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Article

Thermoplastic Elastomer based Phase Change Materials with Enhanced Mechanical Property, Thermal Conductivity and Photo-thermal Performance

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Abstract: Traditional phase change composites usually suffer poor mechanical property and easy collapsing in the phase changing process. Herein, a highly flexible phase change composite is fabricated using thermoplastic elastomer as the basic gel and the expanded graphite/paraffin as the filler. This new phase change composite shows a tensile strength of 2.1 MPa and a breaking elongation of 220%. It has a melting enthalpy of 145.4 $J \cdot g^{-1}$ and a thermal conductivity of 2.2 $W \cdot m^{-1} \cdot K^{-1}$ with 70% of expanded graphite/paraffin. The thermoplastic elastomer based phase change composite exhibits great reversible property after 200 heating/cooling cycles. This flexible phase change composite demonstrates good photo-thermal energy charging/discharging property and shows great potential to be applied in the solar thermal energy systems.

Keywords: Solar thermal systems, phase change materials, thermoplastic elastomer, mechanical property, photo-thermal performance

1. Introduction

Solar thermal energy (STE) is considered to be one of the most prospective renewable energy source. Solar thermal technologyis by far the cheapest method for solar energy utilization[1]. It is widely used in solar thermal water heater[2], solar evaporation[3], solar power generation[4] and solar cooker[5]. Since solar energy is distributed, low thermal grade and intermittent, the large-scale practical application of STE requires effective technology for its capture, conversion and storage. One prospective approach is to use phase change materials (PCMs) with narrow melting temperature and large enthalpy as both light absorber and heat transfer media[6] [7].

Using PCMs to directly absorb the solar energy could decrease the heat lost between the solar energy and absorptive medias[9]. The PCMs with melting temperature above 70℃ have high thermal grade of energy and large enthalpy[8], hence could be used to be a media to absorb solar thermal energy and transfer to another media for heating systems. The photo-thermal charging capacity of PCMs depends on the optical property, thermal storage capacity and thermal conductivity. In addition, the PCMs need to have good mechanical property since the heat exchange process is usually accompanied by pumping systems[10]. However, most of the PCMs suffer poor optical property, low thermal conductivity and poor mechanical property. To address this, carbon materials such as expanded graphite(EG)[11], graphene[12], carbon nanotubes[13], carbon forms[14] were used to absorb the PCMs to form phase change composites. Among these porous materials, EG

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could largely increase the thermal conductivity and optical property of the PCMs, the EG based phase change composites showed high photo-thermal performance[15]. Nevertheless, the reported EG based phase change composites are in the form of powders with poor mechanical property in the phase changing process. The composites could easily collapse when heat transfer fluid flow past it.

To enhance the mechanical property of EG based PCMs, polymers are used as the basic gel to encapsulate the powders with mixing method. Various polymers such as polyethylene[16], Ethylene-Propylene-Diene mischpolymer[17], polymethyl methacrylate[18] and melamine resin[19] were applied as the basic gel for encapsulating the EG based PCMs. The polymer based PCMs demonstrated good mechanical property to resist the impact of heat transfer fluids. Nevertheless, the aforementioned polymers are rigid materials with high stiffness whereas the PCMs have volume expansion (~10%) in the solid-liquid process[20]. This results in unexpected leakage or shape changing in the solid-liquid process. Therefore, developing flexible polymers is essential for encapsulating EG based PCMs. Thermoplastic elastomer (TPE) is a kind of flexible, high elastic polymer with large tensile strength and elongation, which is widely used as the basic gel for flexible device [21,22].

In this work, we first adopt TPE gel to encapsulate the EG based PCMs to form a EG/PCM-TPEs composite through a simple mixing method. The EG/PCM-TPEs composite EG/PCM-TPE have high tensile strength and breaking elongation, large thermal storage capacity, high thermal conductivity, and good reversible property. The EG/PCM-TPEs composite EG/PCM-TPE shows great photo-thermal charging/discharging capacity and exhibits great potential for STE application.

2. Materials and Methods

2.1. Materials

Technical grade paraffin (OP70, Tm of ~65℃) was purchased from Shanghai Joule wax Co, Ltd, PR. China. Expanded graphite (EG) was obtained from Qingdao Herita graphite product Co, Ltd., PR. China. The thermoplastic elastomer (TPE) was provided by The Dow Chemical Company. All chemicals were used as received without further purification.

2.2. Preparation of EG/PCM-TPE

The EG was added to absorb the liquid OP70 with mass ratio of 1:9. Then, different mass fraction of the obtained EG/OP70 composite was blended with a fixed ration of TPE gel by open milling (XH-401, Dongguan Xihua Co., Ltd., PR. China), as shown in Table 1. The as-prepared form-stable PCMs were made into sheets by a hot press (XH-406B, Dongguan Xihua Co., Ltd., PR. China). For the leakage test, the samples were placed on a filter paper and kept in an oven with temperature controlling from 40-100-40℃ for 24 h. The weight of samples was measured to calculate the leakage percentage of the samples.

Table 1. The mass fraction of as-prepared EG/PCM-TPE

Samples	EG/OP70 (%)	TPE (%)
S1	30	70
S2	40	60
S3	50	50
S4	60	40
S5	70	30

2.3. Characterizations of EG/PCM-TPE

The morphology and microstructure of EG/PCM-TPE were observed by a field emission scanning electron microscopy (SEM SU8020, Hitachi, Tokyo, Japan). The structure of the EG/PCM-TPE was characterized by XRD(D8, ADVANCE, Bruker, Karlsruhe, Germany). The XRD pattern was scanned from 10–70° with an interval of 0.2°. The phase change temperature and latent heat of the EG/PCM-TPE were measured using a differential scanning calorimeter (Q200, TA Instruments, New Castle, Pennsylvania, USA). Specifically, 5~8 mg of each sample was sealed in an aluminum pan. The heating rate was 10 °C·min−1 and the N2 flow rate was 50 mL·min−1. The

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thermal conductivity of the EG/PCM-TPE was tested using a thermal constants analyzer (Hot Disk TPS 2500 S, Hot Disk AB, Gothenburg, Sweden).

2.4. Photo-thermal performance management of EG/PCM-TPE

The photo-thermal performance of the EG/PCM-TPE was conducted with solar simulator. The experimental devices contain solar simulator (Microsolar300, Perfectlight, Beijing, China), samples, thermocouples and data acquisition systems (Agilent, 34970A, Agilent Technologies Inc, Santa Clara, CA, USA). The EG/PCM-TPE were placed 10 cm under the solar simulator. The thermocouples were used to record the temperature of the samples. When the light was turned on, the composites underwent the heating storage process, followed by the heating release process when the light was turned off. The irradiance of solar simulator was measured with an irradiatometer (ST-80C, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China).

3. Results and discussion

3.1. Mechanical property of EG/PCM-TPE

The tensile strength and elongation of EG/PCM-TPE were shown in Figure 1. As shown in Figure 1a, the tensile strength of S1~S5 is 0.7, 0.9, 1.2, 1.6 and 2.1 MPa, which increases with the mass ratio of the EG/OP70. While the elongation of S1~S5 is 220%, 170%, 75%, 27% and 11%, decreasing with the mass ratio of EG/OP70. Increasing the mass ratio of EG/OP70 could largely improve the tensile strength since the TPE is a flexible gel with low tensile strength and large elongation, the filler in the samples has an advantage to avoid impact and shape change. As the mass ratio of EG/OP70 increases, the flexibility of samples decrease, since the EG/OP70 powders are irregular. The TPE gel could not encapsulate the EG/OP70 powders completely when the mass ratio reached 70%.

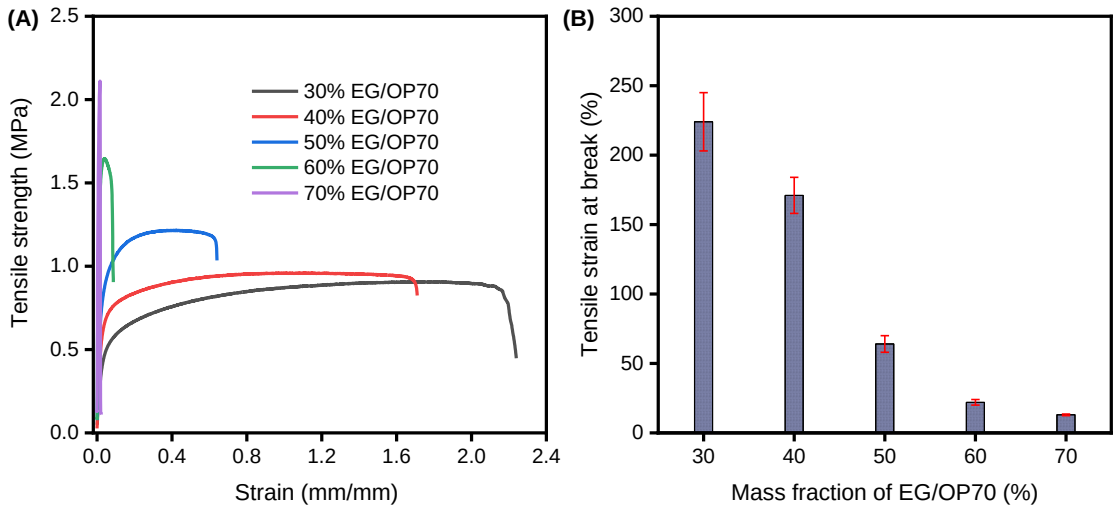

Figure 1. Tensile strength (A) and tensile strain at break (B) of the as-prepared EG/OP70-TPE.

The flexibility of the as-prepared EG/OP70-TPE is important for universal application in solar thermal systems, thermal management systems and waste heat recovery systems. In addition, the OP70 showed a large volume expansion in the melting/freezing process, using the polymer with flexibility could prevent leakage of OP70 in the PCMs. Figure 2 shows that the samples exhibited good flexibility, all samples could be stretched and folded without breakage at 70℃.

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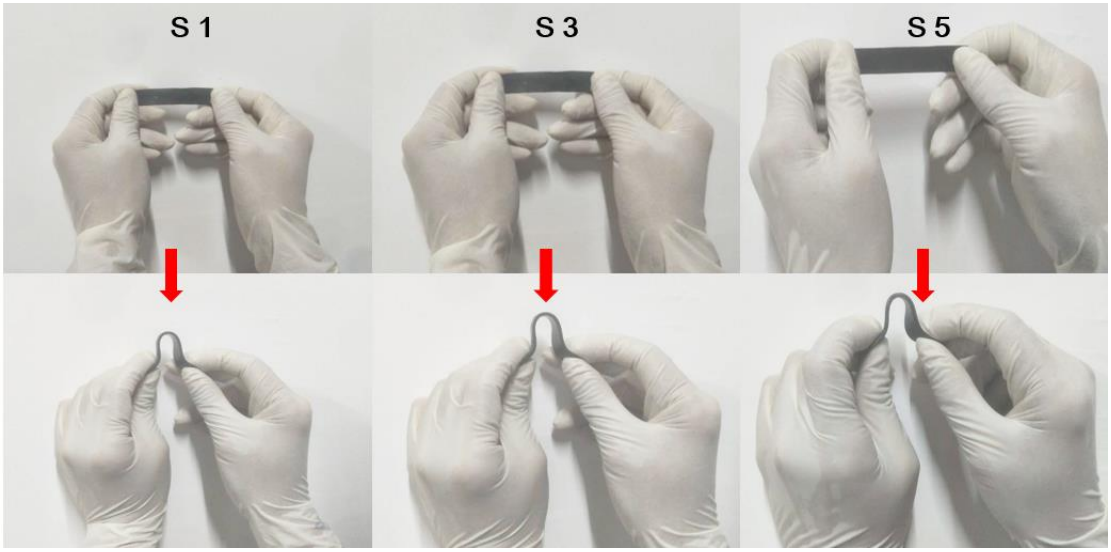

Figure 2. Flexibility test of the as-prepared EG/OP70-TPE.

3.2. Morphology and Structure of EG/PCM-TPE

To verify the mechanical property of EG/PCM-TPE, the morphology was tested by SEM and the images were shown in Figure 3. As described in the experimental section, the OP70 was absorbed in the EG powders, and the EG/OP70 was encapsulated with the TPE gel. Figure 3 showed that the TPE gel covered the EG/OP70 with smooth surface. The scaly EG was observed under the TPE gel. For sample S1, most of the EG/OP70 powders were covered by TPE gel, and the surface was smooth. When increasing the mass ratio of the EG/OP70, the surface became coarse. For sample S3, the scaly EG could be seen obviously. While for sample S5, a lot of EG/OP70 powders was observed, implying that the TPE gel could not completely encapsulate the EG/OP70. The morphology changes provided further explanation of the positive correlation between the mechanical property of the S1-S5 and the mass ratio of the TPE gel.

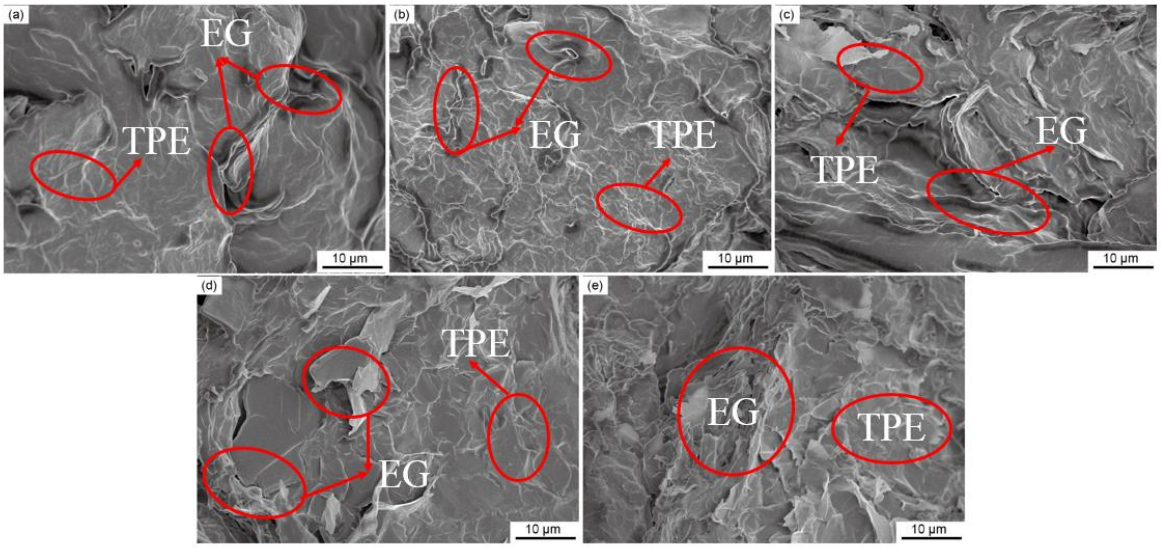

Figure 3. SEM images of the as-prepared samples 30%-EG/OP70- TPE (a), 40%-EG/OP70- TPE (b), 50%-EG/OP70- TPE (c), 60%-EG/OP70-TPE (d) and 70%-EG/OP70-TPE (e).

To further investigate the microstructure of EG/PCM-TPE, XRD was carried out and the patterns of the samples were shown in Figure 4. The EG appeared only one peak at 26.5°, while the TPE showed not obvious peak since it is an amorphous gel. For OP70, peaks appeared at 4.2°, 11.3°, 19.7°, 21.3° and 23.8°, which correspond to different lattice planes. For EG/OP70showed all peaks of OP70 and EG appear and the intensity did not obviously decrease, because the EG powders with macropores range from several micrometer to hundreds of micrometer did not affect the crystallization of OP70. For EG/OP70/TPE, all peaks also appeared, while the intensity decreased

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largely as compared to the OP70 and EG/OP70, which is due the coverage of the EG/OP70 by the TPE gel. The XRD results demonstrated that the EG/PCM-TPE had a compact structure with physical combination.

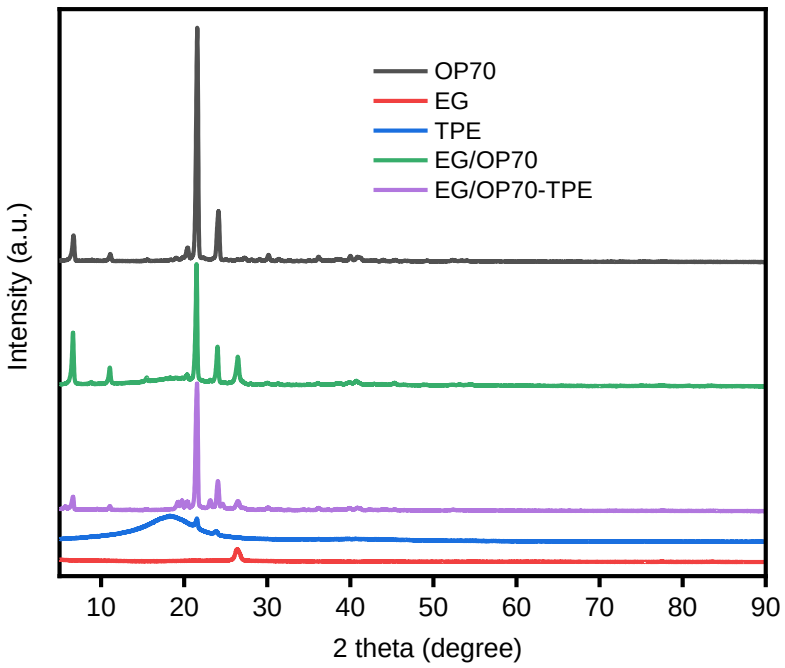

Figure 4. XRD patterns of the as-prepared EG/OP70-TPE.

3.3. Thermal property of EG/PCM-TPE

Figure 5 and Table 2 showed the melting and freezing property of EG/PCM-TPE. For OP70 and EG/OP70, the melting temperature was 65.2 and 65.3℃and the melting enthalpy was 230.8 and 207.7 J·g-1. For S1~S5, the melting temperature was 50.4, 50.4, 53.8, 57.8 and 59.0℃and the melting enthalpy was 62.3, 83.1, 103.5, 124.6 and 145.4 J·g-1, respectively. It can be clearly seen that the melting temperature of EG/PCM-TPE was lower that of the OP70 and EG/OP70. This is because the TPE is composed of alkanes with low melting temperature, these alkanes could be well coupled with the OP70 to form a mixture with lower melting temperature. The melting enthalpy of EG/PCM-TPE was also lower than that of the OP70 (equivalent mass), because the alkanes in the mixtures have low melting enthalpy than OP70. Nevertheless, the melting enthalpy decreased less than 5%, sample S5 showed the largest melting and freezing enthalpy and good mechanical property.

Table 2. Melting–freezing properties for OP70/EG/TPE with different addition of TPE

Samples	**T_m/ ºC**	**ΔH_m/J g^{-1}**	**T_f/ ºC**	**ΔH_f/J g^{-1}**
OP70	65.2	230.8	65.9	230.5
EG/OP70	65.3	207.7	65.2	207.5
S1	50.4	62.3	56.0	61.9
S2	53.0	83.1	57.4	83.8
S3	53.8	103.5	59.6	102.4
S4	57.8	124.6	61.7	123.8
S5	59.0	145.4	62.5	144.6

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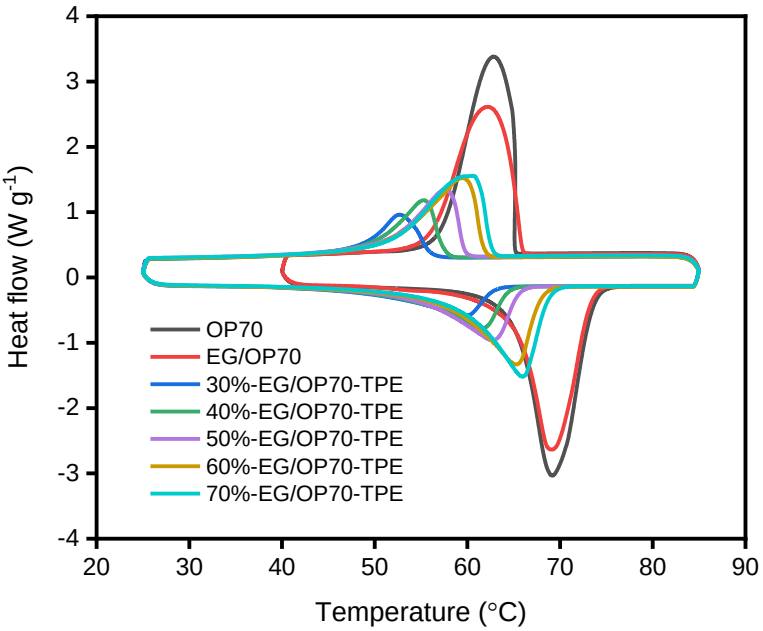

Figure 5. DSC curves of the as-prepared EG/OP70-TPE.

The thermal conductivity of EG/PCM-TPE was also measured and the results were shown in Figure 6. The thermal conductivity of EG/PCM-TPE increases from 0.6 to 2.2 $W \cdot m^{-1} \cdot K^{-1}$ as the mass ratio of EG/OP70 increased from 30 to 70%. The thermal conductivity increased linearly with the mass ratio of EG/OP70. The equivalent mass ratios of EG was 3~7% for S1~S5, adding small mass fraction of EG could largely increase the thermal conductivity. The polymer based PCMs with large thermal conductivity had great advantage of increasing the thermal energy charging/discharging rate in thermal utilization systems. The polymers and paraffin usually poses thermal conductivity lower than 0.2 $W \cdot m^{-1} \cdot K^{-1}$, therefore adding EG could largely improve the thermal conductivity.

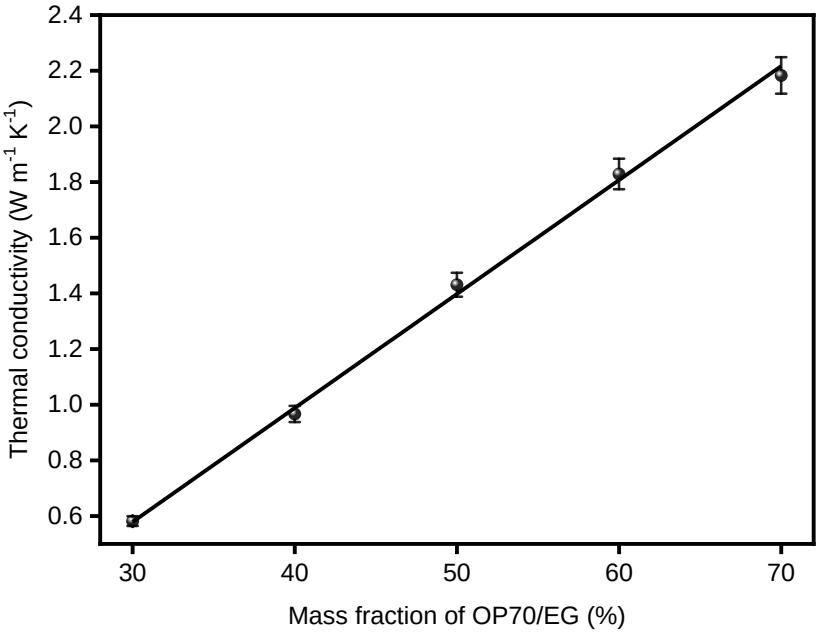

Figure 6. Thermal conductivity of the as-prepared EG/OP70-TPE.

3.4. Reversible property of EG/PCM-TPE

To test the reversible property of EG/PCM-TPE, 200 heating/freezing cycles(30-90-30 ºC) of sample S4 was carried out on the filter paper, after which the morphology and thermal property were investigated. The filter paper did not impregnate the liquid paraffin and no weight loss of the samples was observed, indicating that the samples have no leakage after heating/cooling cycles. Figure 7a showed the SEM image of S4 after 200 heating/freezing cycles. Obviously, sample S4

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showed almost the surface appearance before and after the heating/freezing cycles(Figure 3d), indicating that there was no leakage in the heating/freezing process. To further verify the reversible property, the melting/freezing property of S4 was measured by DSC. As shown in Figure 7b, the results showed that the melting temperature and enthalpy were 57.6 ºC and 124.1 J·g^{-1}, respectively which were approximately the same to the values before the heating/freezing cycles. The EG/PCM-TPE exhibited good reversible property for long term application in thermal systems.

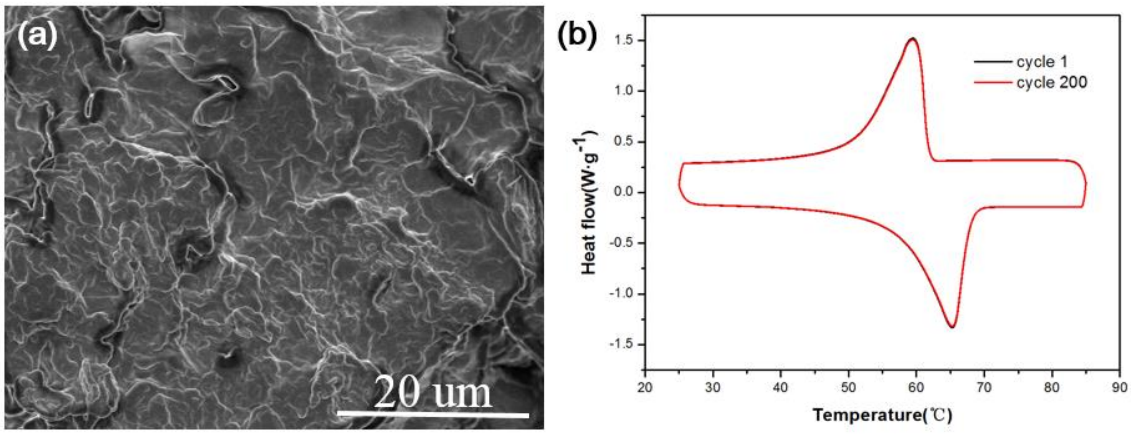

Figure 7. SEM images, melting-freezing curves of sample S4 before and after 200 heating-cooling cycles.

3.5. Photo-thermal performance of EG/PCM-TPE

The photo-thermal performance of EG/PCM-TPE was shown in Figure 8. In the photo-thermal charging process, the temperature of EG/PCM-TPE increased from 30 to 65 ºC quickly, then trended to a temperature stage, and further increased to 95℃. The sample S1 took the shortest time since it contained only 30% of the EG/OP70, and sample S5 with 70% of EG/OP70 took the longest time to increase from room temperature to 95℃. The photo-thermal charging property is dependent on the optical absorptive property and thermal conductivity. The TPE and OP70 have poor optical absorptive property, adding EG powders could largely improve the light absorption. Among these samples, the equivalent mass fraction of EG was 3%, 4%, 5%, 6% and 7% for S1~S5, respectively. To further evaluate the photo-thermal charging capacity of the EG/PCM-TPE, The thermal storage capacity of EG/PCM-TPE was calculated by the following equations:

$$Q_T = m\int_{T=30}^{T=95}\left(Cp+\beta\Delta H\right)dT \qquad (1)$$

$$\beta=\begin{cases}0 & (T<T_m)\\ \dfrac{T-T_m}{T_f-T_m} & (T_m\le T\le T_f)\\ 1 & (T>T_f)\end{cases} \qquad (2)$$

Where Q_T is thermal storage capacity of EG/PCM-TPE, m is the mass of TPE based PCMs, C_p is the heat capacity of PCMs, β is the liquid rate, ΔH is the enthalpy of PCMs, T is the temperature, T_m and T_f is the melting and freezing temperature. The receiver efficiency of the EG/PCM-TPE was calculated by Equation 3.

$$\eta=\frac{Q_T}{G_s A t}\times 100\% \qquad (3)$$

Where η is the receiver efficiency, Gs is the irradiance of solar radiation, A is the irradiation area, t is the irradiation time. The receiver efficiency of all samples decreased with the temperature. The receiver efficiency of S1 was 70% at room temperature, and decreased to 56% at 60 ℃,then stagnated at 48% as the temperature increased to 90℃. For S5, the receiver efficiency decreased from 80% to 75.2% as the temperature ranged from room temperature to 60 ℃,then leveled at 72% at 90 ℃.

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Sample S5 had larger mass fraction of EG and OP70 that could effectively absorb the solar radiation, and hence showed much higher receiver efficiency than S1. The results indicate that the EG/PCM-TPE has great photo-thermal performance, effective thermal storage capacity, and great potential to be applied in solar thermal utilization.

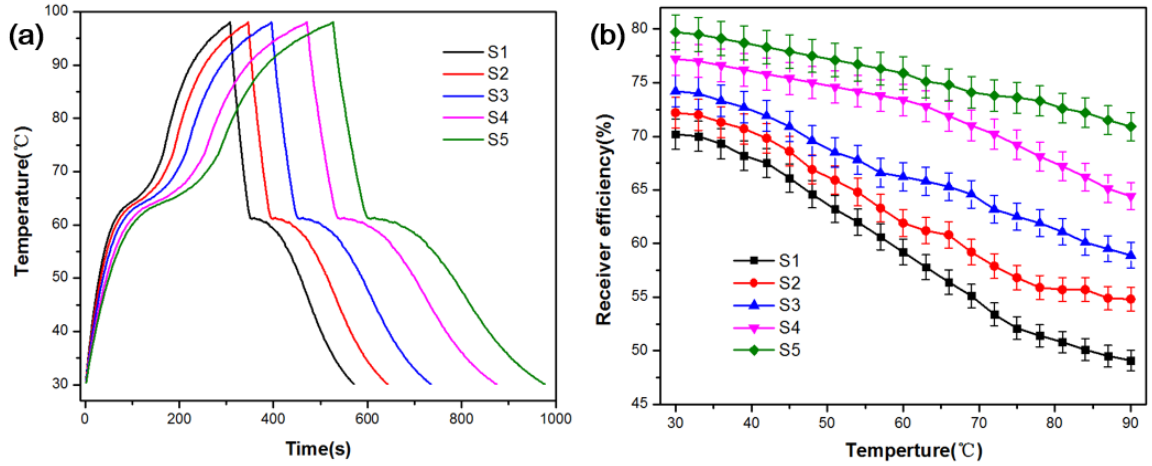

Figure 8. Photo-thermal performance of as-prepared EG/OP70-TPE(a) and receiver efficiency of as-prepared EG/OP70-TPE(b).

4. Conclusions

In this work, a flexible polymer based PCMs were synthesized with TPE as the basic gel and EG/OP70 as the filler. The EG/PCM-TPE shows tensile strength of 1.6 MPa and elongation of 27% with 60% of EG/OP70. The obtained EG/PCM-TPE are highly flexible and could be folded without breakage. The SEM images showed that the TPE gel could completely encapsulate the EG/OP70 powders with continuous smooth surface. The TPE based PCMs with 70% of EG/OP70 has thermal conductivity of 2.2 $W \cdot m^{-1} \cdot K^{-1}$, melting enthalpy of 145.4 $J \cdot g^{-1}$. In addition, The TPE based PCMs with 70% of EG/OP70 demonstrated great photo-thermal performance and reached a receiver efficiency of 72% at 90℃. The flexible EG/PCM-TPE showed great potential in solar thermal utilization.

Author Contributions: W.F. and J.L. conceived the idea. W.F. performed the samples preparation, characterization and measurement of PCMs and wrote the manuscript. X.Z. and Y.C. finished a part of characterization and measurement of PCMs. F.W., X.Z., Y.C. and J.L. discussed and analyzed the results. J.L. revised the manuscript. J.L. supervised the whole research work. All authors read and approved the final version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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