange mediums are desirable characteristics of such a material.

Thermally Form Stable, High-Density Polyethylene-Pellet Phase-Change Material for Thermal-Energy Storage

Phase-change materials having high latent heats of fusion offer an advantage over sensible-heat-only storage materials in terms of energy storage per unit of volume. However, most phase-change materials suffer other drawbacks, such as the incongruent melting behavior of many salt-hydrates, and poor heat transfer in large blocks of paraffin wax. A highly crystalline polymer, such as high-density polyethylene (HDPE), offers definite advantages as a potential thermal-energy storage material if it is crosslinked and thereby rendered form stable so that it does not flow on melting. Thus, thermally form stable crosslinked pellets of HDPE can be used in the form of a low-cost, efficient, pellet-bed heat exchanger. The small size of the pellets and the interstices between pellets combine to provide effective heat transfer to a fluid or air medium.

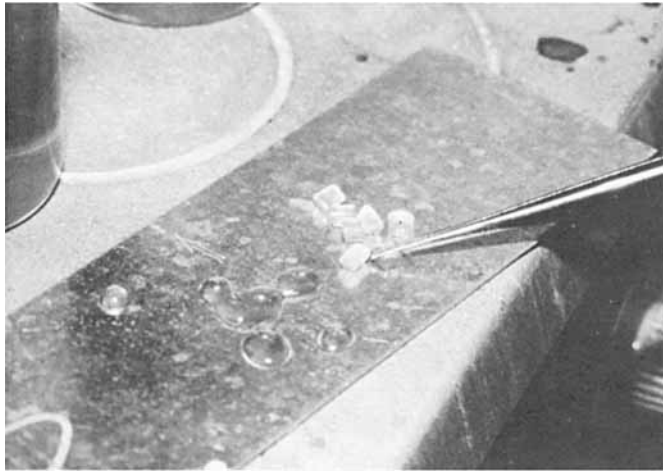
The thermal form stability of crosslinked HDPE pellets is illustrated graphically in Figure 1. The uncrosslinked pellets (left) deform and flow into flattened discs upon melting, whereas the crosslinked pellets (right) maintain their original shape and form through repeated melt/freeze cycles.

Figure 2 shows a differential scanning calorimeter thermogram of a commercial HDPE (Marlex EMN) which has a calculated heat of fusion of 59 cal/g.

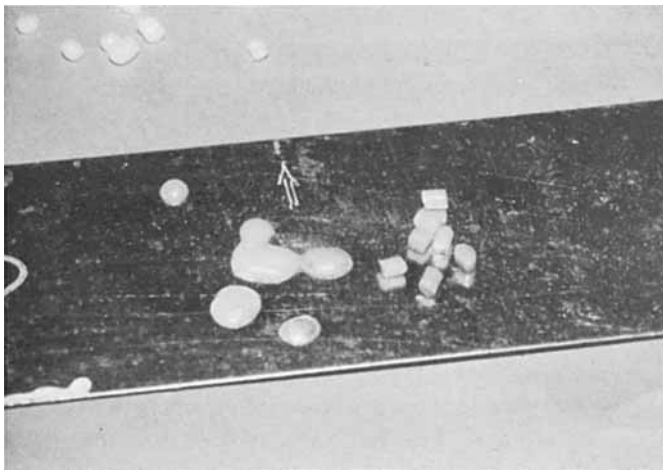
Fundamentals of Crystalline-to-Amorphous Phase Change in Alkyl Hydrocarbons and Polyethylenes

In simple alkyl hydrocarbons, derived from petroleum, there is a direct relationship between linear (unbranched) carbon chain length and dependent properties, such as density, melting point, crystallinity, and heat of fusion. There is a progressive increase in all these properties with increasing chain length until they all plateau in linear molecules of >30 carbon atoms length.

The same relationship between linear carbon chain length and density, melting



(A)



(B)

Fig. 1. Thermal form stability of heated HDPE pellets: uncrosslinked pellets (left) flow into flattened disc; crosslinked pellets (right) retain original cylindrical shape—do not flow. (A) Hot; (B) Cold—after heating.

point, crystallinity, and heat of fusion is also observed in high molecular weight polyethylene hydrocarbons having chain lengths of 2000 carbon atoms or more. Completely linear polyethylenes cannot be readily synthesized by practical techniques, and all commercial polyethylenes are branched to varying degrees. Polyethylenes prepared by mass polymerization at high temperature and high pressure with peroxide catalysts (LDPE) are highly branched and will contain an average of 25–35 branches/1000 carbon atoms. They will have a density of ~ 0.92 g/cc, a melting point of $\sim 115^{\circ}\text{C}$, crystallinity of $\sim 40\%$, and a heat of fusion of ~ 11 cal/g. In contrast, polyethylenes polymerized at low temperature and low pressure using the Ziegler or Phillips catalyst (HDPE) have much greater linearity and contain ~ 0.5 – 1.0 branches/1000 carbon atoms. They will have a density of ~ 0.96 g/cc, a melting point of $\sim 132^{\circ}\text{C}$, and crystallinity of $\sim 95\%$. A

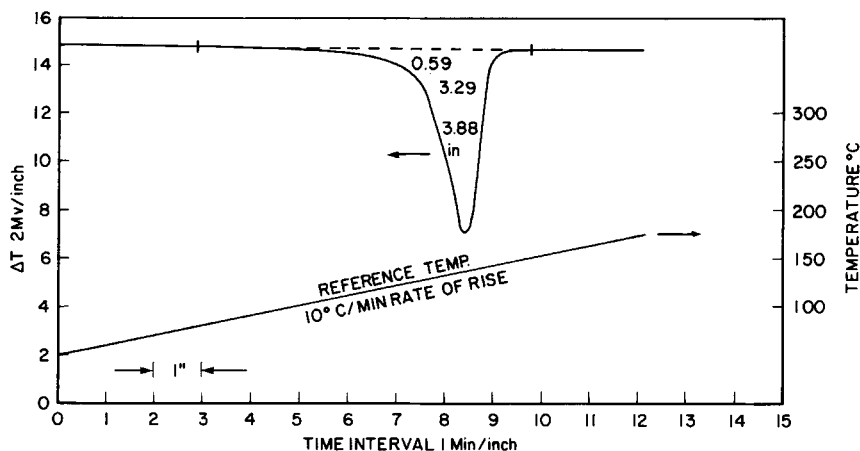


Fig. 2. Differential scanning calorimeter thermogram of Phillips Markx EMN TR-885: $\Delta H = (3.88/4.29)(60 \times 1.0 \times 1.10 \times 1.0) = 59.69$ cal/g; $\langle \Delta H \rangle = 58.61$ cal/g ± 1.63 .

heat of fusion of ~ 50 cal/g can be expected with values of 44–58 cal/g reported.¹

However, the ability of polyethylenes of any type to crystallize is also controlled by molecular weight, since the very high molecular weight molecule is less able to move into the crystal lattice. Thus, in HDPEs of equivalent linearity, the highest crystallinity and heat of fusion is obtained in products of lower molecular weight ($M_v = 30,000$).

Crosslinks are also branch points that, while eliminating melt flow (desirable for "thermal form stability"), also decrease crystallinity and heat of fusion (undesirable for high capacity energy storage). Obviously, then, for highest heat of fusion and best energy storage, branch crosslinking must be kept at a low value (e.g., $< 1/1000$ carbon atoms). This requirement does not impose serious problems since statistically one crosslink branch per molecule of ~ 2000 carbon atoms should be sufficient to eliminate melt flow entirely.

Thus, among polyethylenes, it is only the linear, low-pressure, high melting point, high crystallinity, high heat of fusion (ΔH_f) high-density polyethylenes, which are lightly crosslinked and have a relatively low initial molecular weight, which are of interest as materials for thermal-energy storage from either solar collectors, off-peak electric, or other intermittent sources. There are other crystalline polymers of both higher and lower melting points available, but none are as low in cost as polyethylene.

Both high- and low-density polyethylenes sell in the price range of \$0.52/lb, depending on grade, with the low-density products currently selling at slightly higher prices than high density. More than 4×10^9 lb of HDPE are produced annually in the United States for various uses. Thus, an adequate supply of the pelleted HDPE starting material is assured.

Crosslinking of HDPE Pellets

In the first of two studies funded by DOE,¹⁻⁷ three general methods of controlled cross-linking of HDPE pellets were investigated: (1) incorporation and

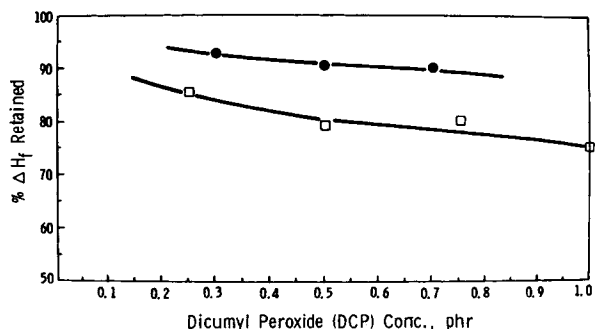


Fig. 3. Percent retained ΔH_f vs. dicumyl peroxide concentration in HDPE Alathon 7040 (\square) and Petrothene LS-606 (\bullet).

thermal activation of a peroxide in the HDPE to produce —C—C— crosslinks; (2) grafting of vinyl triethoxy silane (VTES) onto the HDPE backbone, followed by hydrolysis in an aqueous environment to give —C—Si—O—Si—C— crosslinks; and (3) electron beam irradiation to crosslink through free radical initiated —C—C— bonds. All three methods were successful in that thermally form stable pellets could be obtained that retained $>80\%$ of the initial heat of fusion of the uncrosslinked HDPE. However, the combined raw material and process costs for the peroxide ($\sim\$0.10/\text{lb}$) and VTES ($\sim\$0.20/\text{lb}$) added significantly to the cost of the HDPE-TES system. This led us in the second DOE-sponsored research³ to concentrate exclusively on a detailed study of the variables in the electron beam crosslinking process that had a lower estimated cost of $\sim\$0.01/\text{lb}$ of HDPE pellets processed. For completeness, however, the results obtained in the two chemical crosslinking processes will be briefly summarized, and the electron beam process results presented in more detail.

Peroxide-Initiated, Free-Radical Crosslinking of HDPE. Although three different processes were investigated, the preferred process was to blend the peroxide with the selected HDPE powder (or pellets) at low temperature, followed by extrusion at high temperature, to activate the peroxide and reform the pellets. Several different peroxides were evaluated, but dicumyl peroxide (DiCup) was one of the most effective and was used in the major part of the work. Five different commercial grades of HDPE were also tested, but DuPont's Alathon 7040 was used in most of the tests.

The effect of peroxide (DiCup) concentration on the retention of ΔH_f is shown graphically in Figure 3 for two different commercial HDPEs. As indicated, thermally form stable pellets were obtained at 0.5% wt of DiCup in Alathon 7040 ($\sim 80\%$ retention of ΔH_f), whereas 0.8% wt of DiCup was required in Petrothene LS ($\sim 85\%$ retention of ΔH_f). The percent of ΔH_f retained in HDPEs of five different molecular weights is shown in Figure 4, where the lower initial molecular weights gave significantly higher retention of ΔH_f .

Vinyl Triethoxy Silane Grafting and Crosslinking of HDPE. The second major type of crosslinked HDPE product examined as a TES material was one which contained a siloxane (—C—Si—O—Si—) bond between the polyethylene chains. It was obtained by grafting vinyl triethoxy silane onto the HDPE backbone in the melt, followed by crosslinking in an aqueous environment below the HDPE melting point. In general, the grafting and crosslinking procedures used followed those of Scott.⁸

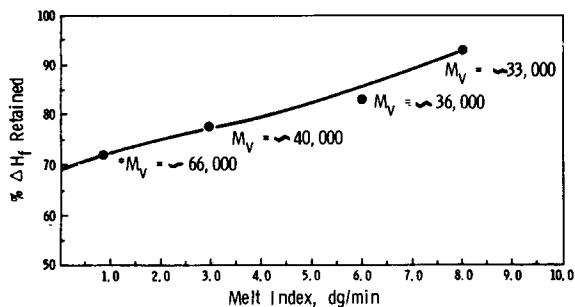


Fig. 4. Percent retained ΔH_f vs. HDPE melt index (mol wt) when crosslinked with 0.5 phr of dicumyl peroxide. * Ref. 5; $\log MI = 16.8 - 3.5 \log M_v$.

Table I summarizes some of the results obtained using Alathon 7040 as the starting HDPE resin. It should be noted that grafting with 3- and 10-phr concentrations of vinyl triethoxy silane (VTES) was carried out on a hot mill roll. This procedure gave inferior results compared to grafting in a Banbury intensive mixer with 8-phr VTES concentration, as shown by the form-stability results in Table I. In subsequent work with the grafting carried out in a Banbury mixer, the VTES concentration was reduced to 6 phr, and form-stable pellets were obtained. This method of silane grafting and crosslinking Alathon 7040 HDPE produced the highest percent ΔH_f retained of any method used while achieving adequate pellet-form stability in the melt. This result may, however, be attributable to the fact that the major portion of the hydrolysis crosslinking takes place at the surface, and only to a lesser extent in the interior of the pellet.

A plot of ΔH_f retained vs. initial polyethylene melt index is shown in Figure 5. In contrast to the results obtained using peroxide, the percent ΔH_f retained shows little change with melt index, and is high for all samples.

Electron Beam Irradiation Crosslinking of HDPE. Electron beam irradiation requires less protective shielding and involves less hazards to operating personnel than gamma irradiation (i.e., Cobalt-60 source). Both processes operate similarly in modification of polymers in that they create free-radical sites which can then further react to cause crosslinking, scission, or unzipping.

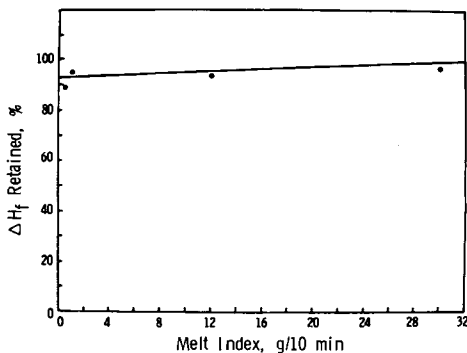


Fig. 5. Percent retained ΔH_f vs. HDPE melt index when crosslinked with 6 phr of vinyl triethoxy silane.

TABLE I
 Thermal Properties of Silane-Grafted and Crosslinked PE

Starting PE resin	Silane-grafting process ^a		Crosslinking process	Pellets Flow ^b on melting	DSC characterization			Melt index ^e (g/10 min/190°C)
	VTES concn (phr)	Grafting/catalyst incorporation			T_M (°C)	ΔH_f (cal/g)	ΔH_f^d retained (%) (crosslinked)	
Norchem XLM	—	Commercial silane-grafted LDPE coextrude with catalyst-containing LDPE (95/5 ratio) at MRC	1. None 2. 30 min/boiling H ₂ O	Yes No	99 100	11 14	— 100	2.0 —
Alathon 7040	3	Graft via hot milling and coextrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5 ratio)	1. None 2. 72 h/boiling H ₂ O	Yes Very slightly	132 131	44 46	— 100	— —
Alathon 7040	10	Graft via hot milling and coextrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5 ratio)	1. None 2. 48 h/boiling H ₂ O	Yes Very slightly	132 132	45 46	— 100	1.8 Not obtainable
Alathon 7040	8	Graft via hot-melt Banbury mixing and coextrude with catalyst-containing (1 phr DBTDL) Alathon 7040 (95/5 ratio) (5-lb batch prepared)	1. None 2. 40 h/boiling H ₂ O	Yes No	131 132	43 43	— 93	1.65 Not obtainable

^a VTES = vinyl triethoxysilane; DBTDL = dibutyltin dilaurate.

^b Pellets heated in air to 200°C in Fischer-Johns mp apparatus.

^c DSC conditions used: 10°C/min heating and cooling rates, range 8, 0.75 in./min chart speed, indium standard, T_M = melting temperature (peak), ΔH_f = heat of fusion.

^d As compared to ΔH_f of starting PE resin.

^e ASTM D-1238.

TABLE II
 Characterization of Radiation Crosslinked Alathon HDPE (0.93 MI) Pellets^a

Radiation dosage (Mrads)	Appearance of irradiated pellets	Form-stability in air ^b		T_M^c (°C)	ΔH_f (cal/g)	ΔH_f retained ^d (%)
		Observations	Rating			
None (control)	White	Pellets "flatten," soften and adhere in the melt—can't readily break them apart when cooled	Fair	132	44.6	—
4.5	White	Pellets retain shape—little "flattening"—adhere slightly in melt, but break apart when cooled	Good	131	41.8	94
9.0	Very faint yellow	No change in pellet shape as they melt and no tendency to self-adhere in melt (do so very slightly on cooling)	Very good	130	39.3	88
13.5	Faint yellow tinge	Pellets very firm in melt—no tendency to self-adhere at all in melt or as cooled	Excellent	129	38.2	86
18.0	Definite yellow tinge	Cycled 30 times around mp in ethylene glycol—no adhesion	Excellent	129	36.1	95
		Pellets very firm in melt and have only a very slight tendency to self-adhere in melt	Very good to excellent	130	37.5	84

^a DSC conditions: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min, indium calibration standard.

^b As determined by heating touching pellets to 200°C on Fischer-Johns mp apparatus.

^c T_M = crystalline melting point; ΔH_f = heat of fusion; values for irradiated PE samples are averages of two separate DSC samples (3 melting cycles each). Percent ΔH_f compared to unirradiated Alathon PE resins, except for sample cycled 30× around mp (compared to ΔH_f before cycling).

^d As compared to ΔH_f of starting HDPE control.

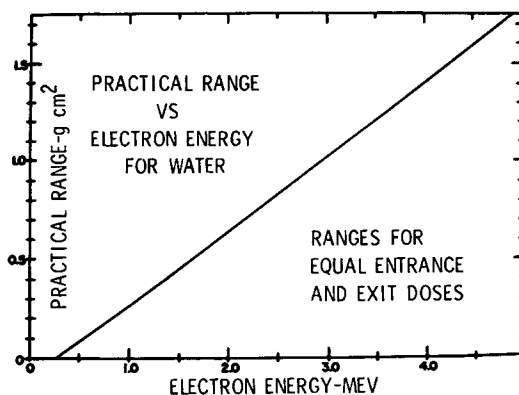


Fig. 6. Electron beam penetration vs. material thickness at various voltages.

Polyethylene is one of the polymers that undergoes progressive crosslinking upon exposure to either electron beam or gamma irradiation. Until recently, electron beam modification of polymers and other materials was severely limited by the depth of penetration of the electrons. However, the advent of the newer machines with operating voltages of $1-5 \times 10^6$ has largely overcome this handicap of E-beam processing. A graph of E-beam penetration vs. voltage is shown in Figure 6.

The electron beam irradiation crosslinking of HDPE pellets was done at the plant of Radiation Dynamics, Inc., Melville, N.Y. In the first DOE program, a single material, Alathon 7040, was irradiated to four different levels of total dosage (4.5, 9.0, 13.5, and 18.0 Mrads) in air medium. Results summarized in Table II showed that, under the conditions used, adequate thermal form stability could be achieved at a total dose of only 4.5 Mrads, but better results were obtained at 9.0 and 13.5 Mrads.

Because of the more favorable economics of radiation crosslinking compared

TABLE III
Commercial Source, Melt Index, and Density of Commercial HDPE Pellets

Supplier	High-density polyethylene	Melt index ^a (dg/min)	Density ^a (g/cc)
1. DuPont	Alathon 7040, pellets	6.0	0.96
	Alathon 7050, pellets	17.5	0.96
2. Phillips Petroleum	Marlex TR-885, powder	30.0	0.964
	Marlex TR-885, pellets	30.0	0.964
	6006, pellets	0.7	0.958
	6030, pellets	3.0	0.960
3. U.S. Industrial Chemicals Co.	LS-556, pellets	8.0	0.955
	LS-606, pellets	10.0	0.962
	LS-630, pellets	32.0	0.962
4. Dow	42060N, pellets	42.0	0.960
	12065, pellets	0.9	0.965
	08064N, pellets	8.0	0.964
5. Gulf	9606, pellets		0.953

^a Nominal values supplied by vendor.

TABLE IV
 Initial Melting Temperature and Enthalpy of Fusion of HDPEs

Sample	Heating cycle			Enthalpy of fusion (cal/g)	Cooling cycle			Enthalpy of fusion (cal/g)
	T_1	Temp (°K) T_2	T_3		T_1	Temp (°K) T_2	T_3	
7040	382	408	412	46.2	393	388	364	48.2
7050	385	406	410	47.3	393	387	370	44.2
TR-855, powder	384	406	409	47.6	395	390	369	50.5
TR-855, pellets	388	407	410	46.6	394	390	377	46.0
6006	384	411	420	47.1	398	392	365	49.1
6030	383	408	412	44.4	396	392	368	47.4
LS-556	385	406	410	38.2	393	390	377	41.2
LS-606	384	407	410	45.6	395	391	372	44.6
LS-630	381	407	411	47.3	394	390	367	45.6
8064	390	407	411	43.7	394	389	375	43.2
1-12065	387	407	411	40.5	395	390	370	42.2
4-2060	389	406	410	42.4	393	386	372	43.4
9606	370	405	410	45.6	394	389	360	43.3

to the peroxide and vinyl triethoxy silane methods, a more detailed study of the E-beam processing was carried out. A total of 13 different HDPE materials obtained from five commercial suppliers were evaluated. The starting polymers were tested for melt index, density, melting point (heating and cooling), and heat of fusion (heating and cooling). The heat of fusion measurements were done on a Perkin-Elmer DSC-2 Calorimeter using a heating and cooling rate of 10°C/min. The results of these measurements are presented in Tables III and IV.

The same HDPE pellets were then irradiated at dosages ranging from 2 to 10 Mrads as shown in Table V. The results were compared to those values which were measured on the HDPE pellets prior to their irradiation. No significant difference was observed in the values of the melting temperature as a function of the radiation dosage. All of the irradiated pellets show that the solid/liquid transformation is still present in their irradiated condition. The results for the values of the heat of fusion do show the expected trend toward lower values with increasing radiation doses. The values for the heat of fusion as a function of the total radiation dose for the DuPont 7040 HDPE pellets are shown in Figure 7.

Four of the commercial polyethylene products were selected for larger-scale electron beam irradiation experiments. These products were the DuPont 7040 pellets, Phillips TR-885 pellets, U.S. Industrial Chemicals LS-630 pellets, and Gulf 9606 pellets. The variables associated with the electron beam irradiation which were studied in our tests were (1) total irradiation dose received by the pellets, (2) accelerating potential of the electron beam, (3) electron beam current, (4) effect of irradiation of the pellets in inert atmospheres, (5) effect of multiple passes and stirring of the pellets during the irradiation, and (6) effect of air vs. other inert atmospheres during irradiation. Results in terms of thermal form stability and retained ΔH_f were obtained on the commercial Alathon HDPEs [Figs. 8(a)–(g)] as reported in Refs. 3 and 4.

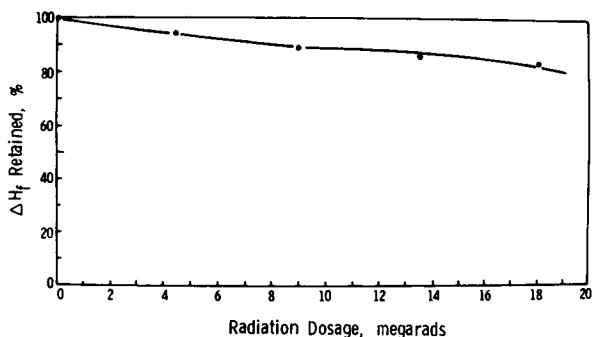


Fig. 7. Percent retained ΔH_f vs. electron beam irradiation dosage in HDPE Alathon 7040, MI = 0.93.

Concerning the effects of all the radiation variables studied, it is now possible to conclude the following:

(1) A total dose of 6–8 Mrads is needed to obtain satisfactory thermal form stability. This is achieved with a decrease in initial heat of fusion of ~ 5 cal/g (e.g., from 45 to 40 cal/g).

(2) Voltages ranging from 1.5 to 4.5×10^6 eV were evaluated and comparable crosslinking obtained at all voltages at the same total dose, provided pellet-bed depth was adjusted to ensure uniform penetration. Thus, accelerating voltage is primarily of economic importance in that higher voltages allow processing of a thicker bed of pellets, and thus results in more product output per unit of time of beam operation (lower processing cost).

(3) Electron-beam current from 5 to 30 mA were investigated. Thermal form stability was unaffected by mean current at equivalent total dose. Higher amperages permit a given dosage to be achieved in a shorter time interval resulting again in lower-cost processing.

(4) Provided that E-beam voltage, amperage, pellet-bed depth, and cart speed are properly adjusted, there is no advantage to multiple passes and stirring of the pellets between passes.

(5) No significant improvement in thermal form stability vs. retained ΔH_f was achieved in our tests of an inert atmosphere over the samples (N_2 , CO_2 , and helium) during processing. However, this inconclusive result may be due to the fact that experimentally it was not possible to completely exclude air (O_2). Typical conditions for economic production of crosslinked HDPE pellets for thermal-energy storage are: voltage 3,000,000 eV; current 33 mA; pellet-bed depth 0.25–0.50 in.; bed velocity ~ 16 ft/min; atmosphere, air; number of passes, 1; dosage 8 Mrads.

Thermal-Energy Storage Tests

The results discussed above regarding crosslinking of HDPE pellets, thermal form stability, and retention of heat of fusion were obtained on very small laboratory-size samples. The differential-scanning calorimeter measurements were made on mg quantities of material cut from individual pellets. To confirm the potential of HDPE pellets for thermal-energy storage, and the stability of the material to repeated thermocycling, larger scale tests in an actual pellet-bed heat

TABLE V
Enthalpy of Fusion and Melting Temperature of HDPE Pellets as a Function of Electron Beam Irradiation

Sample	Radiation level (Mrads)	Heating cycle			Enthalpy of fusion (cal/g)	Cooling cycle			Enthalpy of Fusion (cal/g)
		T_1	Temp (°K) T_2	T_3		T_1	Temp (°K) T_2	T_3	
7040	As received	382	408	412	46.2	393	388	364	48.2
	2	373	408	412	42.8	393	388	362	40.5
	4	373	408	414	43.2	393	387	361	40.9
	6	371	406	411	39.9	393	387	362	38.8
	8	369	407	411	42.9	393	388	363	40.1
	10	373	405	410	40.4	393	387	361	40.0
	12	371	405	410	37.9	393	387	363	35.7
	8 ^a	373	406	412	38.0	393	387	368	36.6
	8 ^b	373	406	412	39.8	392	386	363	38.8
	8 ^c	373	404	409	37.9	393	387	364	36.4
	As received	388	407	410	46.6	394	390	377	46.0
	TR-885	2	376	406	409	48.7	394	390	360
4		377	406	409	48.7	394	390	362	46.7
6		373	407	410	51.0	394	390	360	50.2

LS-630	8	373	406	411	40.7	392	388	360	40.5
	10	373	406	411	40.2	393	388	362	40.2
	12	373	405	411	39.7	398	389	364	41.5
	As received	381	407	411	47.3	394	390	367	45.6
	2	372	405	408	45.4	394	390	361	48.3
	4	373	406	409	47.8	393	389	361	45.3
	6	373	406	410	49.0	393	390	360	46.2
	8	373	406	411	43.6	392	390	360	40.4
	10	372	406	411	42.0	392	388	359	40.7
	12	373	405	409	42.9	393	390	360	38.9
	As received	370	405	410	45.6	394	389	360	43.3
	Gulf 9606	2	369	405	409	41.1	393	389	361
4		368	405	410	41.8	393	388	360	36.3
6		371	404	409	35.2	392	387	360	35.0
8		367	403	407	35.5	392	388	360	33.0
10		366	401	406	35.7	393	387	360	31.7
12		367	401	406	37.0	395	387	360	34.3

^a Electron beam current = 10.30 mA.

^b Electron beam current = 5.65 mA.

^c HDPE stirred during radiation exposure.

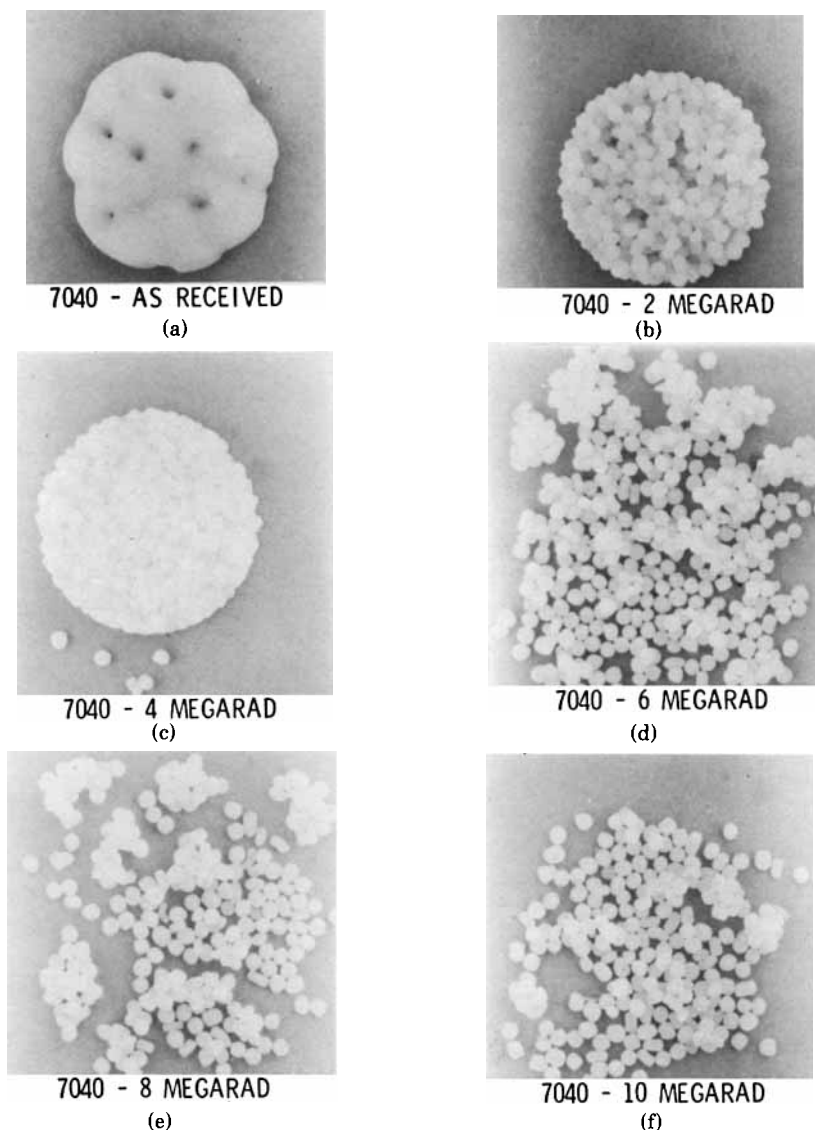
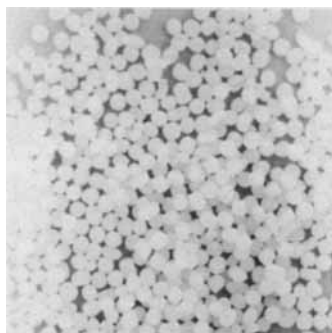


Fig. 8. Thermal form stability of Alathon 7040 HDPE pellets vs. total E-beam dosage after exposure in boiling ethylene glycol. (a) Condition: as received, exposure interval 2 h; (b) condition: 2-Mrad dose, exposure interval 2.5 h; (c) condition: 4-Mrad dose, exposure interval 2 h; (d) condition: 6-Mrad dose, exposure interval 72 h; (e) condition: 8-Mrad dose, exposure interval 72 h; (f) condition: 10-Mrad dose, exposure interval 96 h; (g) condition: 12-Mrad dose, exposure interval 96 h.

exchanger were necessary. A 1-gal (5-lb) laboratory glassware unit (for "screening"), and a 60-gal (250-lb) "pilot-plant" unit (for final evaluation) were used.

Thermocycling (Melt/Freeze) Evaluation of Irradiated HDPE Pellets in a 5-lb Thermal-Energy Storage Test Unit. The performance of the HDPE pellets during repeated melt/freeze cycling was evaluated initially in a 5-lb thermal-energy storage test unit. The 5-lb TES test unit is shown in Figure 9.



7040 - 12 MEGARAD
(g)

Fig. 8 (Continued from the previous page.)

This TES unit was fabricated under an earlier ERDA Contract No. EY-76-C-05-5159, and its operation is fully described in the final report.¹ This report is available from the National Technical Information Service. A block diagram of the TES test unit is shown in Figure 10. The TES test unit consists of four basic components: the storage chamber which holds the HDPE pellets; an electrical heater which heats the heat exchange fluid; a cooling unit for removing heat energy from the system; and a metering pump to control the flow of the heat exchange fluid.

The HDPE pellets which were evaluated in this test unit were the DuPont 7040 pellets, U.S. Industrial Chemicals LS-630 pellets, and Gulf 9606 pellets. A 5-lb quantity of the HDPE pellets were loaded into the storage column, and the unit was filled with Prestone II as the heat transfer fluid. The HDPE pellet bed was thermally cycled between 100°C and 145°C through more than 100 complete cycles. The melting and freezing of the pellet bed was detected by the thermal

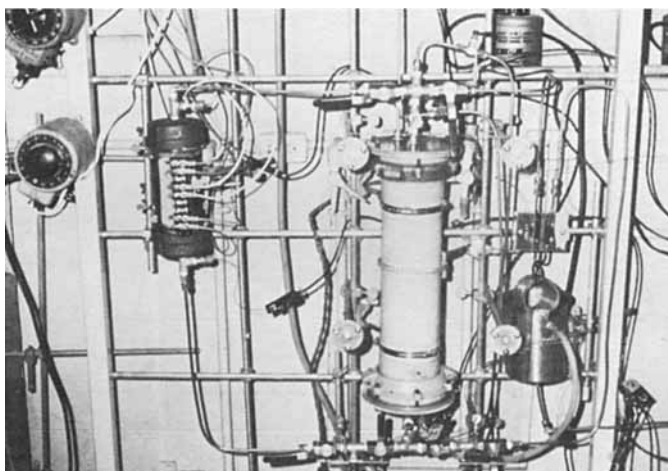


Fig. 9. Photograph of 1-gal (5-lb) lab scale thermal energy storage unit filled with crosslinked Alathon 7040 pellets.

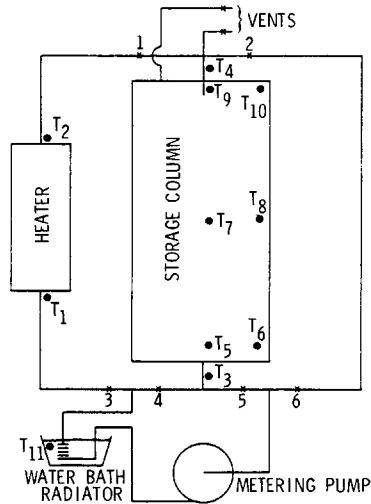


Fig. 10. Schematic block diagram of 5-lb laboratory thermal energy storage unit: (X) flow control valves; (●) thermocouples.

arrest of the thermocouples which sensed the temperatures within the storage column and at the outlet port of the heat transfer fluid. The melting and freezing of the pellet bed was confirmed by visual observation through the viewing ports in the insulation of the storage column. A typical plot of the temperature versus time during a cooling cycle is presented in Figure 11. The temperatures measured at the inlet and the outlet of the heat transfer fluid and within the storage column are shown as a function of time from the initiation of the cooling mode of the cycle. As shown in this figure, the temperature of the heat transfer fluid drops rapidly to 100°C. The temperatures within the pellet bed show the

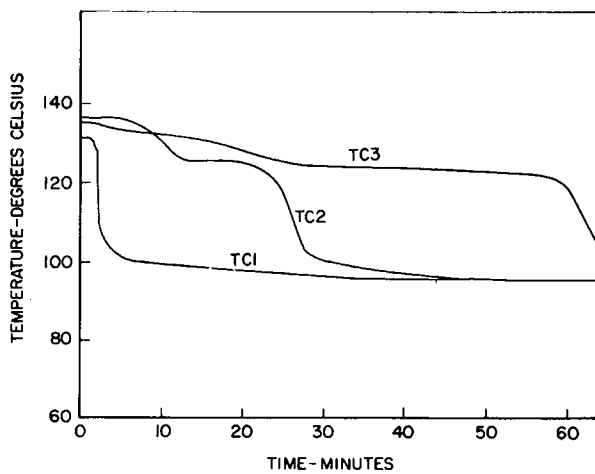


Fig. 11. Graph of temperature vs. flow-through time during a cooling cycle in 5-lb TES unit filled with crosslinked Alathon 7040 pellets on cycle no. 112. Flow rate = 133.2 mL/min; (TC1) inlet; (TC2) storage column; (TC3) outlet.

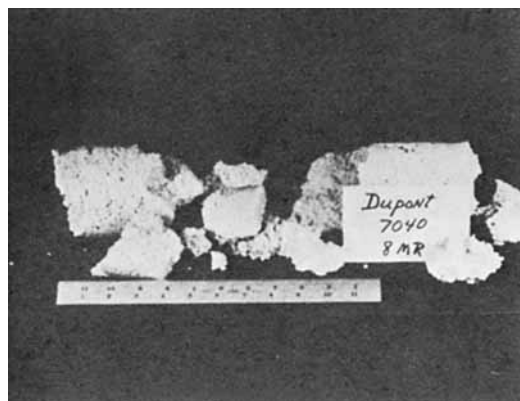


Fig. 12. Photograph of crosslinked Alathon 7040 HDPE pellets after being repeatedly cycled through their melting point in the 5-lb TES unit.

thermal arrest as the pellet bed freezes at 126°C. The temperature of the heat transfer fluid at the outlet remains essentially constant until the freezing of the HDPE pellet bed has been completed. The completion of the freezing of the HDPE pellet bed is observed by the rapid drop in temperature of the heat transfer fluid at the outlet of the storage column. The temperature-time plots of the cooling portion of the cycle after more than 100 cycles were compared to the temperature-time plots which were measured before the accumulation of the heating and cooling cycles. This comparison of the performance of the HDPE pellet bed did not show any significant difference. The condition of the pellets after their removal from the storage column is shown in Figure 12.

Although the pellets had adhered to one another at their points of contact, the pellet bed maintained an open porous structure throughout the thermal-cycling tests. Further, the bonding between the pellets is very small. This observation is based on an experiment which was conducted on a small quantity of the HDPE pellets after they were recovered from the thermal-cycling tests. The clumps of HDPE pellets were heated in a stirred ethylene glycol bath to 150°C. All of the clumps of pellets reverted back to individual pellets within a 30-min time interval.

Thermocycling (Melt/Freeze) Evaluation of Irradiated HDPE Pellets in a 250-lb Test Unit. As a result of the successful demonstration of the HDPE pellet bed in the 5-lb TES test unit, melt/freeze cycling tests on an HDPE pellet bed were performed in a 250-lb prototype TES test unit (Fig. 13). This unit and its operation are fully discussed in the final report cited earlier, and only a brief description is included here. The flow diagram for the 250-lb unit is similar to the 5-lb test unit shown in Figure 11. The principle differences between the two units are: (1) elimination of the water bath radiator in the 250-lb unit, (2) incorporation of a water-cooled heat exchanger in the line between the valves numbered 2 and 6 in the 250-lb unit, and (3) incorporation of an electrically operated control system which automatically controls the heating and cooling portion of the cycles. The storage column was filled with 250 lb of the DuPont 7040 pellets. These pellets were irradiated to a dose of 8 Mrads at the electron beam facility at Radiation Dynamics Inc. The flow of the heat transfer fluid



Fig. 13. Photograph of the 60-gal (250-lb) pilot plant TES unit.

through the storage column was channeled through the HDPE pellet bed by a series of baffles. Since the HDPE pellets have a tendency to adhere to one another at their point of contact, an aluminum screen with a mesh size of 20 openings/in. was used to partition the pellet bed into sizes which facilitate their easy removal at the end of the cyclic testing. In a separate test, the HDPE pellets were observed not to adhere to the aluminum screen.

The HDPE pellet bed was tested through more than 100 complete heating and cooling cycles. The time interval required to cool the pellet bed was typically on the order of 30 min. The temperatures of the inlet, the outlet, and within the pellet bed are shown as a function of the time interval during the freezing portion of one cycle in Figure 14. The inlet temperature of the heat transfer fluid shows a slight decline over the time interval during the cooling portions of the cycle. During the middle portion of the time intervals, the temperature within the pellet bed and in the outlet are reasonably constant. This characteristic is due to the isothermal freezing behavior of the HDPE pellet bed. Upon completion of the freezing of the pellet bed, these temperatures drop rapidly to the value of the temperature of the heat transfer fluid entering the storage column.

The HDPE pellet bed was removed and examined upon completion of 104 cycles. A close-up view of the HDPE pellets after testing is shown in Figure 15. As shown in this view, the pellets had adhered at their points of contact, but had maintained an open porous structure which allowed the free flow of the heat transfer fluid through the pellet bed.

Upon completing the above tests, a total of 15,000 lb of Alathon 7040 HDPE pellets were then crosslinked to the level of 8 Mrads under the optimum condi-

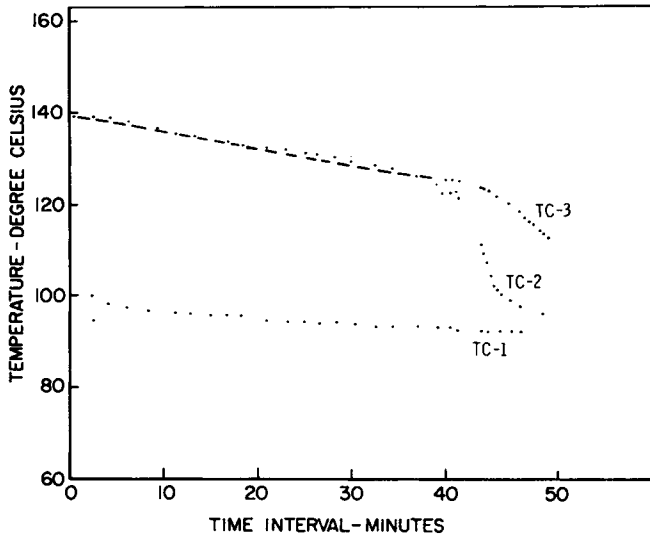


Fig. 14. A plot of the temperatures at the inlet (TC-1) and outlet (TC-3) ports of the storage column (TC-2) and within the storage column as a function of the time interval on cooling cycle no. 82.

tions reported in the prior section. The material was then divided in half (7500 lb), and shipped to Argonne and Oak Ridge National Laboratories, respectively, for larger scale application tests. With the recent catastrophic decrease in DOE's budget, it is our understanding that the scheduled tests have been deferred and may not be completed.

The total thermal-energy storage that could be made available from the insulated 250-lb (60-gal) pilot plant unit is substantial and may be nearly sufficient for 12 h of off-peak electric heating of an average residential house in the Dayton, Oh., area.

For heating, based on using the latent and sensible heat available between the

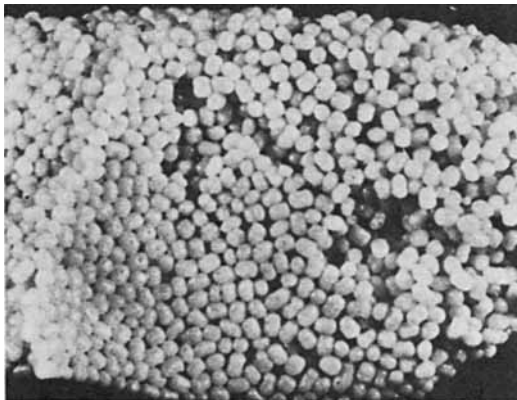


Fig. 15. Close-up view of the HDPE pellet bed. (Note: The HDPE pellets have retained their physical form after more than 100 cycles through their melting point.)

temperatures of 284°F and 104°F, and, ignoring insulation and other losses, the maximum capacity of the HDPE system components is as follows:

Latent heat of HDPE (Btu)		
$\text{lb} \times \Delta H_f = 250 \times 90 =$	22,500	
Sensible heat of HDPE (Btu)		
$1 \text{ lb} \times \Delta T \times C_p = 250 \times 180 \times 0.66 =$	29,700	(1)
Sensible heat of ethylene glycol (Btu)		
$\text{lb} \times \Delta T \times C_p = 85 \times 180 \times 0.66 =$	10,098	
Sensible heat of 250-lb storage vessel (Btu)		
$\text{lb} \times \Delta T \times C_p = 250 \times 180 \times 0.1168 =$	5,256	
Total available (Btu)	67,554	

For cooling, via absorption air conditioning, the total available storage is significantly less (~47,000 Btu) because absorption-unit operation becomes inefficient below ~184°F, and thus, the contribution of the sensible components to system capacity is proportionately less. Nonetheless, a larger unit of the 80-gal size should have sufficient storage capacity for home cooling (and heating) of an average residential house in the Dayton, Oh., area.

An important result of this analysis is that projected raw materials and systems cost for the HDPE storage unit should be sufficiently low to make a 5-year, payback time realistic—with appropriate off-peak incentive (e.g., 1/3) electric power cost.

Cost/Benefit Analysis of the HDPE Thermal-Energy Storage System

In prior research by one of the authors,² a cost/benefit analysis of the HDPE thermal-energy storage system vs. rocks, ethylene glycol alone, and pressurized water was performed. The results obtained in that study are summarized below.

The costs developed for a complete HDPE-*TES* system, including all hardware and labor, operating in its optimum temperature range of 120–140°C, were determined to be \$0.94/Btu for a liquid thermal transfer system (with ethylene glycol) and \$0.79/Btu for air thermal transfer. For liquid thermal transfer systems, these costs are about half that for ethylene glycol alone, and even lower than for rocks or pressurized water.

The overall favorable cost comparisons, in spite of higher initial material costs, result primarily from the larger volumes (and, hence, larger and more expensive storage tanks) required for the other storage media which utilize sensible heat only. Thus, both the importance of the heat-of-fusion contribution and the pellet-bed concept, where the HDPE material serves as its own heat exchanger, were demonstrated.

Importantly, the form-stable HDPE-*TES* material could be made available immediately (1983) in almost any quantity. Two major producers of HDPE have indicated their interest in manufacturing a specific material for thermal-energy storage when a commercial market develops.

The potential savings in energy and capital expenses that could be realized from the use of the HDPE-*TES* system, combined with the demonstrated advantages and favorable economics, should act as stimuli for its implementation in the near future. This is particularly true since relatively little further development work is needed prior to actual introduction into the marketplace.

FUTURE WORK

The validity of the concept of thermal-energy storage in radiation crosslinked pellets of HDPE has been thoroughly established in the research reported herein. A low-cost process for the irradiation has also been developed and demonstrated. However, three tasks remain to be completed before the system is ready for commercial application.

More Extensive Thermocycling Tests

The larger-scale tests of radiation crosslinked HDPE in the 250-lb pilot plant unit were only taken to a total of 100 repeated cycles of melting and freezing. Repeated cycling up to this level showed no change in melting point or heat of fusion. However, more extensive thermocycling of up to at least 1000 successive melt/freeze cycles should be performed to ensure long-term performance.

Development of Improved HDPE Having a Higher Initial Heat of Fusion

In separate prior research, we have shown that high-density polyethylene having an initial heat of fusion of >60 cal/g can be obtained by practical modification of the polymerization process to produce a less-branched, higher crystallinity material with higher heat of fusion. Theoretical considerations indicate that a heat of fusion of 66 cal/g is possible in polyethylene that is completely linear (unbranched). It is, therefore, apparent that there is a practical route to producing an HDPE having an initial heat of fusion of >60 cal/g. After electron beam crosslinking, a retained heat of fusion of ~ 55 cal/g should also be possible. An increase in useable heat of fusion from the present 35–40 cal/g level to a foreseeable 55 cal/g represents a significant increase of at least 25% in thermal-energy storage capacity. This improved storage capacity has two practical advantages:

(1) It reduces the weight and cost of the HDPE raw material required to obtain a predetermined amount of storage capacity.

(2) The volumetric capacity and cost of the storage unit will be reduced proportionately.

Both of these effects make the HDPE–TES system more attractive by reducing initial system costs and subsequent payout time, etc.

This higher storage capacity of the new HDPE–TES system should be investigated—if supporting funds can be obtained from either government agencies or private industry.

Design and Testing of Full-Scale TES Systems That Can Be Used with Off-Peak Electric Power for Home Heating and Cooling

For residential off-peak power utilization, the amount of storage required would be only that needed for heating and cooling for a 12-h time period. If hot water heating is also included, the storage required would increase by the amount of hot water used. The size of the storage unit will also vary with the building size, location, insulation, as well as family size and other factors relating to energy utilization for heating and cooling.

However, for a selected insulated house in the Dayton, Ohio, area, preliminary calculations [eq. (1)] have indicated that the 12-h energy storage requirement could be contained in an insulated vessel of about 80-gal capacity. The storage tank would need to be fitted with all the necessary piping, valves, pumps, and controls. Further, a liquid-type heat exchanger for the heating and cooling (absorption air conditioning) would also have to be designed and integrated into the heating and cooling units. Optionally, a hot-water heating coil could also be included in the design of the storage unit. It should be possible, thereby, to eliminate the conventional hot-water heating/storage unit and to "produce" hot water only "on demand."

Direct passage of air to the TES storage unit for heating is not contemplated since this mode of operation has not been investigated and might cause degradation of the HDPE-TES material.

Once system design has been completed, the remaining task would be to install it in one or more typical homes, and collect actual performance data over a 2- to 3-year time period. Presuming that no major operational problems were encountered, the HDPE-TES system should then be ready for commercial production, sale, and large-scale utilization.

The chemical crosslinking studies summarized in the first part of this paper were carried out at Monsanto Research Corporation with Ruth A. Botham, George H. Jenkins, and George L. Ball, III, as collaborators. The measurements of heat of fusion of radiation crosslinked samples were done by Mr. Daniel E. Miller and Mr. William A. Price of the University of Dayton Research Institute. The contributions of all the above personnel to the research reported herein are gratefully acknowledged.

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