10. Polymers for Solar Energy Storage

Review Article

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Abstract

Energy storage is the need of the hour. We need to conserve our resources to avoid a "power-less" future. The article discusses the use of polymeric materials for solar energy storage and release applications. Mainly focusing on Phase Change Materials (PCMs) as a reliable method of solar energy storage, some other methods have also discussed.

Keywords: Solar energy, PCMs, polymers

1. Introduction

Due to rapid world-wide development, and growing population, the increase in energy demand is inevitable. At the current global energy consumption rate, it is just a matter of time before our energy resources will be exhausted. The need of the hour is to develop high performance, low cost and environment friendly energy conversion and storage systems. This is where application of polymers steps in!

Energy is available in various forms. This energy has to be efficiently managed to make it available at appropriate times and locations, both to balance generation with consumption and to maintain the energy grid stability. For example, wind and solar power installations generate power only intermittently and with a highly variable output. When the wind is blowing or the sun is shining, excess power should be stored and made available during suboptimal generating conditions or during peak demand. This requirement has led to greater demand for alternative energy storage facilities to support the grid.

Thus, energy storage plays a vital role in preventing energy loss and also helps utilizing the energy more efficiently. Most applications require that the energy is stored only for a short period like few hours; however, long term storage of a few months may also sometimes be needed.

When we talk of energy storage, the first thing that clicks, and rightly so, is the battery. This was invented in the 19th century, a time around which the electrochemical devices, fuel cells, were also developed. These fuel cells were light-weight, non-thermal sources of electricity that were required during manned spaceflights. With the passage of time these cells have been getting upgrades to increase the conversion efficiency of chemical energy to electrical energy. Several other technologies have also been investigated such as flywheels, which can store kinetic energy and compressed air storage, which can be pumped into underground caverns and storage. Another method of energy storage is the use of molten salts to store solar energy and deliver it as needed. The system pumps molten salt through a tower that is heated by the Sun's rays. There are a number of other such examples.

The conventional energy storage methods can be summarized as follows (Table 1), categorized based on the type of energy stored:

Table 1: Conventional Energy Storage Methods

Sr. No.	Energy	Storage-Types
1.	Chemical	Hydrogen/ Bio-fuels/ Liquid Nitrogen/ Oxyhydrogen/ Hydrogen Peroxide
2.	Biological	Starch/ Glycogen
3.	Electrochemical	Batteries/ Flow batteries/ Fuel cells
4.	Electrical	Capacitor/ Supercapacitor/ Superconducting magnetic energy storage
5.	Mechanical	Compressed air energy storage/ Flywheel energy storage/ Spring/ Gravitational Potential energy
6.	Thermal	Ice storage/ Molten salt/ Cryogenic liquid air or nitrogen/ Seasonal thermal store/ Solar pond/ Hot bricks/ Steam accumulator/ Fireless locomotive/ Eutectic systems

Taking into account today's increasing energy crisis situation, it becomes increasing necessary to tap the renewable energy sources. The fossil fuels are depleting rapidly. Also their use leads to emissions of large amounts of green house gases have several global impacts. Renewable energy sources like solar energy, wind energy, tidal energy, etc. are all clean forms of energy. The problem is that their use is limited due to time dependence and hence storage is a must. Polymers have proven to be effective materials for energy storage and delivery. Besides renewable energy sources, energy from non-renewable sources can also be stored.

2. Polymers for Energy Storage and Delivery

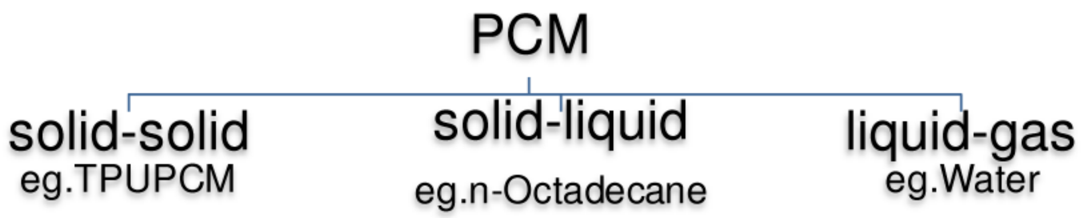
The demand for increasing renewable energy resources implies that storage of energy is a must. The fossil fuel reserves are depleting rapidly and the need of the hour is not only harnessing of cleaner, greener fuels but prevention of loss of any form of energy. Thus, we need to capture and store energy as far as possible.

2.1. Solar Energy: The use of PCMs (Phase Change Materials)

Solar energy is one of the most and abundant widely available energy resources to man: available throughout the Earth’s surface. This reserve needs efficient and economic tapping. The main problem with conventional solar energy harnessing methods is that the captured energy has to be used immediately. This limits the amount of energy that we can capture. However, with the development of effective methods to store this energy it is possible to increase the quantum of energy harnessed. By storage, we can capture solar energy during the day, when the radiant energy received is at its peak and the excess energy collected can be used at night, when the solar power received is negligible. The total rate at which energy enters the Earth's atmosphere is estimated at 174 petawatts. This is equal to the product of the solar constant, about 1,366 watts per square meter, and the area of the Earth's disc as seen from the Sun, about 1.28×10^{14} square meters, averaged over the Earth's surface, which is four times larger. (i.e. the area of a disc with the Earth's diameter, which is effectively the target for solar energy, is 1/4 the area of the entire surface of the Earth.) The solar flux averaged over just the sunlit half of the Earth's surface is about 680 W/m^2. This is a substantial amount of energy which can be efficiently used to reduce the energy crunch. Polymeric materials are well suited for this purpose, especially in the form of PCMs.

2.1.1. What is a PCM?

PCM or Phase Change Materials are those materials which are capable of storing large amounts of latent heat energy with little or no temperature change, and can also release this energy, in a suitable environment, when required. These PCMs can be of the following types:



PCMs use chemical bonds to store and release heat by phase transition. Liquid-gas PCMs are not of much practical importance due to large volume change on phase change. The solid-liquid PCMs are susceptible to leakage on phase change. Hence these are not very economical since they require containment- use containers or microencapsulations which are expensive. Properties of polymers making them good PCMs:

The phase transition temperatures for many polymers are viable for application in around the range of 15-90°C

- The quantum of latent heat stored is significantly high
- Show little or no volume change upon phase change
- The phase transition occurs at a constant temperature
- Have good reliability over several thermal cycles i.e. their thermal properties do not vary much over repeated cycling
- High energy storage density

Poly-ethylene glycol (PEG) is an attractive material to be used as a polymer backbone. It has a suitable phase change temperature, high latent heat capacity, melts uniformly at constant temperature, is non-toxic in, does not undergo super cooling, has low vapor pressure (leads to less loss) and has little or no volume change during the solid-liquid phase change. Depending on the molecular weight of PEG used, the thermal properties are seen to vary slightly. PEG can be used to synthesize thermoplastics, polyurethane solid-solid PCM, named as TPUPCM, one such of which is synthesized from THCD [bis(1.3-duhydroxypropan-2-yl)4,4' methylenebis(1,4-phenylene) dicarbamate].

The TPUPCM has good thermal and mechanical properties. The thermal stability is good, repeated thermal cycling studies [1] show very slight variation in the thermal properties over a thousand cycles. This indicates that it has great potential for thermal energy storage.

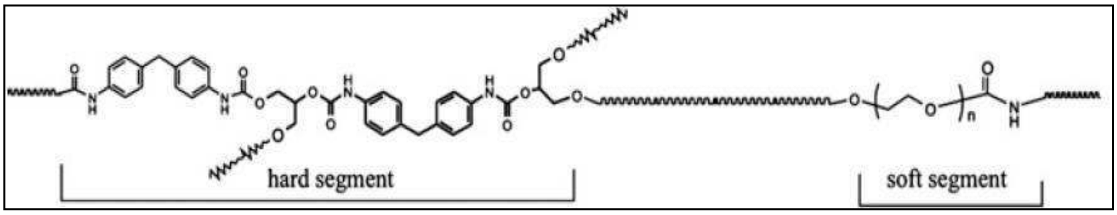


Figure 1: The structure of TPUPCM [1]

Table 2: Thermal Properties of TPUPCM

Sample	$\Delta H_{Heating\ Cycle}$ J/g	$T_{p,\ Heating}$ °C	$\Delta H_{Cooling\ Cycle}$ J/g	$T_{p,\ Cooling}$ °C
TPUPCM2000	97.5	56.3	88.9	31.8
TPUPCM4000	126.4	55.8	112.4	33.4
TPUPCM6000	137.4	57.1	127.6	31.2
TPUPCM8000	127.1	57.5	115.2	30.1

Trying to capitalize on the suitable properties of PEG, a number of PCMs are being developed. Polymer PCMs are now under use to store and release energy, by incorporating them in building structures, to improve the thermal comfort within [1]. PEG has a property: it can directly be incorporated into porous materials. Making use of this, PEG/ diatomite composite was synthesized and is seen to have good thermal properties for the above mentioned application. Diatomite is a white crumbly, porous rock. It is light weight, rigid and inert. These properties coupled with the fact that it is abundantly available and relatively cheap make it a very viable energy storage material. According to studies [2] carried out, this composite has good thermal properties and with very slight variation over 1000 thermal cycles.

Table 3: Thermal Properties of PEG/diatomite composite

Sample	$\Delta H_{Heating\ Cycle}$ J/g	$T_{p,\ Heating}$ °C	$\Delta H_{Cooling\ Cycle}$ J/g	$T_{p,\ Cooling}$ °C
PEG(50wt%)/ diatomite	87.09	27.7	82.22	31.8

This polymer composite can be applied for temperature regulation and reduce the overheating in buildings. This composite used as energy storing wallboard/ plaster stores extra energy thus reducing cooling requirements in the premises.

Talking of energy storage applications in buildings, another set of polymers that have made their ground are those with a palmitic acid backbone. Palmitic acid has the advantage of a suitable phase change temperature in the range 58-64°C besides having other prerequisites. One such polymer is the palmitic acid/ expanded graphite composite PCM. It has high energy storage density with excellent thermal reliability as studies [3] suggest. For a Palmitic Acid/ Expanded graphite (80/20 w/w%) composite the thermal properties are in Table 4 below.

Table 4: Thermal Properties of PA/Eg composite with thermal cycling

Cycle No.	$\Delta H_{Heating\ Cycle}$ J/g	$T_{p,\ Heating}$ °C	$\Delta H_{Cooling\ Cycle}$ J/g	$T_{p,\ Cooling}$ °C
0	148.36	60.88	149.66	60.81
1000	147.39	60.85	146.55	60.98
2000	151.81	60.94	150.58	60.84
3000	140.38	60.78	139.97	60.98

In recent years, several other polymeric solid-solid PCMs have been synthesized for energy storage and release. Another such one is polystyrene-graft-palmitic acid copolymer. The advantages of these are as follows:

- Fairly good thermal properties (enthalpy and transition temperature)
- Good thermal conductivity (which would mean the device using this material will be more compact)
- Good thermal reliability and stability.

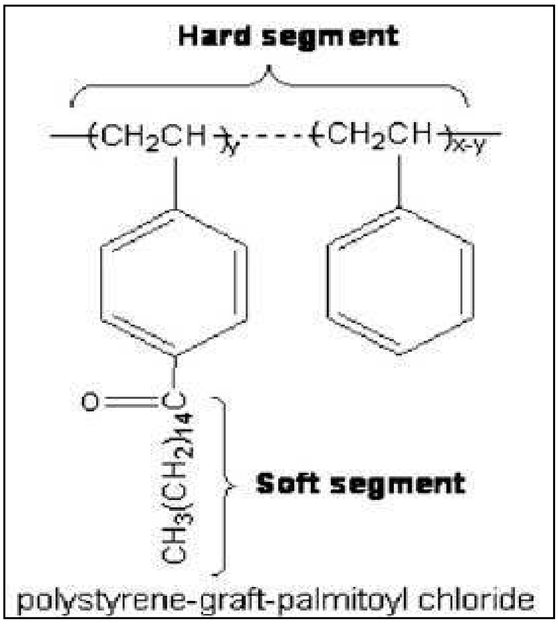


Figure 2: The structure of polystyrene-graft-PA-copolymer [4]

The thermal properties as reported in literature [4] are as in Table 4. The effect of varying the palmitic acid percentage on these properties can also be seen as follows:

Table 5: Thermal Properties of polystyrene-graft-PA-copolymer

Sample	$\Delta H_{Heating\ Cycle}$ J/g	$T_{p,\ Heating}$ °C	$\Delta H_{Cooling\ Cycle}$ J/g	$T_{p,\ Cooling}$ °C
25% mol PA	26.20	21.47	20.02	17.65
50% mol PA	31.16	18.72	28.04	18.51
75% mol PA	39.78	19.18	39.19	18.72

The excellent thermal reliability of these materials makes them ideal phase change materials. Even after 5000 thermal cycles, the variation in properties is minimal [4]. E.g. For 75% Palmitic Acid copolymer, less than 1% change was observed in the enthalpy value.

Almost all polymer material matrices could be tweaked so as to form a stable PCM. The electrospinning technique provides a viable and versatile method to prepare ultrafine fibers of diameters ranging in the nano-micrometer range (Provides for greater surface area for energy storage applications). New techniques such as coaxial electrospinning allow for fibers with a hydrocarbon core and a TiO_2 or polyvinylpyrrolidone sheath (McCann et al., 2006). An important example in this class of polymers is polyamide6 (PA6). This material has good properties such as high strength and toughness, low coefficient of friction and good chemical resistance. Lauric acid acts as a composite material for the PCM (taking into account that PA6 has a higher melting point than Lauric Acid, PA6 makes for a good supporting matrix). For fibers of approximately 1 micro meter diameter, studies [5] were carried out for various composition of the fibers and the results are tabulated as follows. The first column indicates the mass ratios of the components of the composite.

Thus PCMs find major applications in solar energy storage, waste heat recovery, building energy conservation [e.g. use of porous building materials to micro-encapsulate polymers for use as PCM (Li et al., 2009)], temperature control for greenhouses, in kitchen utensil for electric energy storage, clothing thermal insulation and so on. These are next generation materials for thermal energy storage and retrieval. Below is a comparative plot for the various polymeric solar energy materials discussed. It summarizes their working temperature and enthalpy values.

Table 6: Thermal Properties of PA 6/LA composite fibers

Sample	$\Delta H_{Heating\ Cycle}$ J/g	$T_{p,\ Heating}$ °C	$\Delta H_{Cooling\ Cycle}$ J/g	$T_{p,\ Cooling}$ °C
LA/PA680/100	63.66	44.57	54.64	40.28
LA/PA6100/100	70.44	44.53	57.14	40.67
LA/PA6120/100	73.01	44.87	58.35	40.57
LA/PA6150/100	74.12	44.71	62.48	40.09

ΔH: J/g

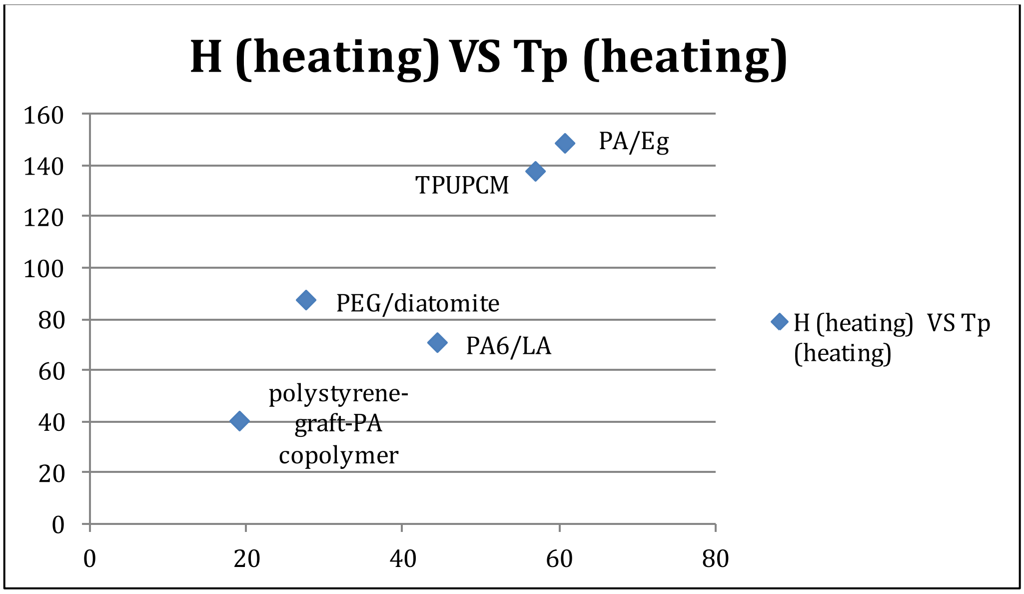


Figure 3: A comparison of PCMs [1],[2],[3],[4],[5]

After looking at PCMs, it is worthwhile looking at another class of polymers that are capable of solar energy storage but function differently. These polymers work using "Valence Isomerization."

This method has proven itself to be one of the most promising systems for the harnessing of solar energy – its conversion and storage. A good example of this is norbornadiene in polymer systems [6]. The wavelength of sunlight received by us ranges between 300-700 nm. This energy cannot be harvested directly by norbornadiene – we have to introduce auxiliary groups like chromophores, sensitizers etc. The structure variation during energy storage has been studied [7] and is in the figure below:

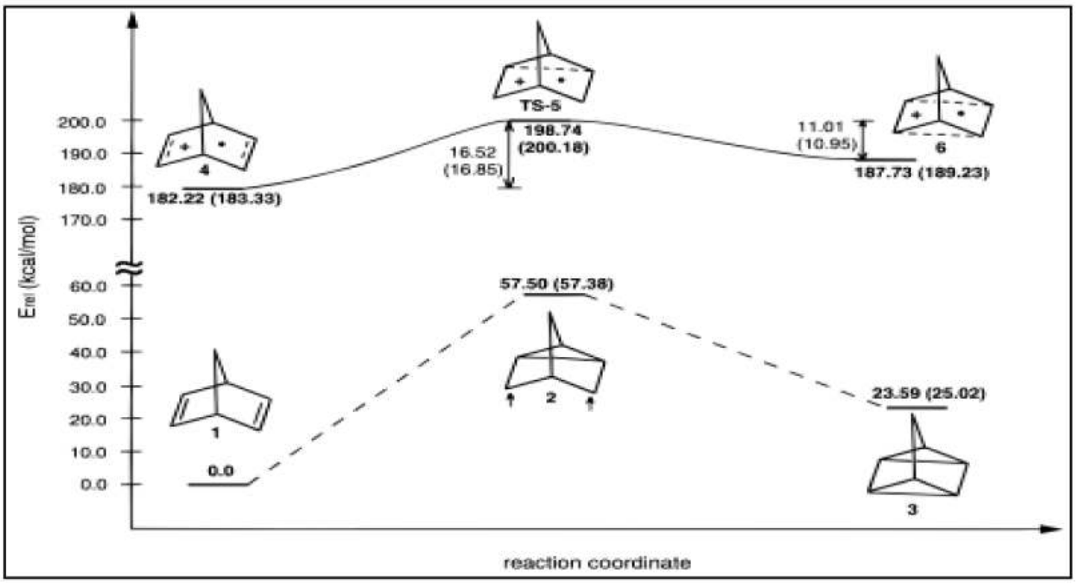


Figure 4: Valence Isomerization as seen in Norbornadiene[7]

3. Conclusions

Energy storage is the need of the hour. We need to conserve our resources to avoid a "power-less" future. As discussed and cited in the report, it is rather clear that polymeric materials are very capable materials for energy storage and release.

In solar energy harnessing, the implementation of proper energy storage remains crucial to achieve energy security and to reduce environmental impact. No

because of the lower mass and volume of the system and the energy is stored at a relatively constant temperature and energy losses to the surrounding are lower than with conventional systems. These

phase transformation is associated with a significant volume change. This increases the working cost using these polymers as

single type of storage method can be used universally to store energy. For specific situations, geological locations (temperature being a major factor), and existing facilities, different storage methods are possible and must be considered. PCMs store latent heat within their structure. The quantum of energy stored for organic PCMs ranges from 10kJ/kg to 300kJ/kg. Energy storage in PCMs has a lot of advantages over conventional systems

materials are viable to use provided their peak phase change temperature is within practical limits (15-90°C). In certain PCMs (solid-liquid & especially liquid-gas), the

we need to take into account a variable volume system in our design. Liquid PCMs are susceptible to leakages –

microencapsulation technique can be applied to prevent the same. PCMs have varied applications from heat and coolness storage in buildings to thermal storage in satellites and protective clothing. Recently, many developments in latent heat storage have been observed, mainly because the utilization of solar and industrial heat is a promising method to save energy and reduce CO_2 emission. Incorporating these materials into building structures during construction phases can reduce the energy requirement for years together as solar heat stored can be used for electrical purposes or even for warming the structure during later hours of the day.

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