Thermal characterization of polyurethane foams with phase change material

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Abstract

Taking the joint advantages of the thermal insulation capacity of polyurethane foams (PU) and the thermal energy storage capacity of phase change materials (PCMs), it is possible to produce PU composite foams that can be incorporated as a functional layer into buildings components, designed as latent heat thermal energy storage systems (LHTES), that improve the thermal comfort and the energy consumption of buildings. In this work, PU composite foams containing microencapsulated PCMs (mPCMs) were produced by polyol synthesis. The major aim of the present study was to improve the thermal characteristics of PU foams, by incorporating PCMs, taking advantage of their thermal energy storage capacity. The thermal and energy storage properties were evaluated for three different PU composite foams (hard foam without and with melamine and expandable graphite) with the addition of different percentage of mPCMs. The comparative characterization of the energy storage properties of the PU composite foam formulations is measured using a dynamic scan calorimeter and the thermal conductivity using the transient plane heat source method. The addition of flame retardants to the PU foam slightly influenced the latent heat storage capacity of the PU foam with mPCMs and the addition of mPCMs increases the final thermal conductivity.

Keywords: latent heat storage; phase change material; polyurethane foam; thermal conductivity.

1. Introduction

In the last two decades, the European Union (EU) has been working on new and stricter legislation to control the consumption of energy. The building sector is responsible for consuming 40% of the total final energy use of the EU and produces nearly 40% of the total CO_2 emissions [1,2]. This sector, as one of the major energy consumers, generates pollution and consumes natural resources [3,4]. Therefore, it is necessary that the energy consumption of buildings decreases, but without compromising thermal comfort and indoor air quality [5].

In this context, phase change materials (PCMs) appear as a potential solution to increase the thermal efficiency in buildings since they can store more energy, in the latent form, than the typical sensible energy stored by common materials [6-9].

Phase change materials are divided into two main categories: organic and inorganic [10-13]. This classification depends on different properties: thermal, physical, chemical, kinetic, as well as their economic value. These types of materials have been studied during the last 40 years, mainly hydrated salts, paraffin waxes, fatty acids and eutectics mixtures of organic and non-organic compounds.

To enhance the integration and compatibility of PCMs

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into existing and new building solutions, commercial companies base their solutions mainly on microencapsulated PCMs (mPCMs) composed by microscopic polymer capsules with a diameter approximately of 1-20 micrometres [14,15]. The main advantages of mPCMs are: a) easy incorporation into conventional building materials; b) increase of heat transfer area; c) protection against their destruction and loss of properties; d) good control of the volume change during the phase change [15-19]. The incorporation of mPCMs in PU foams to improve the thermal behaviour and to enhance the energy efficiency in the buildings was firstly undertaken and developed in 1990s [20-23]. As many authors present, the main advantage of the PCMs integration into buildings solutions is the high storage density for small temperature range [7,13,24-26]. This storage capacity increases the building thermal inertia, and it is expected to contribute to solving the time mismatch between the energy supply and the consumption.

Hard polyurethane foams (HPU) are widely used as insulation layers incorporated or associated to opaque building envelope solutions for construction, as well as for other applications such as transportation, decoration and appliances, accounting for almost one-third of the polyurethane market [27,28].

These cellular materials are made by reacting polyols with isocyanates with the proper amount of catalysts, additives and blowing agents. In general, preparation of highly cross-linked polyurethane (PU) material requires a reactive polyol that has a relatively high hydroxyl number ranging from 200 to 800 mg KOH/g. The interest in using bio-based polyols, especially natural oil polyols, in the manufacture of PU products has increased significantly in the recent years [29]. In order to increase the substitution level of bio-based polyols, it is often required that bio-based polyols have good compatibility with the conventional petrochemical-based PU systems and consistent composition. Oil extracted from a plant consists mostly of a composition of various fatty acids. The plant, the seeds of growth conditions and the season have an effect on the composition of the oils. Due to the diversity of fatty acids in biological raw materials, the synthesis of well-defined PU systems presents a problem. For these reasons, polyols based on dicarboxylic acids, instead of fatty acids are still in need of evaluation. Bio-based raw materials of dicarboxylic acids are carbohydrates such as cellulose and glucose. Despite the extensive research and commercialization efforts relating to the development of bio-based polyols or "biopolyols" from renewable resources, petroleum-

based polyols still dominate the global polyol market. You et al. [30] studied the influence of mPCMs on the fabrication of PU foams. Results revealed no significant influence in terms of the thermal stability of PU foam and the enthalpy of the foam rise with the increase of the content of mPCMs, above 12 J/g for the foam containing 12.59 wt% mPCMs. You et al. [22] fabricated PU composite foams containing microencapsulated n-alkanes with general polyether and a combination of polyether polyols. Results revealed the enthalpies of the foam rises steadily as the content of microcapsules increased from 6.4 to 25.2 wt% (28 J/g). Sarier and Onder [27] studied two paraffin waxes (*n*-hexadecane and *n*-octadecane) directly incorporated into the PU foams with different ratios. Results revealed that the PCMs enhance the foams thermal energy storage (TES) capacity. Borreguero et al. [31] incorporated different percentages of microcapsules containing Rubitherm® RT27 into PU foams. Borreguero et al. [32] incorporated up to 18 wt% of two different kinds of thermo-regulating microcapsules having different shell material into the HPU foam. The results showed that the type of microcapsules and their content effect the final foam height, which decreased with the content and particle size. And showed a TES capacity similar to those reported in the literature (16 J/g). In the present work, it was observed that the increase of the microcapsules content in the foams decreases the final foam height rise but increases its density and TES capacity.

Most current research focuses on how the percentage of PCMs influences the thermal energy storage capacity of PU composite foams without paying attention to the thermal insulation performance of these formulations with the presence of different flame retardants This paper gives an overview of the experimental work in order to demonstrate the thermal characteristics of three PU composite foams (hard foam without and with melamine and expandable graphite) containing various quantities of mPCMs and compared resourcing to the transient plane heat source method and the dynamic scan calorimeter (DSC). The main aim of this work is to gain new insights on thermal characteristics of PU foams with mPCMs.

2. Experimental

2.1. Materials

Microencapsulated PCM powder purchased from BASF (Ludwigshafen, Germany) was used in this

study, (Micronal®DS 5001X). It contains a paraffin wax with a melting point of 26°C as the core material and the shell of PMMA (polymethyl methacrylate).

The PU components Purotherm 463 RG 48 (polyol) and puronate 900 (isocyanate) of the HPU foam formulation were purchased from Rühl Puromer GmbH (Friedrichsdorf, Germany). The polyol component includes different proportions of bio-polyols, catalyst and stabilizers. Melamine (99 %) was purchased from Sigma Aldrich (Munich, Germany) as a fine power. Ammonium polyphosphate (APP) with an average grain size of 20 μm was purchased from Clariant (Oberhausen, Germany) under the sales designation Exolit AP 462. Expandable graphite (EG) was purchased from Nordmann/Rassmann (Hamburg, Germany) under the sales designation NORD-MIN FP.

2.2. Preparation of HPU composite foams

The standard HPU foam was prepared using 100 parts polyol (Purotherm 463 RG 48) and 130 parts isocyanate (puronate 900). Both components were mixed with a blade stirrer at 2000 rotations / second for 10 s. Afterwards the mixture was put in a foaming mould under a fume hood until final foaming. The foam remained at room temperature for at least 24 h before performing out any measurement, to ensure complete reaction between polyol and isocyanate.

The mPCM (up to 12.5 parts = 5%) and flame retardant (melamine, APP or EG) were incorporated in the polyol fraction prior to the HPU foam formation by mixing for 55 s. To avoid high shear forces, a blade stirrer with a lower rotation rate (1000 rotations/second) that does not touch the bottom of the beaker was used.

2.3. Characterization

To evaluate the influence of mPCMs incorporated into the HPU foam, it was taken into account the tests referred in the literature review. The selected experimental characterization tests were: *i)* DSC, *ii)* thermal conductivity, *iii)* foaming behaviour, *iv)* SEM, and *v)* flame retardancy testing, all carried out over all the produced foams (see Table 1).

The foaming of the HPU foams was investigated using the foam qualification system FOAMAT, an electronic measuring device, which is equipped, inter alia, with an ultrasonic sensor (pulse-echo method).

Thus, the steep slope performance of flammable mixtures can be measured without contact. In addition, the rising pressure and the dielectric polarization of the expanding foam can be measured.

Table 1. Treatment compositions.

Samples	mPCM (wt%)	Flame retardant
mPCM	100	-
HPU	0	-
HPU_PCM2%	2	-
HPU_PCM5%	5	-
HPU_M	0	melamine
HPU_M_PCM2%	2	melamine
HPU_M_PCM5%	5	melamine
HPU_EG	0	expandable graphite
HPU_EG_PCM2%	2	expandable graphite
HPU_EG_PCM5%	5	expandable graphite

The measurements were made in a 20 cm high cardboard tube with 15 cm internal diameter.

SEM images of the incorporated mPCM in the HPU foams were recorded to investigate whether the stirring process destroys the mPCM and how those particles are fixed in the HPU matrix. The recording SEM device was a scanning electron microscope (Zeiss Supra 55 VP) with an Everhard Thornley secondary electron detector and in addition a backscattered electron detector.

Flame retardancy measurements were performed using a small burner according to the Airbus test (AITM 2002 F2). This Airbus test is very well suited for samples on a laboratory scale. PU foam test specimens of 10 cm x 25 cm x 2 cm were cut from the foamed HPU block fabricated. The samples were clamped vertically in a frame (sample holder) and exposed to a defined flame (38 mm high) for 12 seconds and the combustion behaviour was documented.

To characterize the energy storage properties of the HPU foams (melting and solidification temperature and enthalpy), a dynamic scan calorimeter (DSC 4000, PerkinElmer) was used, at a heating and cooling rate of 1ºC/min, in the range of 10ºC to 50ºC under a nitrogen atmosphere. The thermal conductivity of the composites was measured using a transient plane heat source method (Hot Disk Analyser, TPS 2500 S).

3. Results and discussion

3.1. Foaming rate

As seen in Fig. 1, it was possible to incorporate mPCM in HPU without destroying them due to low shear forces using a blade stirrer with a low rotation rate. With this method it was possible to incorporate mPCM up to a loading of 25%.
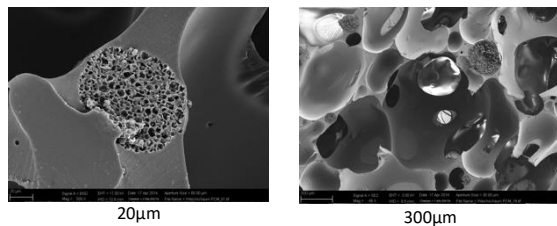
Fig. 1. SEM images of incorporated PCM in PU foam.

However, the foaming behaviour is decreased based on the thermal storage behaviour of the mPCM, which escapes the system energy. The HPU foams with incorporated mPCM exhibits higher densities. The foaming behaviour remains similar to untreated HPU foam, as shown in Fig. 2 for the pure HPU foam, PU foam with melamine and up to 5 wt% of mPCM incorporation. Nevertheless the starting and rise time is shifted to higher values and the final height decreases. In addition, it takes much longer to reach the so called sticky free time (foam is not sticky any more). The standard foam needs approximately 5 min, the foam with 5 wt% mPCM incorporation roughly 20 min.
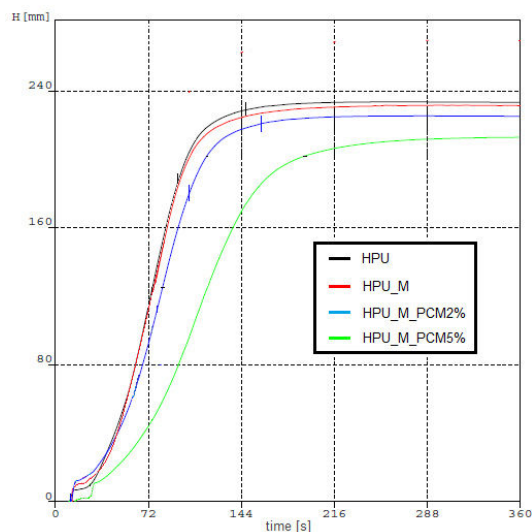
Fig. 2. Steep slope performance of HPU foam with and without flame retardant (melamine) and mPCM.

3.2. Flame retardance

The chosen HPU foam already exhibits good flame retardant properties (Fig. 3a), what can be seen from the fact that the HPU foam without incorporated additives hardly burns down, but mainly is charred. In a first step, possible flame retardants were evaluated for the HPU foam to evaluate possible interactions, for example on the foaming behaviour and, in addition, to further increase the flame retardancy. Fig. 3 shows that

expandable graphite and melamine can be used in the chosen HPU foam formulation to reach high flame retardancy without additional additives since the HPU foam only charred. By using ammonium polyphosphate (APP) the HPU foam burns down completely (Figure 3.d). Based on these results, further measurements were carried out only with melamine and expandable graphite (EG).
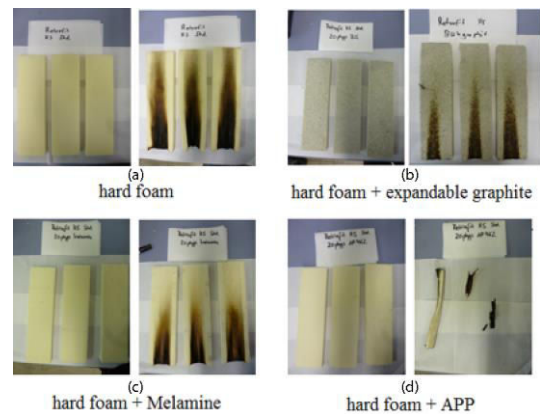

Fig. 3. Flame retardant testing of HPU foams with various incorporated flame retardants.

Besides testing of the pure HPU foam with incorporated flame retardants, also fire testing with incorporated mPCMs was carried out. It was found that the flame retardancy decreases significantly with increasing mPCM content. Even for very low (1-2 wt%) mPCM loading, the HPU foam burns down completely. This was expected, since the paraffin of the mPCMs can act like candle wax.

In order to achieve reasonable flame retardant values with incorporated mPCM, further tests were carried out with the HPU foams with mPCMs. It was found that the HPU foam passed the F2 test by incorporation of up to 5 wt % of mPCM content using 20 hpp melamine or respectively 20 hpp EG. Based on these results, all further measurements were carried out with HPU foams with mPCM content not exceeding 5%.

3.3. Heat capacity

DSC analyses of HPU foam specimens resulted in well-performed endothermic enthalpy changes during heating and cooling in between 10ºC and 50ºC at the rate of 1ºC/min. The measurements were made using three samples for each treatment composition. Fig. 4 shows the specific heat capacity versus temperature for the pure mPCM microencapsulated. It can be seen that the peak melting point of the mPCM is about 26ºC,

which is the value given by the manufacturer's data sheet.

Table 2 summarizes the results of specific heat capacity versus temperature for the HPU foams specimens containing different amount of mPCM and the ΔH (J/g) values for melting and solidification curves.
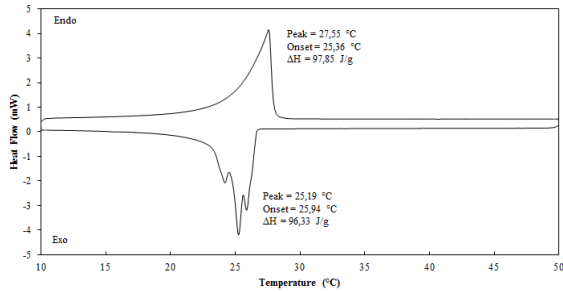

Fig. 4. DSC curve of pure mPCM (Micronal®DS 5001X).

The main conclusions from the results presented in Fig. 4 and Table 2 are:

- The composite foam HPU_M_PCM5% shows the highest latent heat storage capacity (4.29 to 4.86 J/g);
- Comparing the improvements of the latent heat capacity according the PCM additions, the samples with flame retardants increases significantly the latent heat improvement (between 1.77 and 3.07 J/g in comparison with the simple HPU_PCM samples that have between 0.43 and 0.47 J/g);
- The latent heat capacity for the melting and solidification process presents similar behaviour however slightly values differences. This is due to the DSC temperature rate (1°C/min) that should be smaller to minimize this effect/difference.

3.4. Thermal insulation

Fig. 5 shows the apparatus (Hot Disk Analyser, TPS 2500 S) used to measure the thermal conductivity by a transient plane heat source method (hot disk) suitable for testing homogeneous and isotropic materials. The measurements were carried out according to the ISO 22007-2:2008 test method procedure for the determination of thermal conductivity and thermal diffusivity.

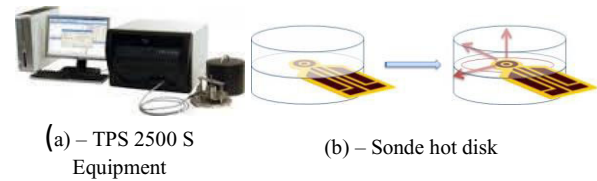(a) – TPS 2500 S Equipment   (b) – Sonde hot disk

Fig. 5. The apparatus used for thermal conductivity measurement by hot disk method.

The sensor/heater used in this test method consists of a thin nickel foil in a double spiral pattern, which is embedded in between two thin layers of Kapton polyimide protective films. This sensor/heater is sandwiched by two identical HPU foam composite sample disks with a diameter of 50 mm and a thickness of 10 mm (the samples may have other dimensions and shapes). During the measurement, electrical heat current passes through the nickel spiral and creates an increase in temperature. The heat generated dissipates through the sample on either side at a rate dependent on the thermal transport characteristics of the material.

Table 2. DSC results of HPU foams with different types of flame retardants and content of mPCMs.

| Samples	mPCM (wt%)	Melting			Solidification		
		Transition temperature $T_{t,m}$ (°C)	Melting temperature T_m (°C)	Melting latent heat ΔH_m (J/g)	Transition temperature $T_{t,s}$ (°C)	Solidification temperature T_s (°C)	Solidification latent heat ΔH_s (J/g)
HPU_PCM2%	2	22.45±0.10	24.45±0.02	2.05±0.26	23.14±0.01	22.68±0.04	1.45±0.09
HPU_PCM5%	5	22.60±0.21	24.46±0.01	2.52±0.32	23.09±0.01	22.66±0.08	1.88±0.46
HPU_M_PCM2%	2	22.95±0.57	24.12±0.48	1.80±0.06	24.98±0.65	22.67±0.12	1.22±0.21
HPU_M_PCM5%	5	22.92±0.28	24.53±0.04	4.86±0.22	23.06±0.01	22.69±0.01	4.29±0.89
HPU_EG_PCM2%	2	22.40±0.41	24.47±0.01	1.87±0.69	23.13±0.04	22.65±0.05	1.49±0.52
HPU_EG_PCM5%	5	23.08±0.37	24.54±0.08	3.85±0.66	23.04±0.05	22.69±0.04	3.26±0.69
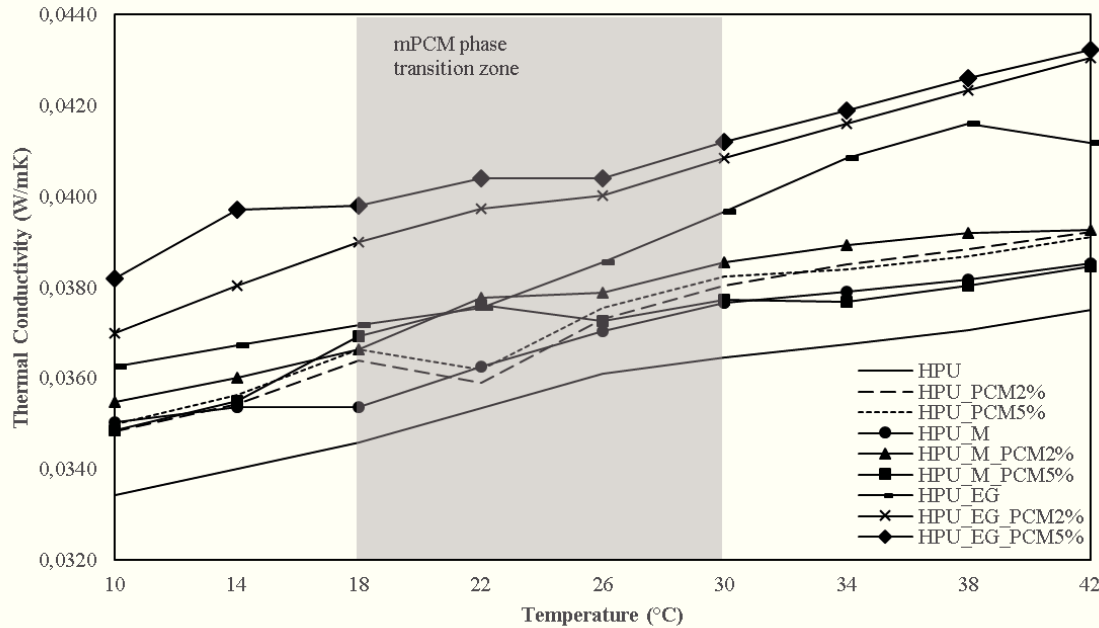
Fig. 6. Thermal conductivity versus temperature of HPU foams with different types of flame retardants and content of mPCMs.
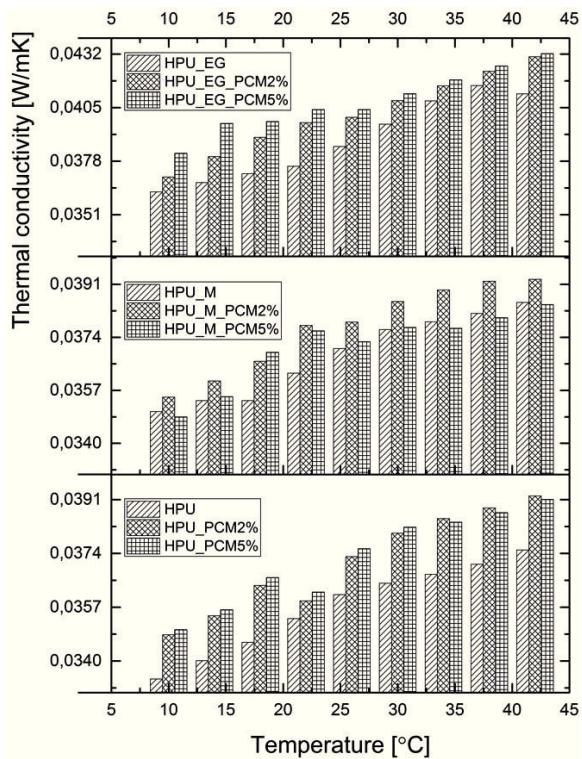

Fig. 7. Thermal conductivity increment per degree operating temperature raise of HPU foams with different types of flame retardants and content of mPCMs.

By recording the temperature versus time response in the sensor, these characteristics can accurately be calculated by a computational algorithm based on Hot Disk Thermal analyser software. The measurements were made using three samples (50x50x25mm) for each treatment composition. Fig. 6 and Fig. 7 summarizes the results for thermal conductivity versus temperature for the HPU foams specimens containing different amount of mPCM and the thermal conductivity (W/mK) values.

In the temperature range before and after phase transition of mPCM (18°C to 30°C), the thermal conductivity values are close to those expected.

The enhancement of the thermal conductivity increased with the increment of mass fraction of mPCMs in the HPU foam matrix. This enhancement is visible in the temperature range before and after phase transition of mPCM (18°C to 30°C) and in the HPU foam with or without flame retardants.

Comparing the HPU foams and the HPU foams with mPCM the thermal conductivity is higher and the addition of melamine and expanded graphite to the HPU foam influenced the thermal conductivity of the HPU foam with mPCM.

In addition, the results present slight differences of the thermal conductivity profiles shown in Fig. 7. To minimize this behaviour the sample size should be increased.

4. Conclusions

Based on the steep slope performance test, DSC analyses and thermal conductivity tests, the results reveal that the thermal characteristics of HPU foams are enhanced by the mPCM additions.

These results suggest that the addition of melamine and expanded graphite into HPU foams slightly influence the latent heat storage capacity. The addition of mPCMs into HPU foam increases the thermal conductivity and the introduction of flame retardants agents does not affect the phase transition intervals of the DSC curves.

In conclusion, the preliminary results of the PU foams shows their potentially for the indoor thermal regulation, e.g. an application for building external envelopes, particularly for hot climate regions associated to the range of melting and solidification temperatures of the testing mPCM. In addition, the samples with the melamine and expanded graphite improve the flame retardancy in case of fire.

Optimization of the content of mPCMs into the PU composite foams needs further research, including other issues such as the mechanical strength and the thermal transmittance measurements using the hot box method.

Acknowledgements

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