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Thibault Harlé, Giao T.M. Nguyen, Béatrice Ledesert, Yannick Melinge, Ronan L. Hebert. Cross-linked polyurethane as solid-solid phase change material for low temperature thermal energy storage. *Thermochimica Acta*, 2020, 685, pp.178191 -. <10.1016/j.tca.2019.01.007>. <hal-03489323>

HAL Id: hal-03489323

<https://hal.science/hal-03489323v1>

Submitted on 7 Mar 2022

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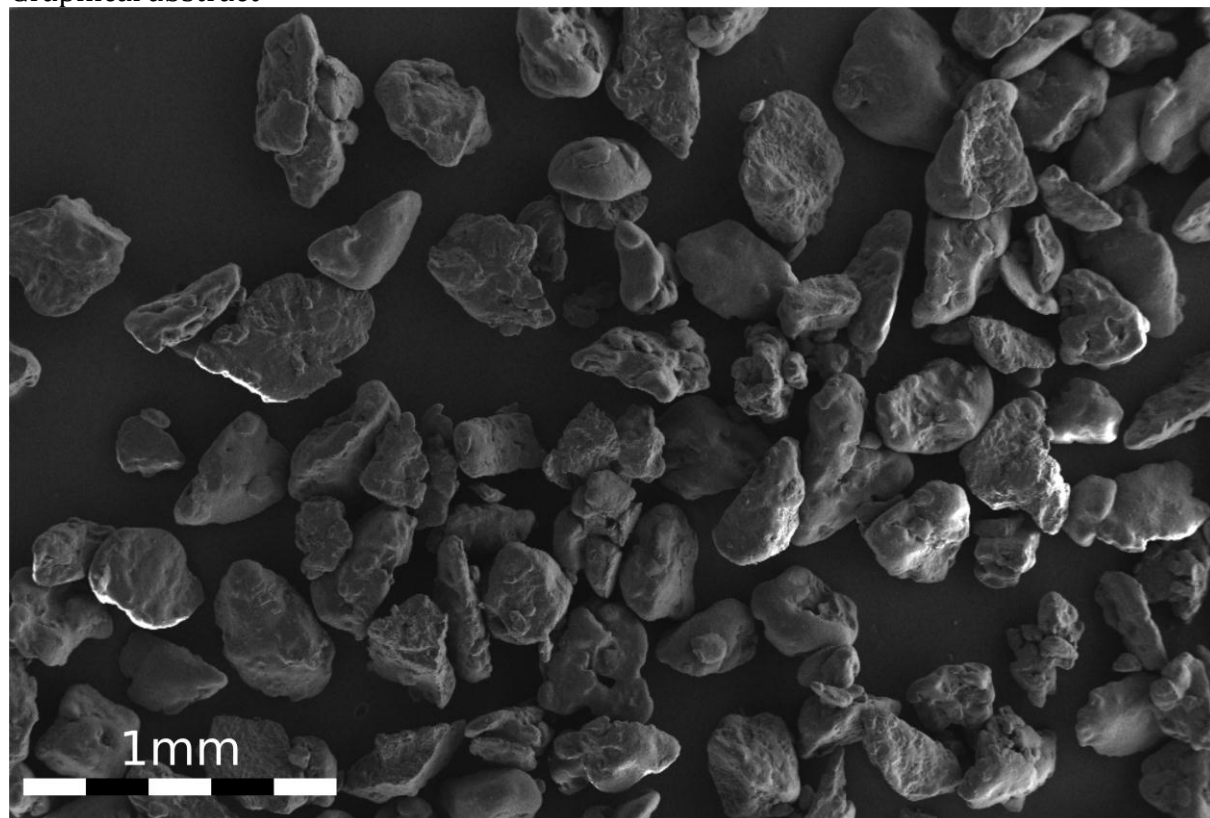
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Cross-linked polyurethane as solid-solid phase change material for low temperature thermal energy storage

Harlé Thibault

Université de Cergy-Pontoise, 1 rue Descartes, 95000, Cergy-Pontoise, France,
0618981048
thibault.harle@u-cergy.fr

Graphical abstract



Highlights

- Low temperature linear and crosslinked PUs as solid-solid PCMs.
- Multicriteria characterization of thermo-physical properties.
- Phase change temperature between 20°C-36°C and latent heat between 76-103J/g.
- Crosslinked PCM can be reduced into powder thanks to specific physical properties.
- PCMs show excellent long-term stability through 500 cycles.

1 Introduction

Phase Change Materials (PCMs) are materials capable of exchanging thermal energy with their environment by phase transition. The phase transition can be a state change, such as solid-liquid (s-l PCMs) [1] and conversely, or from a crystalline solid to an amorphous solid (s-s PCMs) [2,3,4,5,6,7,8,9,10,11,12,13]. PCMs are commonly used for thermal energy storage, solar energy utilisation, clothing and textile insulation [14], and food transport [15]. They are also considered into building materials in order to increase the thermal inertia of buildings and to regulate indoor temperatures [16,17].

Solid-liquid PCMs are the subject of numerous studies, which are reviewed in [1]. They are suitable for various applications due to a wide range of available transition temperature, high latent heat, good stability, and low cost. However, the phase transitions of s-l PCMs present some major disadvantages: (i) exhibiting high volume change (up to 12%) [18], (ii) requiring containment in macro- or micro-capsules in order to avoid fluid to flow away [19,20], (iii) additional cost due to encapsulation, and (iv) damage of PCM capsules during the fabrication or the implementation of composite materials. Then, liquid leakage from the PCMs can occur, and potentially modifies the features and the properties of the host material (e.g. odour problems, colour change, increase in flammability, decrease in mechanical strength [16, 21, 22]. This leakage issue can be incompatible with certain domains of application. Solid-solid PCMs (s-s PCMs) are a promising alternative, overcoming the disadvantages of s-l PCMs; they are often reported as s-s PCMs for Thermal Energy Storage (TES). For this reason, they have received a great deal of attention over the last decade [13,23,24,25,26,27,28,29,30,31,32]. The phase transition from a crystalline phase to an amorphous-solid phase and reversely enables avoiding encapsulation. The leakage issue is then removed as long as the operation temperature remains within the range of the solid-to-solid transition and below the temperature of amorphous solid to liquid transition. Among s-s PCMs, polymer PCMs based on poly (ethylene glycol) (PEG) are among of the most studied. PEGs, semi-crystalline polymers, are often reported as precursors for s-s PCMs synthesis due to their high crystallinity, high latent heat [33], good biodegradability [34], low cost [35], and especially due to the chemical reactivity of their glycol end groups. Depending on the molecular weight, the thermal properties of PEGs can be modulated. PEGs are characterised by a solid to liquid transition. To produce s-s PCMs from PEGs, several solutions have been reported in the literature, for example: (i) In [4], PEG 6000 is embedded in a poly(polyethylene glycol 400 diacrylate) (PPGD) network via a semi-interpenetrating polymer network (semi-IPN) architecture. While the PEG 6000 exhibits a s-l transition, the solid state of the material is ensured by PPGD network. This structure is able to preserve the thermal properties of PEG. High latent heat reaching up to 116 ± 1 J/g can be achieved with transition temperatures of 58.5°C (for melting) and 37°C (for crystallisation); (ii) Form-stable PCMs can also be obtained by grafting of PEG chains onto a supporting polymer, such as polystyrene [5,29]. In this structure, polystyrene ensures the solid state of the PCM, and the thermal exchanges are performed by PEG or other s-l PCMs, such as palmitic acid [24]. Among the reported methods for the synthesis of PCMs from PEGs, the formation of polyurethanes (PUs) has been the most described [3,6,7,13,23,30,36]. In general, these PUs consist of hard segments based on diisocyanate structure, i.e. 4,4-diphenylmethane diisocyanate MDI [8,9,10,11,12,13], ensuring the material solid state and soft segments based on PEGs providing thermal properties. The synthesis parameters allow producing s-s PCMs with different thermal properties. These syntheses are generally realised in dimethylformamide (DMF) as the solvent. Several more environmentally friendly syntheses of PUs as s-s PCM are described in [6,7,37] with solvent-free methods. In these syntheses, the PEG is previously melted. When it is fully liquid, other reactants are added without using any solvent or catalyst. In [6], the synthesis of a polymer network involving PEG 4000 or PEG 6000 has been described in three steps: (i) In the first step, an isocyanate-terminated prepolymer "component A" was prepared by reaction between PEG and MDI; (ii) Next, PEG and MDI were mixed to produce an isocyanate-terminated intermediate, and then diethanol amine was added to form tetrahydroxy-terminated prepolymer "component B"; and (iii) third, the reaction between the

prepolymers "A" and "B" was realised to produce s-s PCM with latent heats (melting: PCM-4K = 172 J/g, PCM-6K = 174.6 J/g) that are about 60% that of the initial PEGs (melting: PEG-4K = 79.6 J/g, PEG-6K = 102 J/g) [6]. In the present work, we report the synthesis of PUs as s-s PCMs for TES. Inspired by [3], we propose a way to improve the synthesis, physical properties, and solubility of s-s PCM. The synthesis of linear PUs and cross-linked PUs is carried out using a one-step solvent-free synthesis. We first synthesize linear polyurethanes from PEGs and hexamethylene diisocyanate. To improve the physical properties of the resulting polyurethanes, glycerol is used as cross-linker to produce a cross-linked PU network. The s-s PCMs synthesis kinetics are studied by Fourier transform infrared spectroscopy (FTIR). Morphological, thermal, and physical properties of the different produced PCMs are described and compared to each other. The resulting PUs showed thermal and physical properties that are suitable for various applications such as TES at low to moderate temperature conditions.

2 Experimental

2.1 Materials and methods

2.1.1 Materials

Poly(ethylene glycol) (PEG-1K: $M_n=1000 \text{ g.mol}^{-1}$, PEG-1.5K: $M_n=1500 \text{ g.mol}^{-1}$ and PEG-2K: $M_n=2000 \text{ g.mol}^{-1}$) and glycerol (purity $\geq 99\%$) were purchased from Carl Roth GmbH+ Co, and hexamethylene diisocyanate (HMDI) MERCK MILLIPORE from VWR (purity $\geq 99\%$). All reagents were used as received.

2.1.2 Synthesis of linear PUs

Linear PU synthesis was conducted in a 500 ml four-necked round-bottom flask under argon atmosphere. A quantity of 100 g of PEG was placed into the reactor. The temperature was raised to 70 °C to melt the PEG. Once the melting of PEG was completed, HMDI was added. Different molar ratios of isocyanate group/hydroxyl group [NCO] were used: 1, 1.05, and 1.1. After the addition of all the reactants was completed, the mixture was homogenised, and kept for 45 minutes at 70 °C. The obtained polymer was then poured into moulds and post-cured in an oven at 100 °C for 5 hours to ensure the good formation of all polymers chains [38]. A linear PU made of PEG-1K was named PUL-1K, PEG-1.5K named PUL-1.5K, and for PEG-2K, PUL-2K.

2.1.3 Synthesis of cross-linked PUs

The synthesis was realised in a 500 ml four-necked round-bottom reactor under argon atmosphere. A total of 100 g of PEG were placed into the reactor. The temperature was then raised to 70 °C to allow the total melting of PEG. Glycerol (0.818 g corresponding to 20% of glycerol hydroxyl function, compared with that of PEG) was blended with the melted PEG before the incorporation of HMDI to realise a one-step solvent-free synthesis. The molar ratio of isocyanate group/hydroxyl group [NCO] was fixed at 1. After the complete incorporation of all reactants, the mixture was homogenised, and kept for 45 minutes at 70 °C. As previously, the synthesised polymers underwent a post-cure in an oven at 100 °C for 5 hours. A cross-linked PU with PEG-1K and 20% of the cross-linker was called PUX-1K-20.

2.2 Characterisation

2.2.1 Thermogravimetric analysis

Thermogravimetric analyses (TGA) were performed with a TA instruments Q50 on synthesised s-s PCMs as well as PEGs, at a heating rate of 20 °C.min⁻¹ under constant

argon flow ($60 \text{ mL}\cdot\text{min}^{-1}$) and from 20°C to 700°C . Platinum pans were used for the analysis with the mass sample $10 \text{ mg}\pm 2$.

2.2.2 Differential scanning calorimetry

A differential scanning calorimeter (DSC), TA instruments Q100, calibrated with Indium wire, was used to determine the transition temperature and latent heat of the different synthesised PUs. Powdered samples of $6\pm 1 \text{ mg}$ were placed into aluminium closed crucibles. A first heating stage to 80°C (above melting temperature) was performed to erase the thermal heritage of the sample. Samples were then analysed from -10°C to 80°C , with cooling and heating rates of $5^\circ\text{C}\cdot\text{min}^{-1}$. Each sample was analysed three times, and the presented results correspond to the mean values and standard deviation of the three measurements.

2.2.3 Polarising optical microscopy

The crystallisation and the melting of PUs and PEGs was observed under a Polarising Optical Microscope (POM), OLYMPUS BX50, equipped with a digital camera for image acquisition. Samples of the PCM were placed between a glass section and a cover slip, then heated/cooled at temperatures above and below phase transition.

2.2.4 X-ray diffraction

X-ray diffraction was performed on the PUs' powder using a X'Pert3 Powder from PANalytical with Cu $K\alpha$ at 35 kV and 30 mA. Data were collected between 3° and $50^\circ - 2\theta$.

2.2.5 Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were performed on a BRUCKER spectrometer in attenuated total reflectance (ATR). The synthesis advancement was followed by the observation of the isocyanate peak at 2250 cm^{-1} .

2.2.6 Accelerated thermal cycling for thermal durability testing

To estimate the thermal durability of cross-linked PUs, the chemical stability of the PCMs was tested through accelerated thermal cycles. Thermal cycles were performed in a stove (Mettler ICP 110) between 15°C and 40°C with a cooling rate of $0.6^\circ\text{C}\cdot\text{min}^{-1}$ and a heating rate of $1.1^\circ\text{C}\cdot\text{min}^{-1}$ (maximum heating and cooling capacities specified by the stove manufacturer). Samples were analysed by DSC before thermal cycling and after 500 thermal cycles.

2.2.7 Hardness test

The physical characterisation of s-s PCMs was made through a hardness test performed on a ZWICK durometer, using Shore D scale. Hardness characterisation was performed on 1 cm^3 s-s PCM samples. Thirty measurements were realised on each sample, and the presented results are an average of these measurements.

2.2.8 Thermal conductivity measurement

Thermal conductivity measurement was performed using hot disk TPS 1500 at ambient temperature (20°C) with Kapton sensor. The sensor used for measurement was included directly in the centre of a prismatic block ($8.5 \times 8.5 \times 4 \text{ cm}$) of PCMs casted at the end of the synthesis. The results presented in this paper are the average values calculated from five measurements.

Thermal conductivity measurement has been performed using hot disk TPS 1500 at ambient temperature (20 °C) with a Kapton-insulated sensor (ref. 5501 with a 6.4 mm radius). Internal calibrated procedure is automatically running when the apparatus is switched on. The apparatus is also annually revised. With the aim to increase the quality measurement and to prevent against the contact resistance, the sensor was directly placed in the centre of a PCM prismatic sample (8.5 x 8.5 x 4 cm). Thermal conductivity measurements were taken under isothermal conditions at 20±1 °C (4 hours cooling period between two measurements). The measurement procedure starts automatically once the sample temperature is stabilized at 20±1 °C (2%).

3 Results and discussion

3.1 Synthesis of s-s PCM

In this work, s-s PCMs were synthesised through the reaction between diisocyanate and dihydroxyl, as commonly reported in the literature [3,6,7]. For environmental and health reasons, limiting the use of solvent was an objective of our study. Thus, the syntheses were realised with neither solvent nor catalyst. First, the synthesis described in [3] was adapted to our requirements to produce PUs as s-s PCMs. Second, the synthesis was improved to meet specifications such as hardness and water insolubility.

3.1.1 Synthesis of linear PUs

For this purpose, the reaction between HMDI and PEG (Figure 1) in a stoichiometric quantity of isocyanate and hydroxyl function was realised at 70 °C under inert atmosphere.

The kinetics of reaction was followed by FTIR for all synthesised PU. After the homogenisation of the reaction mixture, FTIR analysis was performed on the reaction mixture every 15 minutes. An example is provided in Figure 2 for the synthesis of a PU made from PEG-1K and HMDI in stoichiometric proportions ([NCO]=1). On one hand, the reaction is characterised by a decrease in the absorbance of the stretching vibration of isocyanate at 2250cm⁻¹ and that of PEG's hydroxyl function at 3400cm⁻¹. Alternatively, the formation of urethane function is observed through an increase in intensity of the vibration at 1717cm⁻¹, corresponding to the resulting carbonyl stretching, and at 1538cm⁻¹ of N-H urethane bending. In Figure 3, the conversion of isocyanate function is plotted as a function of reaction time. One may notice that the reaction is nearly quantitative after 45 minutes with a conversion of about 99%. As a result, for this mixture (PEG-1K and HMDI in stoichiometric proportions), 45 minutes at 70 °C has been chosen as the reaction conditions. The obtained PU underwent a post-curing at 100 °C for 5 h. According to FTIR analyses, the kinetics may differ slightly from one mixture to another.

The synthesis of linear PUs (PULs) can be successfully realised without any solvent or catalyst. The obtained PULs appeared like a solid with low physical properties, particularly hardness (easily scratchable by nail). They were also completely soluble in water. To limit the PUs' solubility, the formation of polymer network from PU chains has been considered.

3.1.2 Synthesis of cross-linked PUs

Synthesis of cross-linked PUs (PUXs) was investigated using glycerol as cross-linker to counterpart the issue of water solubility and poor physical properties observed with PUL (Figure 4).

To balance out the lower reactivity of the secondary alcohol in glycerol, the latter was introduced in the reaction mixture at the beginning of the synthesis. In this study, the quantity of glycerol was calculated so as to be 20% of total PEG's hydroxide function. The total hydroxide function is kept in stoichiometric quantity with isocyanate function. As in the case of PULs, the kinetics of reaction were followed by FTIR. Similar evolution was observed after 45 minutes at 70 °C. This similarity seems to indicate that the presence of glycerol does not have significant impact on the reaction kinetics. The reaction was then followed by a post-curing at 100 °C for 5 h. To ensure that the obtained PUXs were s-s PCMs, samples were heated at 50 °C in a stove and observed through infrared thermography. According to Figure 5, the synthesised PUs remain in solid state above and below temperature transition (see Table 1).

3.2 s-s PCMs characterisation

3.2.1 POM observation and crystalline morphology

S-s PCMs undergo a change from crystalline to amorphous-solid phase and reversely. The study of crystalline morphology allows a better understanding of thermal material behaviour. The crystalline morphology of PEG, PUL, and PUX can be observed under POM. Figures 6A, B, and C show micro-photos of PEGs with growing molecular weight at 20°C. The PEG crystals appear as spherulites whose size increases with molecular weight as expected [3]. Similar evolution has been observed with PUs, as a function of PEG molecular weight. The relationships between crystal size and PEG molecular weight are also observed in PUs, as shown in Figures 6D and E at 20 °C under POM. Whatever the sample, the crystalline morphology appears as spherulites like pristine PEG. However, a significant reduction of the crystal size, as well as the lamellae size [6], is observed. The spherulite size is between 150 µm-200 µm for pristine PEG, and around 50 µm for PUL or PUX. Compared to PEGs, the crystallisation of PUL and PUX is limited due to the organisation of the hard segments within the PUs, which constrains the nucleation sites of soft segments (PEGs). This phenomenon is observable under POM, as shown in Figure 7, where a microscopic preparation of PUX-1.5K-20 was heated in an oven to 50 °C and then placed under the microscope. The formation of spherulites during the cooling at room temperature can then be observed. At the oven exit (i.e. close to 50 °C), the PU showed no birefringent property indicating that the material was in a solid amorphous state. As shown in Figure 7, spherulites appeared progressively with cooling. Numerous nucleation sites occurred, leading to the formation of many small crystals rather than large crystals from a liquid phase, as is the case for pure PEG.

Both PEG-1.5K and PUX-1.5K-20 were characterised in X-ray diffraction (XRD) to compare their crystalline structure (Figure 8). The diffraction signals at 19.28 °, 23.40 °, 27.23 ° and 36.20 °2θ are attributed to PEG, according to [39]. These peaks are also observed for PUX-1.5K-20. Both diffractograms are very similar, indicating that the crystalline morphology of PEG was found in PUX, which suggests that cross-linking has a minor impact in that regard. The only difference between the two diffractograms that could be from cross-linking was found at 27.23 °2θ, where PEG-1.5K showed two well-defined peaks while PUX-1.5K-20 showed a single poorly defined peak with a lower intensity. These diffractograms showed that the crystalline structure of both compounds can be considered to be very close to one another.

3.2.2 Thermal analyses

The thermal stability of the different s-s PCMs was first investigated by thermogravimetric analysis (TGA). Figure 9A presents the thermogram of PULs as a

function of the initial PEG's molecular weight. Figure 9B shows the influence of the cross-linker on the thermal stability of the PUs. As shown in these figures, the molecular weight of the initial PEG and the presence of cross-linker have no significant influence on the degradation temperature of the PCMs. Whatever the PU composition, a progressive and continuous thermal degradation is observed, suggesting a high homogeneity of the PUs. Of weight loss, 5% is reached at 280 °C, and a 90% advancement of the degradation is reached at 430 °C. The total degradation is complete at 450 °C in all cases. This high temperature stability of the s-s PCMs allows their consideration in various applications. This behaviour is similar to that of other cross-linked PUs [9,10].

The thermal properties (latent heat and transition temperatures) of s-s PCMs were determined by DSC. These thermal properties are controlled by the crystallisation of poly (ethylene oxide) part. The formation of polyurethane restricts the movement of polymer chains, and thus their crystallisation. Consequently, one could expect lower transition temperatures and latent heat in PU when compared to corresponding PEG. These values depend on three parameters: the molecular weight of the initial PEG, the stoichiometry (isocyanate group/ hydroxyl group call [NCO] ratio), and the cross-linking. The PEG's molecular weight is a major parameter acting directly on the heat storage capacity, as well as on the transition temperatures. The increase in PEG's molecular weight shifts the transition phase towards higher temperatures of melting and crystallisation and increases the latent heat. As shown in Figure 10 and Table 1, PUL-1K has a latent heat lower than PUL-1.5K, which has a latent heat lower than PUL-2K. The molecular weight of PEG impacts temperatures of phase change (crystallisation and melting temperatures). Thus, it seems that for similar crystallisation conditions (i.e. room temperature in our case): the higher the molecular weight of the PEG, then the longer the polymer chains, the larger the size of the spherulites, the higher the latent heat, and the higher the temperature of phase transition. This evolution is general for both PEG and PUL. The formation of polyurethane does not seem to produce an additional impact on these evolutions, as reflects the "remaining crystallinity". The latter, calculated from the ratio of latent heat of PUL to corresponding PEG, remains quasi-constant in the range of PEG molecular weights and in the same studied conditions.

The stoichiometry ([NCO] ratio) is another major parameter that influences the final properties of resulting PUs. An excess of isocyanate function is generally used to cover any loss of isocyanate due to volatilisation, dimer formation, and unintentional urea formation due to reaction with humidity [34]. Table 1 shows the influence of the stoichiometry on the thermal properties of the PUL based on PEG-2K. Whatever the [NCO] ratio, PUL-2K has a latent heat lower than the corresponding PEG from which it was synthesised. The higher the [NCO] ratio, the lower the latent heat. A diminution of the transition temperature was also observed with an increase of the [NCO] ratio. The excess of isocyanate function appears to improve the network formation reducing the PEG chains movement, which constrains the size of crystallisation sites. This behaviour is somehow similar to POM observations described in 3.2.1. However, very efficient polymerisation tends to reduce latent heat. As a consequence, the [NCO] = 1 is retained for further study.

The influence of cross-linker on thermal properties is shown in Figure 11 and Table 1. A decrease of transition temperature and latent heat is observed with the introduction of cross-linker into the system. This decrease is consistent with POM observations (Figure 6), where a decrease in spherulite size is observed with cross-linking.

Accelerated thermal cycles (between 15 °C and 40 °C) were performed on PUX-1.5K-20 to assess thermal durability, i.e. the ability of PUX to maintain TES capacity. Quantities of 6 ± 1 mg of powdered PUX-1.5K-20 underwent 500 thermal cycles and were analysed by DSC at $t = 0$ (before thermal cycling), $t = 100$, $t = 200$, $t = 300$, $t = 400$, and $t = 500$ cycles. As shown in Figure 12, latent heat and phase change temperatures remained unchanged after 500 cycles, suggesting a good chemical stability of PUX-1.5K-20. A similar chemical stability is expected whatever the molecular weight of the PEG used for PUX.

The mean thermal conductivity of PUX-1.5K-20 is $0.231 \pm 0.0085 \text{ W.K}^{-1}.\text{m}^{-1}$. The reproducibility of the measurement is close to that provided by the manufacturer (i.e. 1%). The thermal conductivity of PUX-1.5K-20 is compared to other PCMs conductivity available in the literature (Table 2). The corresponding PEG-1.5K has a thermal conductivity of $0.297 \text{ W.K}^{-1}.\text{m}^{-1}$. This observation suggests that PUs have a lower thermal conductivity than that of PEG from which it is synthesised. Paraffin, largely used as a s-l PCM, has a thermal conductivity of $0.22 \text{ W.K}^{-1}.\text{m}^{-1}$, and DC6Br, a s-s PCM, has a low thermal conductivity of $0.12 \text{ W.K}^{-1}.\text{m}^{-1}$ [40]. The preliminary results of PUX-1.5K-20 thermal conductivity are comparable to other materials used as PCMs which behave as good insulators.

3.2.3 Physical properties

As shown previously, PULs and PUXs differ from their thermal properties, but they also presented some physical differences. Soft materials that are very easy to deform manually at ambient temperature, PEGs show a ductile behaviour at room temperature, and their hardness is given on Shore durometer A scale. In comparison, PULs and PUXs, synthesised from PEGs in this study, appeared as solid materials that were comparatively hard and impossible to deform manually. They did not show a ductile behaviour but rather a fragile behaviour. PULs and PUXs also presented some physical differences from each other that were less obvious but remained perceptible. The most striking difference concerned hardness. Indeed, PUXs clearly appeared much harder and more brittle than PULs. Hardness tests were performed on different PUs to quantify this hardness difference. Linear and cross-linked PUs using the same PEG are compared in Table 3, as well as the effect of cross-linker content. Their hardness is given on the Shore durometer D scale used for hard materials. While PUX-1.5K has a mean hardness of 30 ± 1 , PUL-1.5K has one of 10 ± 1 , which confirmed the qualitative impressions. Comparatively, PUX-1.5K-30 and PUX-1.5K-40 have a hardness of 38 ± 3 and 39 ± 2 respectively. These results show that cross-linking modified and increased the hardness of the synthesised PUX and that the higher the cross-linker content, the greater the hardness of the PUX, for a constant PEG. The hardness of the s-s PCMs is a very interesting feature, especially for some application domains where PCMs require being ground to very fine particles so as to be disseminated or incorporated into a composite material. Thanks to this hardness property, grinding was performed on different PUXs with a knife mill GM200 from Restsch®. As a result, a fine powder with grain size varying between $50 \mu\text{m}$ and $600 \mu\text{m}$ was obtained, suggesting the possibility of adjusting grain size as wished. An example of ground PUX-1.5K-20 is given after sieving at $300 \mu\text{m}$ in Figure 13. Grains of PUX showed an angular shape with sharp edges. Reducing PUL into powder with the same knife mill was also tested. Unfortunately, it had been impossible to realise, as the PUL behaviour is not brittle enough to accommodate this grinding process in particular.

Figure 13: Photo of PUX-1.5K-20 grains after grinding and sieving at $300 \mu\text{m}$.

4 Conclusions

In this study, linear (PUL) and cross-linked (PUX) s-s PCMs based on PEG with different molecular weights (1K, 1.5K, and 2K) have been synthesised successfully via one-step bulk polymerisation. PEGs react with HMDI at different [NCO] ratios to produce PUL, and glycerol was used as cross-linker, at different ratios, to produce PUX. These syntheses were performed solvent free, which provided an extra value to them from the environmental and health perspectives. Three parameters were varied for the synthesis of PUs: (i) PEG molecular weight, which determine the thermal properties (phase change temperature and latent heat); (ii) the stoichiometric, which played a minor role on thermal properties and spherulites size of PUL (at constant molecular weight of PEG); and (iii) the cross-linker content, which provided the physical properties of the PUX (hardness and solubility). It was possible to produce different s-s PCMs with different properties: latent heat ranges between 79 J/g and 108 J/g and the temperature of phase change between 22 °C and 50 °C. These PUs degraded at high temperature (from 290 °C), this relatively high temperature stability allows a wide range of utilisation. Furthermore, thermal conductivity of PUX-1.5K-20 was found at 0.231 W.K⁻¹.m⁻¹. The PUXs seemed to be the most interesting because of their physical and thermal properties. Their hardness, improved by cross-linkage, was between 30 and 39 on Shore D scale; this property allows grain size reduction into a fine powder. As a result, PUXs seem to be s-s PCMs particularly suitable for direct incorporation into composites materials dedicated to TES within low to medium temperature application.

5 Acknowledgements

The authors thank the University of Cergy-Pontoise, its Foundation and the Chaire Eco-Quartiers et Villes Durables for their financial support (PhD grant and scientific environment) and the SATT IdF innov for patent deposit. We also thank the "Institut de Recherche Criminelle de la Gendarmerie Nationale" for XRD access.

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Figure 1: Synthetic scheme of polyurethanes.

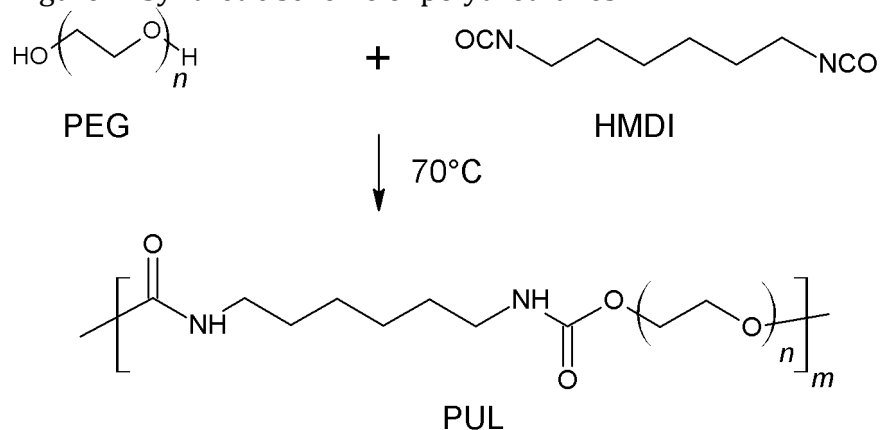


Figure 2: FTIR spectra performed on a PEG-1K, HMDI in stoichiometric proportions mixture. $t_0=0$ mn (blue), $t_1=15$ mn (red), $t_2=30$ mn (purple), $t_3=45$ mn (green).

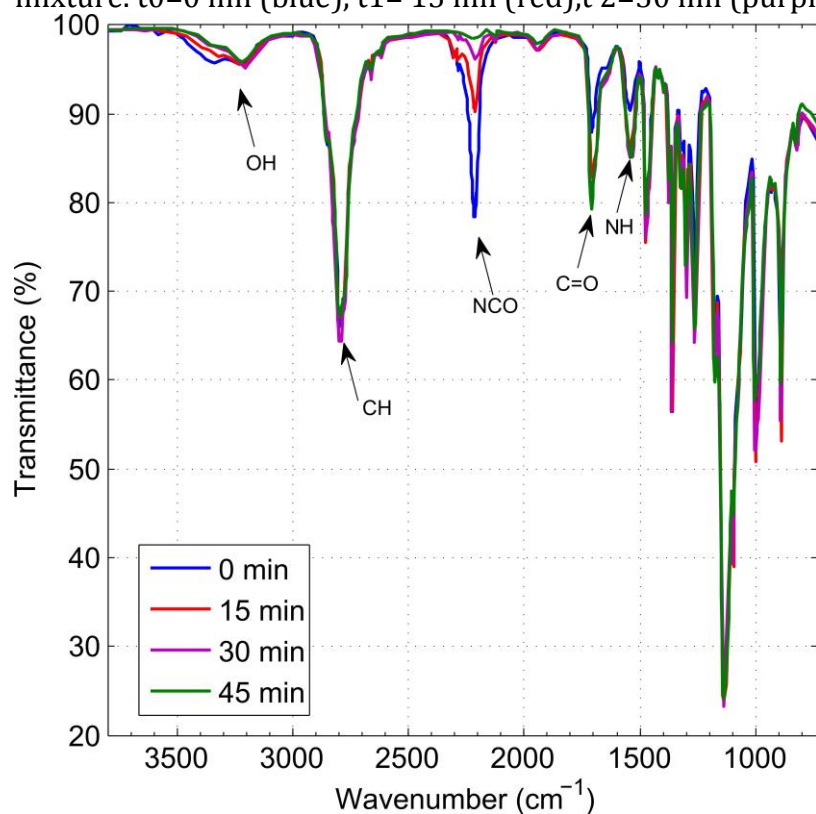


Figure 3: Conversion of isocyanate as a function of reaction time.

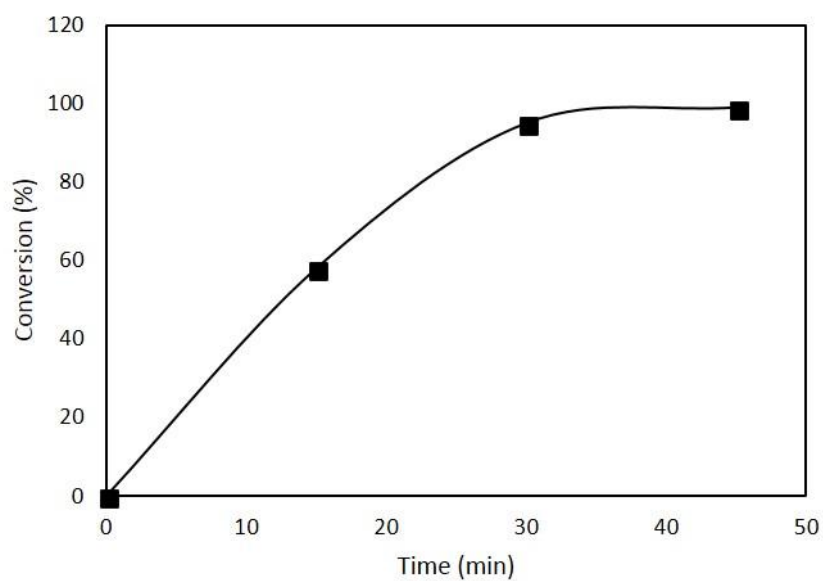


Figure 4: Synthetic route of cross-linked polyurethanes.

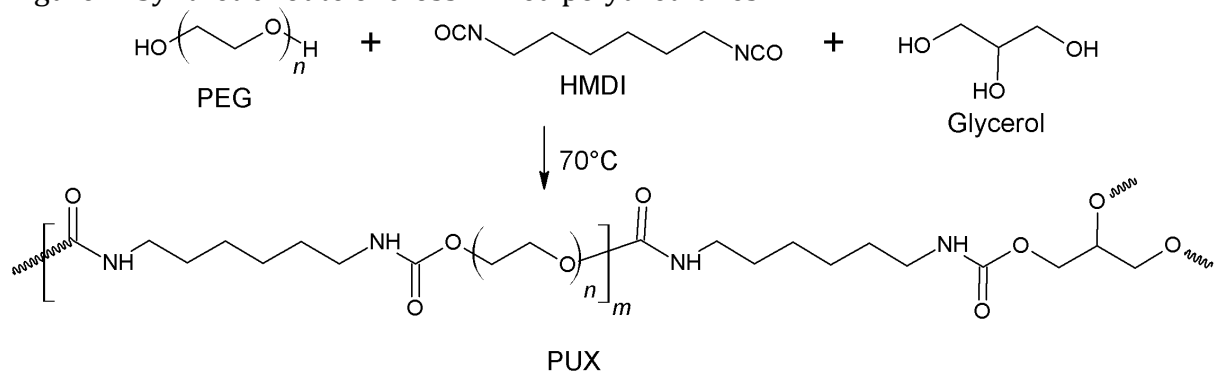


Figure 5: Photographies of PUX-1.5K-20 at ambient temperature (A) and 50 °C (C); and infrared thermography at ambient temperature (B) and 50 °C (D).

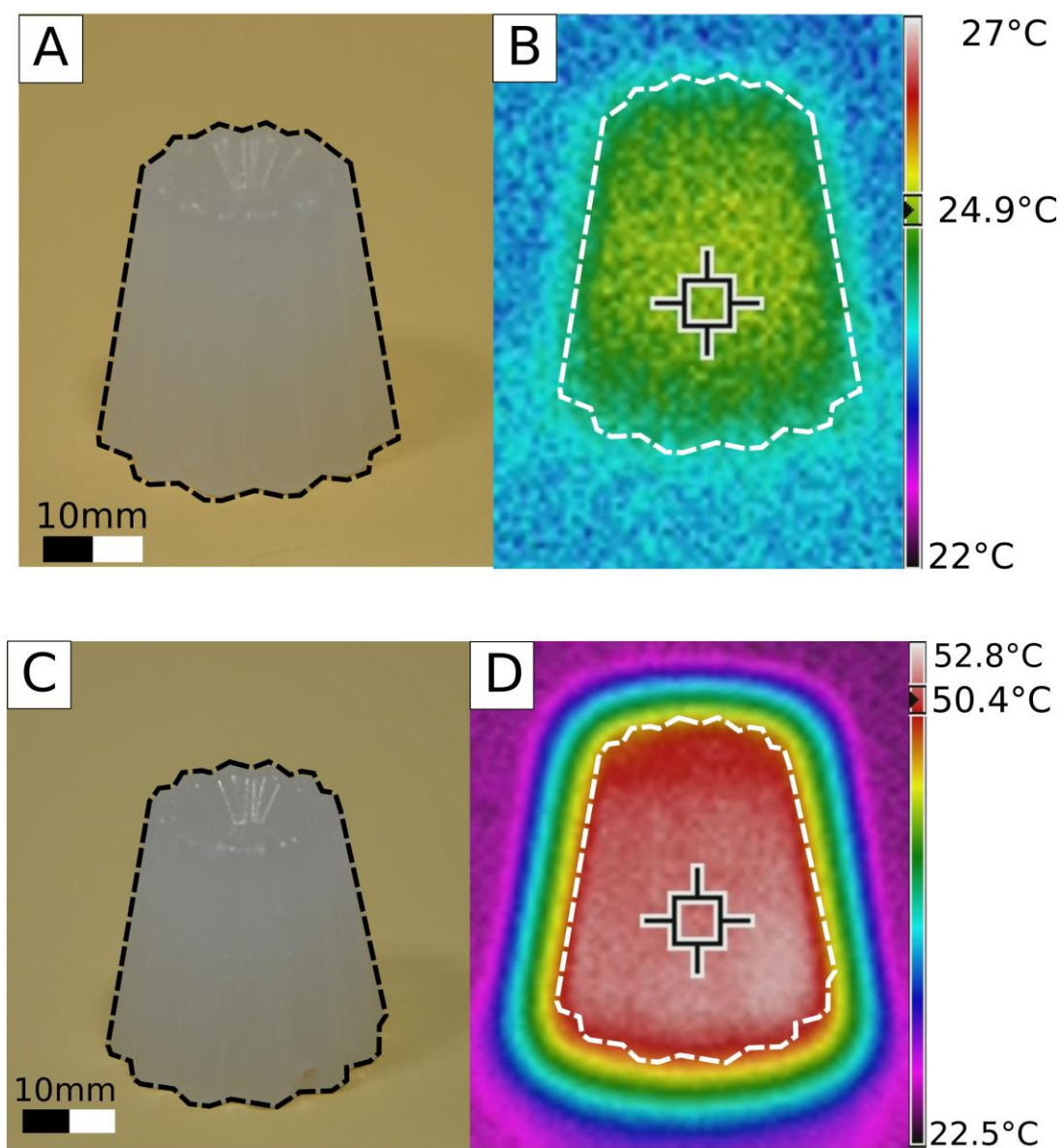


Figure 6: PEG-1K (A), PEG-1.5K (B) and PEG-2K (C) under POM at 20 °C; PUL-1.5K (D) and (E) PUX-1.5K-20 under POM at 20 °C

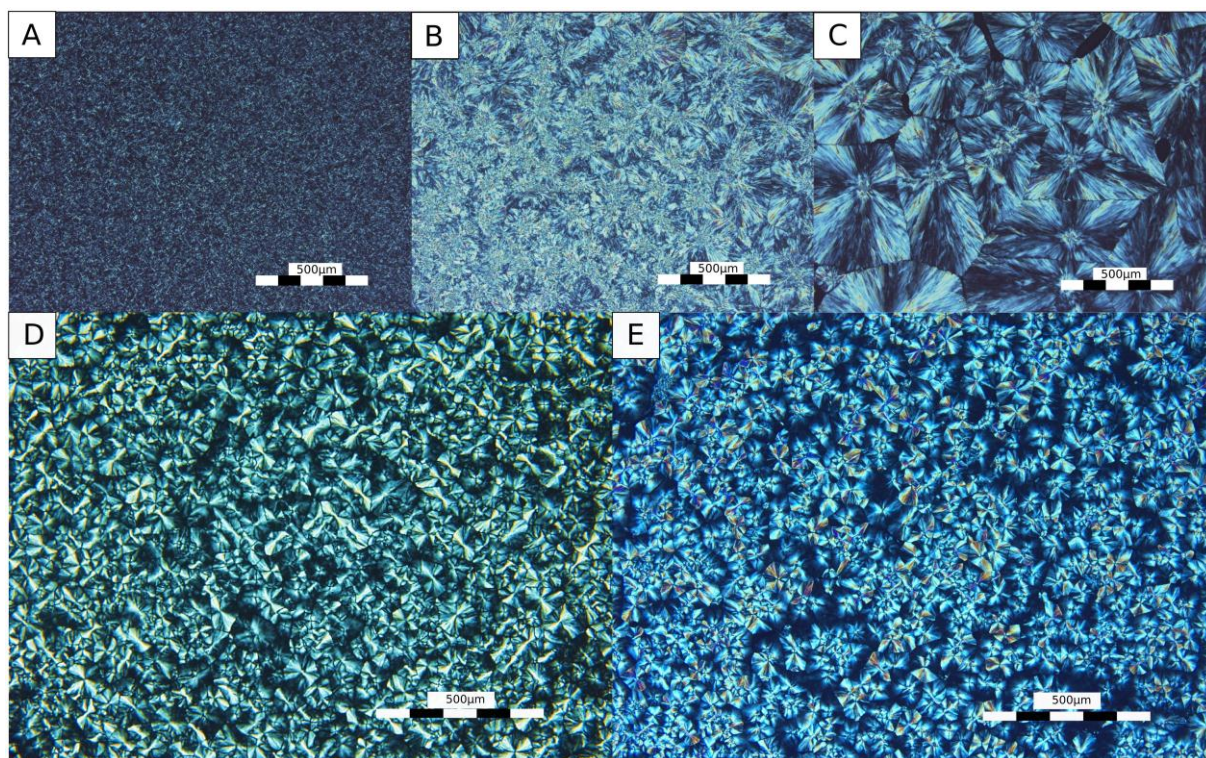


Figure 7: Crystallization of PUX-1.5K-20 from 50 °C (A) to room temperature (F) under POM.

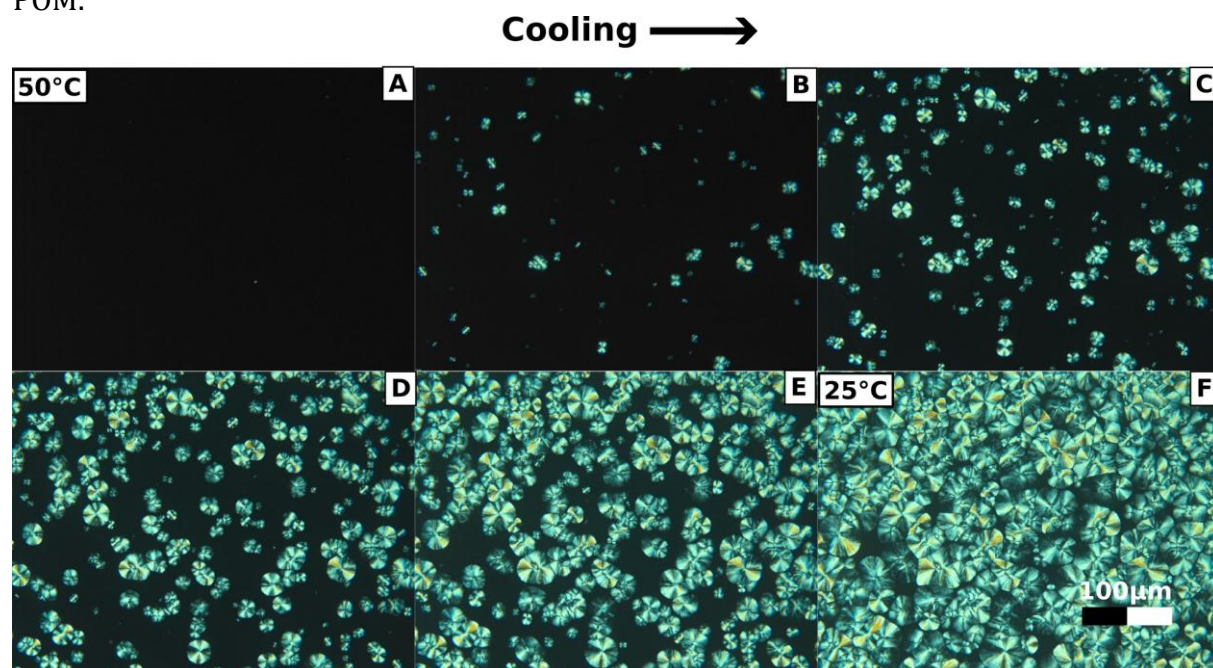


Figure 8: XRD curve of PUX-1.5K-20 and PEG-1.5K.

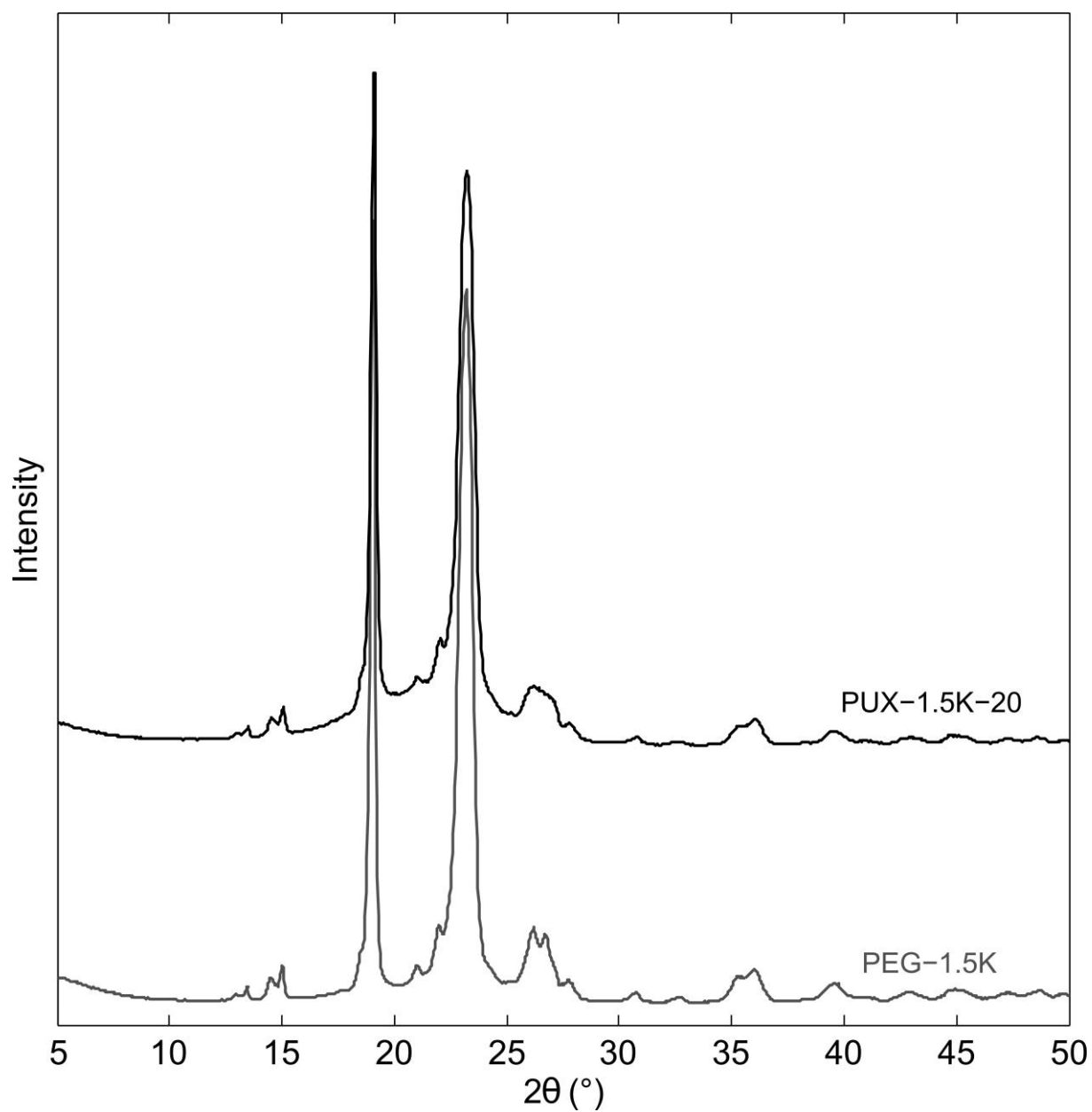


Figure 9: Thermogravimetric analyses of PUL-1.5K A: as a function of the initial PEG molecular weight; B: as a function of cross-linker content (0 or 20%).

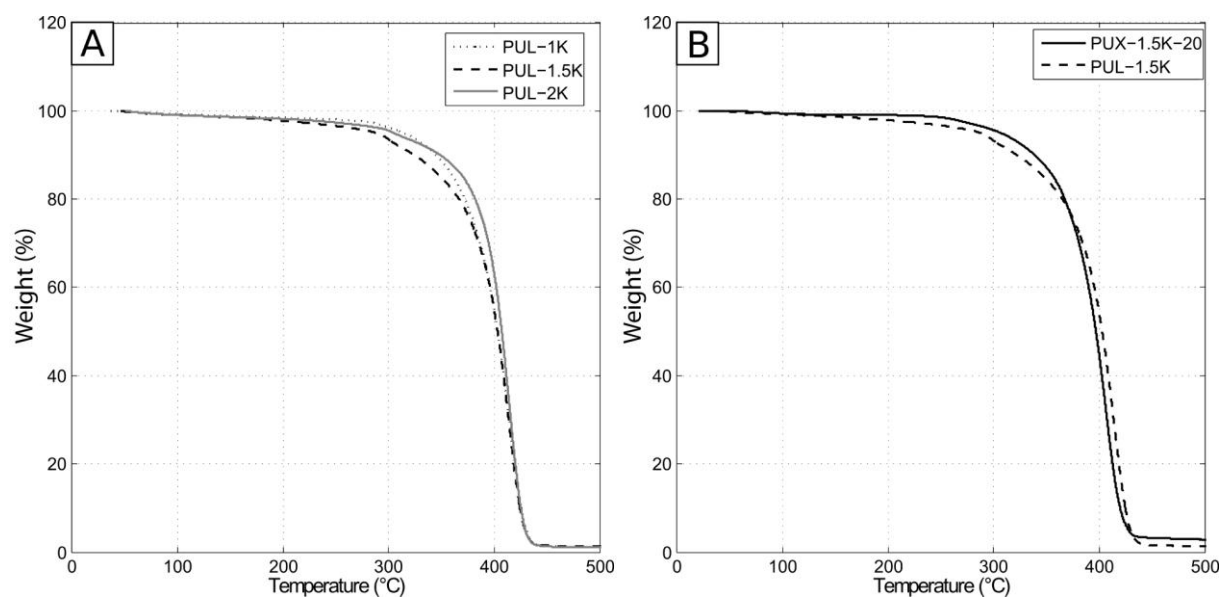


Figure 10: DSC analyses of PUs as a function of initial PEG's molecular weight. Left: crystallisation, right: melting.

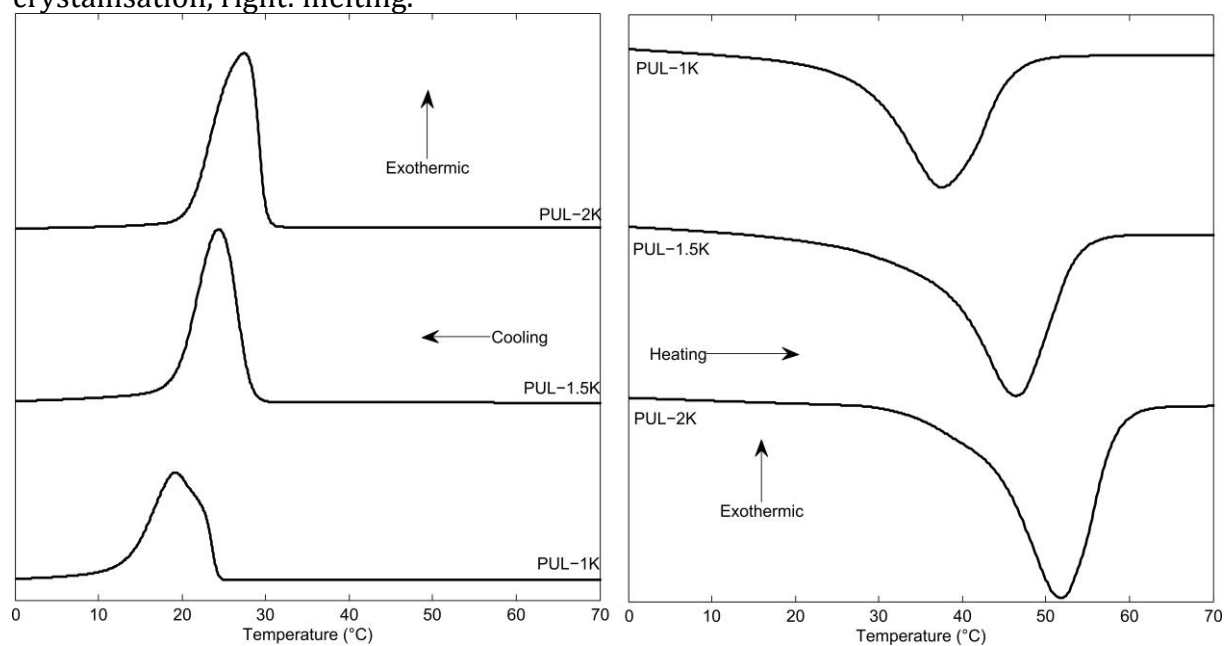


Figure 11: DSC analyses of PUL-1.5K and PUX-1.5K-20.

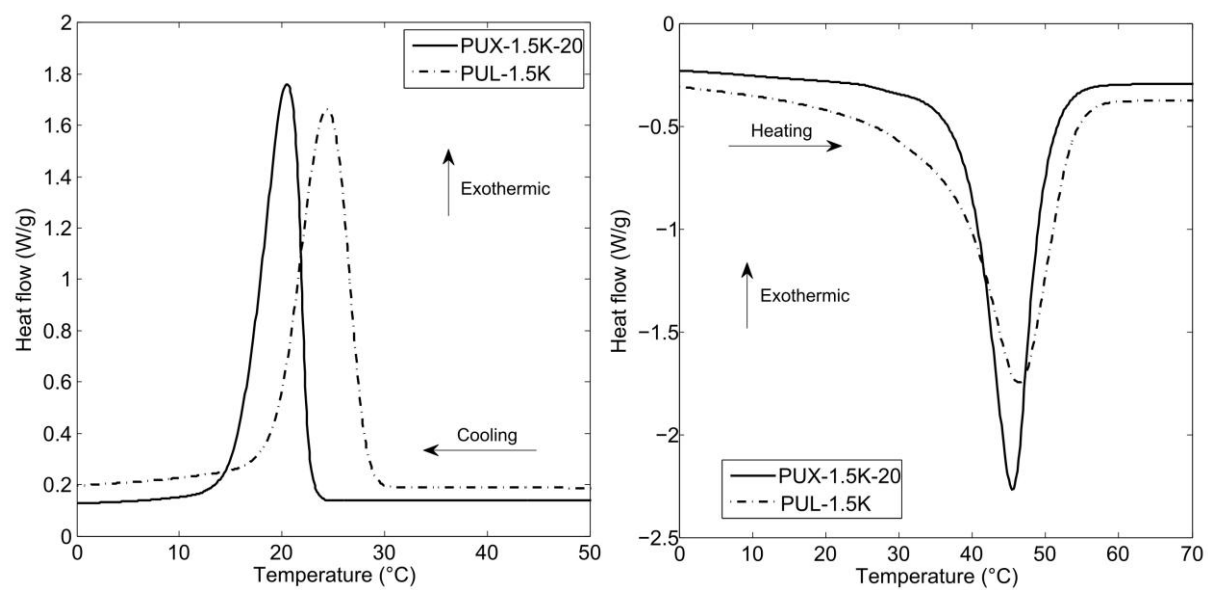


Figure 12: DSC analyses of PUX-1.5K-20 before thermal cycling, after 100, 200, 300, 400 and 500 thermal cycles.

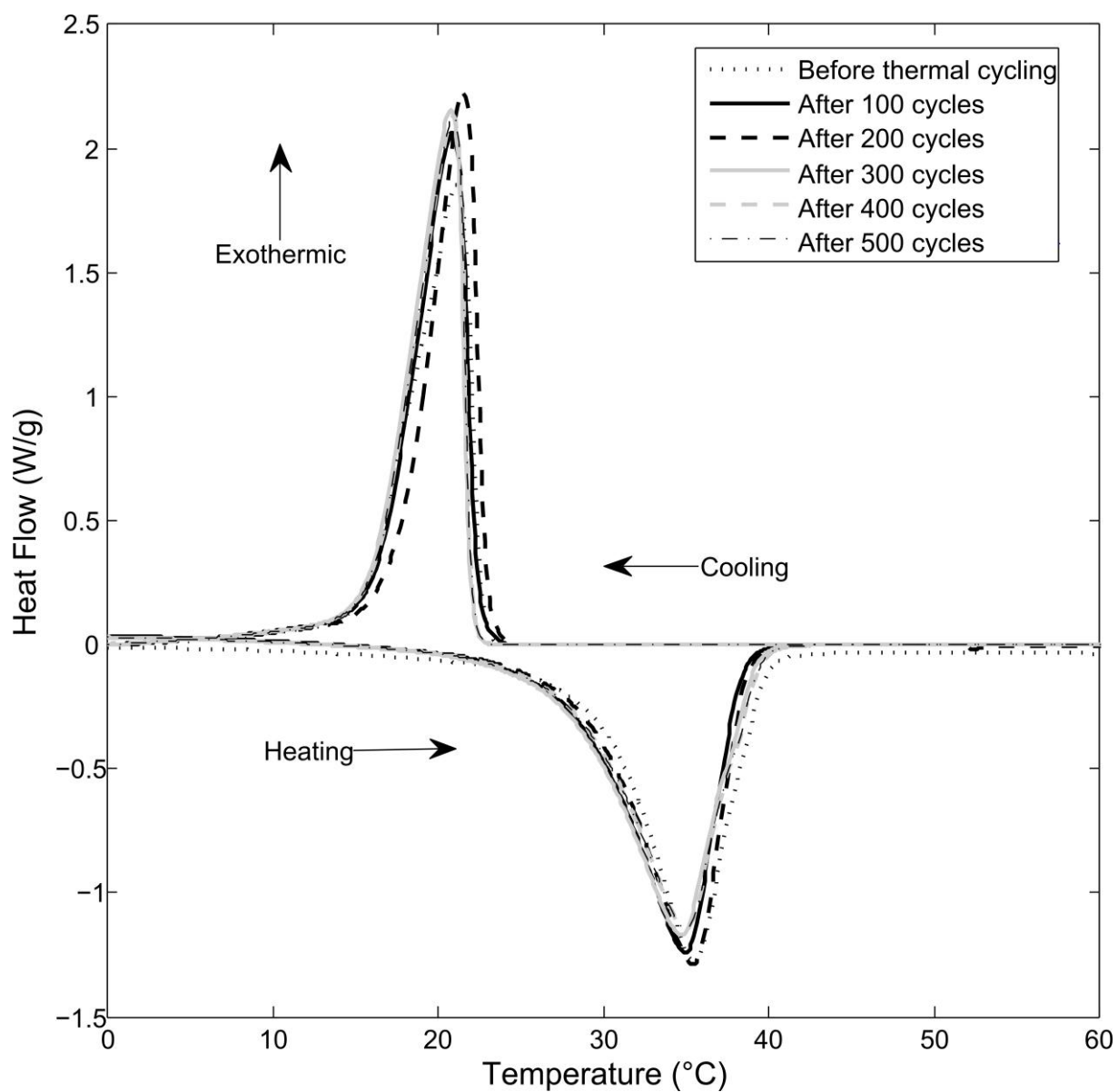


Table 1: DSC results of PEGs, PUL and PUX.

Sample	[NCO]	Melting			Crystallisation			Remaining crystallinity
		T_{Peak} (°C)	T_{Onset} (°C)	ΔH (J/g)	T_{Peak} (°C)	T_{Onset} (°C)	ΔH (J/g)	
PEG-1K	/	40.0±1	33.0±1	151±1	22.8±1	26.5±1	150±1	1
PEG-1.5K	/	52.8±1	50.0±1	166±2	32.3±1	34.5±3	167±1	1
PEG-2K	/	56.1±1	49.8±1	169±1	36.9±1	40.5±1	169±1	1
PUL-1K	1	37.7±0.2	28.2±0.5	80±4	19.9±0.7	24.8±0.6	79±5	0.64
PUL-1.5K	1	47.0±2.8	34.8±2.3	95±5	22.8±1.3	28.1±1.4	94±4	0.64
PUL-2K	1	51.7±1.1	39.5±2.2	108±5	24.9±2	29.4±0.5	104±4	0.68
PUL-2K	1.05	46.4±0.4	35.1±0.4	88±4	23.0±0.6	25.6±0.4	87±5	0.575
PUL-2K	1.1	45.3±0.9	28.7±2.3	87±2	17.2±0.6	25.2±1.1	87±2	0.570
PUX-1.5K-20	1	45±0.7	38±1.3	91±2	20.2±0.4	22.3 ±0.4	89±2	0.57

Table 2: Thermal conductivity of PEG, PUX-1.5K-20 and other PCMs

Sample	Thermal conductivity (W/(K.m))
PEG-1.5K	0.297
PUX-1.5K-20	0.231
Paraffin [41]	0.22
DC ₆ Br [40]	0.12

Table 3: Results of hardness test performed on sample of PCM at 25°C.

s-s PCM	Hardness (Shore D)
PUL-1.5K	10 ±1
PUX-1.5K-20	30 ±1
PUX-1.5K-30	38 ±3
PUX-1.5K-40	39 ±2