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3D printable thermoplastic polyurethane blends with thermal energy storage/release capabilities

elongation at break.



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ARTICLE INFO	A B S T R A C T
Keywords:	The aim of this work was to develope novel 3D printable thermoplastic polyurethane (TPU) blends with thermal
Thermoplastic polyurethane (TPU)	energy storage (TES) capabilities. The target are potential applications for winter sport equipment. Different
Phase change materials	amounts of an encapsulated paraffin were added to a TPU matrix, and the resulting blends were then used to produce 3D printed samples. FESEM observation evidenced a homogeneous distribution of the capsules in the polymer matrix and a good adhesion between the layers in the 3D printed parts. DSC tests indicated that an
Thermal energy storage	
3D printing	
Fused deposition modeling	

1. Introduction

Thermal energy storage (TES) refers to different types of technologies focused on the possibility to store thermal energy in excess and release it when needed. TES techniques are in fact able to balance peak energy demands, thus reducing the energy consumption and the pollution, increasing at the same time the efficiency of thermal energy management [1]. TES systems can be classified according to three main mechanisms: i) sensible heat storage, based on heating or cooling a liquid or solid storage medium; ii) latent heat storage, based on the possibility to store and release thermal energy by accumulating and releasing latent heat developed during a phase change (phase change materials (PCMs)); and iii) thermo-chemical heat storage, based on the storage and the release of thermal energy through chemical reactions [2]. The most important parameters for a TES system are its heat evolution capacity, the thermal power developed, the heat storage period, the temperature range and its cost [3].

In the last 40 years, different classes of materials including hydrated salts, paraffin waxes, fatty acids, the eutectics of organic and non-organic compounds and polymers have been considered as potential TES. It is possible to classify PCMs on the basis of the different phase transition modes, i.e. gas-liquid, solid-gas, solid-liquid and solid-solid. The applications of solid-gas and liquid-gas phase transitions are limited because of the large volume change during these phase transition [2]. Solid-liquid transitions are perhaps the mostly used. Paraffins are PCMs produced from petroleum cuts, they have good chemical and thermal stability, together with low vapor pressure [4]. These organic compounds can also store a c amount of latent heat, that is readily available with a limited super-cooling and with good reliability (i.e. they can have stable thermal properties for 1000-2000 cycles). A technical limitation of paraffins as PCMs is represented by their limited thermal conductivity, that is around $0.2 \text{ Wm}^{-1} \text{ K}^{-1}$ [5]. Another problem of this solid-liquid phase change materials is the leakage when the paraffin is in the molten state [6]. The commonly adopted solutions to limit this problem are i) micro-/nano-encapsulations, i.e. the encapsulation of the PCM inside a polymeric or inorganic shell [7]; ii) shape-stabilization, that involves the addition of a supporting material able to stabilize the shape of the organic PCM (i.e. carbon nanotubes [8], nanosilica [9], sugar [10]); and iii) intercalation methods, consisting in the PCMs stabilization through intercalation in layered structure such as lamellar silicates, phosphate, layered double hydroxide and graphite. In microand nano-encapsulation technology, the shell is a container for the phase change material in both solid and molten states and, depending from the production method, can have different shapes. Several techniques are nowadays available for the encapsulation [10].

effective energy storage/release capability was obtained in the 3D printed parts, with melting enthalpy values up to 70 J/g. The hard shells of the microcapsules, made of melamine formaldehyde resin, induced an increase of the stiffness, of the creep stability and of the Shore A hardness of the material, accompanied by a decrease of the

In sport applications, PCM are mainly used in the textile industries to provide thermal comfort to the athletes. The aim of PCM is to help human thermoregulation, that is an important issue in competitions characterized by extremely hot or cold temperature conditions [7]. Typical situations in which warming is required are winter sports like skiing, skating, bobsledding and so on. PCM can be also incorporated in clothes for winter sport applications in order to release heat when the

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Fig. 1. SEM micrographs of 3D printed samples. (a) TPU, (b) TPU_30M6D, (c) TPU_40M6D and (d) TPU_50M6D.



Fig. 2. Melt Flow Index of neat TPU and relative blends.

external temperature decreases [11,12]. On the other hand, cooling could be necessary in summer sports, such as marathons or bike races. PCMs can be also useful in firefighter turnout coats with the aim of absorbing as much heat as possible to protect the human body from excessive temperatures [13]. Many factors influence the effectiveness of PCM incorporation in warming and cooling effect: the total heat developed/release, that is proportional to the amount of PCM embedded in the matrix, the area on the human body covered by PCM, and the

part of the body covered by PCM [14]. Various explorative research activities have been performed in this field. For instance, Borreguero et al. prepared nonwoven fabric, foams and leather doped with PCM microcapsules [15]. A stable and reproducible bi-component melt spinning process on an industrial scale incorporating PCM into textile fibres has been successfully developed by Cherif at al. [16].

Thermoplastic polyurethane (TPU) presents a low stiffness and high strain at failure [13]. TPU closes the gap between rubber and hard thermoplastics, it has properties of thermoplastics and so it can be deformed plastically under the influence of heat, showing very high elasticity and good adhesion without sticking as rubbers. If compared with common cross-linked elastomers that have strong chemical bond in between different polymer chains, thermoplastic elastomers have weak secondary chemical bonds like hydrogen bonds that give to them the possibility to be re-melted [11,17]. The relative concentration of hard and soft segments within the main chains determines the mechanical properties of TPU [18].

In additive manufacturing (AM) a 3D virtual model is directly transformed into a physical prototype by slicing the model into a determined number of cross-sections that will be the layers of the physical object. AM, in general, describes a group of technologies able to build three dimensional objects by adding layer by layer a material such as polymers, metals and ceramics, but also food [19], bone tissue [18] or nanocomposites [20–22] are under investigation. By a social point of view there is an increasing interest for the open source availability of AM concepts, the "Maker Movement" [23]. This movement envisage a new industrial revolution based on digitalization, online share of material and democratization. The thermoplastic behavior of TPU gives



Fig. 3. DSC thermograms of 3D printed samples at different M6D concentrations. (a) Heating stage and (b) cooling stage.

the possibility to this material to be processed by additive manufacturing, and TPU is thus one of the few materials for AM technologies that can combine an excellent tear and wear resistance together with high impact strength and considerable flexibility [24]. TPU is mainly applied in AM technology for fused filament fabrication (FFF) manufacturing processes. FFF or fused deposition modeling (FDM) or simply 3D printing (3DP) represents one of the most widespread AM technologies. Therefore, TPU could offer unique capabilities to make tailorable, flexible cellular structures and so can be used to produce specific energy absorbing parts. The energy absorbing efficiency is defined as the ratio between cumulative absorbed energy up to a given stress divided by the stress and it is a value in between 0 and 1. With 3D printed TPU it is possible to obtain a maximum energy absorbing efficiency of 0.36, that is comparable to that of closed cell polyurethane foams [25]. This leads to the possibility of using this 3D printed material for tailor-made cellular architectures that are not constrained like those made from traditional manufacturing. Even if TPU is a very versatile material that can be used for fashion design, for insole and shoes design [26], there are some technical drawbacks to apply TPU in 3D printing. The main disadvantage is the flexibility of the filament and so the difficulty to transmit through the filament the pressure needed for the extrusion in the nozzle. However, it is possible to find various solutions to this problem that include an optmization of the printing temperature and the envelop of the TPU filament into polyethylene tubes [27]. In a

previous paper of our group [28], flexible systems for the thermal energy storage were obtained by encapsulating a paraffin with a melting point of 6 °C in a thermoplastic polyurethane, and the resulting blends were then microstructurally and thermo-mechanically characterized. In that work, high melting enthalpy values (up to 95 J/g) were reached for polymer blends with elevated capsules contents (60 wt%), and their energy storage release/capability was preserved even after several (at least 50) repeated thermal cycles [29].

On the basis of these considerations, the objective of the present work is the production of extruded filaments made of TPU containing paraffin microcapsules at different concentration, to be used as feedstock for a commercial FDM machine. 3D-printed samples were then characterized to investigate their mechanical, rheological and thermal properties and to understand how the different processing parameters affected the 3D printed process. The final goal of this project is the development of 3D printed materials with thermal energy storage/release capabilities based on TPU/paraffin blends, to be applied in sport applications.

2. Experimental part

2.1. Materials

Desmopan[®] 6064A thermoplastic polyurethane (density 1.09 g/cm³, melting temperature 200 °C) was kindly provided by Covestro Srl (Milano, Italy). This injection molding grade of TPU finds application in many different areas, such as automotive interior and shoe soles due to the excellent mechanical properties and microbial resistance, low abrasion and absence of plasticizers. Microtek MPCM6D microencapsulated paraffin (named M6D in this work), provided by Microtek Laboratories Inc. (Dayton, OH, USA) was used as phase change material. In this PCM a paraffin wax characterized by a melting temperature (T_m) of 6 °C and a crystallization temperature (T_c) of about -10 °C is encapsulated in a stable melamine formaldehyde shell. The resulting particles have a mean diameter of 17–20 µm, a density of 0.9 g/cm³, and are constituted by 85–90 wt% of paraffin. Their melting enthalpy according to the datasheet is 157–167 J/g.

2.2. Samples preparation

2.2.1. Compression molded samples preparation

Compression molded samples were prepared to compare the thermal and mechanical properties of the resulting materials with those of the 3D printed samples. A Thermo Haake Rheomix^{*} 600 was used to compound TPU granules and M6D powder in different proportions. The materials were mixed at 200 °C with a rotating speed of 60 rpm for 5 min. The obtained compounds were compression molded in a Carver hot plate press at 180 °C for 15 min, applying a pressure of 1 MPa. Neat TPU and TPU/PCM blends at different concentrations (from 30 to 60 wt %) were thus obtained.

2.2.2. Filament extrusion

TPU granules were finely grinded and mixed with the microcapsules using a mechanical stirrer to avoid any leakage of paraffin from the capsules. The obtained powder was then extruded by using a Estru^{*} 13 single screw extruder, provided by Friul Filiere SpA (Udine, Italy). This extruder was characterized by a screw diameter of 14 mm and an extrusion head of 3.0 mm. The screw rotation speed was set at 30 rpm and the temperature profile was varied from 105 °C in the feeding section to 180 °C in the die zone. Temperature profile in the extruder was selected to optimize the surface quality and to avoid porosity inside the filaments. Filaments with a constant diameter of about 1.75 mm were thus obtained.

2.2.3. 3D printed samples preparation

The 3D printed specimens were prepared starting from the extruded



Fig. 4. Comparison between DSC results of the prepared blends as a function of the composition and of the adopted processing technique. (a) Heat of fusion, (b) normalized heat of fusion, (c) heat of crystallization and (d) normalized heat of crystallization.

filaments by using a Sharebot Next Generation desktop 3D printer. A 3D model of ISO 527 1BA specimen was built by using SolidWorks^{*} software, it was then exported in a .STL format, processed by Slicer^{*} and finally exported in a GCODE format. A rectangular infill with a density of 100% was selected, while the infill angle was set in configuration 0°/0°, to maximize the density and the mechanical properties of the resulting samples. Considering that increasing the percentage of microcapsules inside the TPU matrix made the printing stage more difficult, a feeding configuration with a 0° angle resulted the best choice for the preparation of the printed materials. After several trials the following optimized parameters were set for the 3D printing process: layer height 0.20 mm, nozzle temperature 240 °C, bed temperature 40 °C, deposition rate 40 mm/s.

The neat matrix was denoted as TPU, while the blends were named indicating the matrix and the weight percentage of PCM. For instance, TPU_30M6D denotes a polymer blend with 30 wt% of microcapsules.

2.3. Experimental techniques

Microstructural observations of the cryo-fractured surfaces of the 3D printed specimens were carried out to understand the quality of the printing process and the interaction between microcapsules and the TPU matrix. A Zeiss Supra 40 high resolution field emission scanning electron microscope (FESEM) with an accelerating voltage of 2.5 kV was used. Samples were observed after the deposition of a thin platinum palladium conductive coating on their surface.

Melt flow index (MFI) values were determined according to ASTM 1238-04 standard for all the compositions. A Kayeness Co. 4003DE

capillary rheometer was used, and the tests were carried out at a temperature of 180 $^\circ C$ with a load of 2.16 kg.

Differential scanning calorimetry (DSC) measurements were performed by a Mettler Toledo DSC30 calorimeter. Samples of about 10 mg were analyzed under a nitrogen flow of 150 ml/min, applying a first heating run from -100 to 220 °C, followed by a cooling run from 220 °C to -100 °C and by a second heating run until 220 °C. All runs were performed at 10 $^{\circ}$ C/min. The glass transition temperature (T_a) was evaluated as the inflection point of DSC thermographs. The melting (T_m) and the crystallization (T_c) temperatures were determined in correspondence of the endothermic and exothermic peaks, respectively. The enthalpy values were evaluated as the integral of their corresponding peaks: area under exothermic peak to estimate enthalpy of crystallization (ΔH_c) and area under endothermic peak to estimate enthalpy of melting (AHm). Normalized melting and crystallization enthalpy values were obtained dividing the ΔH_m and ΔH_c values for the melting/crystallization enthalpy of the M6D capsules, taking into account the effective microcapsule content in the composites.

Dynamical mechanical thermal analysis (DMTA) measurements were performed by using a DMTA Q800 device (TA Instruments, New Castle, USA) under tensile configuration. Samples cut from the central part of dog bone specimen were tested in a temperature range between -60 °C and 100 °C at a heating rate of 3 °C/min and a frequency of 1 Hz, to determine the temperature dependency of the storage modulus (E'), loss modulus (E'') and loss tangent (tan δ).

The mechanical behavior of the obtained materials was investigated through quasi-static tensile tests at room temperature. These tests were carried out according to ASTM D638-14 standard with an Instron 5969



Fig. 5. Results of DMTA tests on 3D printed samples. (a) Storage modulus, (b) loss modulus and (c) loss tangent.

universal tensile testing machine, equipped with a load cell of 50 kN. A long-travel extensometer (Instron mod. 2603-080/656) was used to monitor the deformation during the tensile tests. At least five specimens were tested for each sample, in order to determine the chord modulus at a deformation of 10%, the stress and the strain at break. All the samples were tested with a crosshead speed of 100 mm/min.

The viscoelastic properties of the prepared materials were investigated also by examining the creep behavior of the material. Creep tests were carried out by a DMA Q800 analyzer, supplied by TA Instrument (TA Instruments, New Castle, USA). The tests were performed for a total duration of 3600 s at a temperature of 30 °C and under a constant stress of 0.25 MPa. The creep compliance D(t), calculated as the ratio between the time dependent deformation $\varepsilon(t)$ and the applied stress, was thus evaluated.

Shore A hardness tests were performed according to the ASTM D2240 standard by a Hildebrand D-72644 durometer. The hardness values were collected after 1 s from the beginning of the test, to avoid any relaxation phenomenon.

3. Results and discussions

3.1. Microstructure and rheology

Morphological features of the cryo-fractured sections of 3D printed samples of neat TPU and of the relative blends at different microcapsule contents were investigated by FESEM, and the most representative micrographs are reported in Fig. 1(a–d).

No welding lines are visible between extruded filaments in the neat TPU sample (Fig. 1a), meaning that a good adhesion between different layers was achieved. As often observed for 3D printed objects, a triangular porosity is present in correspondence of the edges of the filaments, and it is possible that this feature could negatively affect the mechanical properties of the resulting materials. Considering FESEM micrographs of the blends prepared at different M6D concentrations (see Fig. 1(b–d)), it is possible to notice the presence of capsules with dimensions ranging from 1 to $20 \,\mu\text{m}$, with a rather good adhesion with the surrounding TPU matrix. No microcapsules agglomerates can be detected, and the uniform distribution of M6D allows to retain the morphological continuity of the matrix even at elevated M6D concentrations. This feature is important both for the mechanical behavior and for the thermal diffusivity of the resulting blends.

MFI determinations were performed in order to evaluate how the presence of various amounts of microcapsules affects the processability of the materials. The results of these tests are summarized in Fig. 2. MFI increases with the microcapsules content, this means that the material becoms less viscous and its flowability is thus enhanced upon M6D addition. It is important to remind that the stiffness of microcapsules strongly decreases when the temperature is above the melting temperature of the paraffin, with an evident influence on their rheological behavior [30]. It can be therefore concluded that the processability of the prepared materials is retained upon microcapsules addition since the viscosity in the molten state is reduced upon microcapsules addition.

3.2. TES behaviour

The thermal energy storage/release capability of the prepared blends is a key feature for their intended applications. Therefore, DSC was performed on the prepared materials in form of compression molded samples, filaments and 3D printed samples, in order to assess if the thermal efficiency of the microcapsules could be preserved in the 3D printed samples after two subsequent extrusion processes. In



Fig. 6. (a) Representative stress-strain curves of quasi-static tensile tests of 3D printed samples. Comparison between the tensile properties of compression molded and 3D printed samples. (a) Chord modulus, (b) stress at break and (c) strain at break.

Fig. 3(a,b) representative DSC thermograms of the 3D printed samples of neat TPU and of the relative blends during the heating and the cooling stage are respectively reported.

It is possible to note that neat TPU presents a rather flat signal with no crystallization or melting peaks in the temperature range from -100to 220 °C, and an inflection point corresponding to the glass transition temperature (T_g) is detectable at -48 °C. Regarding the M6D blends, an evident endothermic/exothermic peak, due to the absorption/release of latent heat when the core material of the microcapsules undergoes a phase change transformation from solid to liquid (and viceversa), can be detected. The melting peak (T_m) is located at 5 °C in the heating stage, while the crystallization temperature (T_c) is set at -9 °C in the cooling run. It is also evident that the intensity of these peaks is proportional to the M6D concentration, while their position is not affected by the microcapsules concentration. In Fig. 4a and b the values of the heat of fusion and crystallization of the blends prepared with the different techniques are respectively reported, while in Fig. 4c and d the normalized melting/crystallization enthalpy values, evaluated taking into account the relative M6D weight concentration, are reported.

It is important to notice that no substantial variations between the melting enthalpy values of compression molded and filament samples can be detected, while a slight decrease can be detected in 3D printed materials at elevated M6D amount (higher than 50%). This is mainly due to the fact that during the 3D printing process the material is forced to sustain a high draw ratio (passing from a diameter of 1.75 mm down to 0.35 mm) at elevated temperature (240 °C). In these conditions, part of the microcapsules inside the matrix were probably damaged, with a consequent paraffin leakage within the matrix. However, the thermal efficiency of the prepared blends is rather good, being the relative values of crystallization and melting enthalpy higher than 70% for all the

tested compositions.

3.3. Mechanical behaviour

Viscoelastic properties are very important for several applications and the evaluation of the role of microcapsule addition on the dynamic behaviour of the resulting materials could be thus very interesting from a technical point of view. In Fig. 5(a-c) the trends of the dynamic moduli (E', E'') and of the loss tangent (tan δ) as a function of the temperature for the 3D printed samples are reported.

Storage and loss modulus are not strongly influenced by the M6D addition, and only a slight E' increase over the whole testing temperature interval can be detected at elevated M6D concentrations (see Fig. 5a,b). Moreover, the increase of microcapsules content has a marginal effect on the TPU glass transition temperature (Tg), and only a slight shift towards higher temperatures can be detected in tan δ trends (see Fig. 5c). According to the indications of the producer, the T_{a} identified at about -32 °C as the tan δ peak corresponds to the glass transition of PU soft segments within the macromolecular structure. It is clear that the intensity of this $tan\delta$ peak decreases with the M6D content. Interestingly, the incorporation of microcapsules inside the TPU matrix results in a shoulder in tan8 curves located at about 10-15 °C, with a magnitude that increases with the M6D content. Comparing these results with those of DSC tests, it is possible to conclude that this signal can be attributed to the phase transition of the paraffin wax that constitutes the core of the microcapsules. It is thus clear that the viscoelastic response of the material near ambient temperature could be strongly influenced by the melting of the paraffin inside the capsules.

The effect of the microcapsules addition on the tensile properties of the 3D printed samples is represented in Fig. 6(a-d). Representative



Fig. 7. Creep compliance curves of (a) compression molded and (b) 3D printed samples (T = 30 °C, $\sigma_0 = 0.25$ MPa).



Fig. 8. Shore A hardness values of (a) compression molded and (b) 3D printed samples.

stress-strain curves are reported in Fig. 6a, while a comparison between the tensile properties of compression molded and 3D printed materials as a function of the M6D concentration is shown in Fig. 6(b–d).

Stress-strain curves clearly put in evidence how M6D addition

promotes a strong stiffening of the materials, accompanied by an evident embrittlement of the samples. Considering the shape of the curves of the blends at different concentrations, it can be hypothesized that the failure of the material is probably due to the interfacial debonding between the TPU matrix and the polymeric shell of the microcapsules. Further microstructural analyses will be performed to have a better comprehension of the failure mechanisms in these materials. The elastic modulus increases with the M6D content (Fig. 6b), and this stiffening effect is probably due to the higher elastic modulus of the melamine formaldehyde shell of the capsules with respect to that of the TPU matrix. This result is in accordance with the slight E' increase detected in DMTA analysis (see Fig. 5a). As said before, this stiffening of the material is accompanied by a clear embrittlement, as shown in Fig. 6(c,d), for both compression molded and 3D printed samples. Stress and strain at break are negatively affected by M6D addition, especially at elevated microcapsules concentration. The lack of adhesion between the M6D capsules and the matrix during the straining process and the consequent discontinuity of the TPU matrix promotes the creation of points with high stress concentration and the nucleation of microcracks that can cause the premature failure of the material. It is also important to underline how the tensile properties of the 3D printed samples are systematically lower than those of the corresponding compression molded samples. However, considering standard deviation values, it can be concluded that the 3D printing process does not lead to a heavy deterioration of the mechanical properties of the materials. This means that the printing quality of the samples was rather good even at elevated M6D amounts. The relatively low void content evidenced in FESEM micrographs (see Fig. 1) could confirm this conclusion.

Creep analysis was carried out to understand what is the viscoelastic response of the material under a constant load. The creep curves of compression molded and 3D printed samples are respectively shown in Fig. 7a and b. It is interesting to note how no tertiary creep can be detected, in fact at the selected testing conditions all the samples reach the secondary creep plateau without reaching the failure point. For the CM and 3D samples there is a clear correlation between creep resistance and microcapsules concentration. In particular, by increasing the M6D content the creep compliance decreases, and this result is in agreement with the conclusions reported for quasi-static tensile tests.

The Shore A test was useful to determine the hardness of the prepared elastomeric materials. As it is possible to see from Fig. 8, there is a linear increase of the hardness, both for compression molded and 3D samples, by increasing the content of microcapsules. Also this result reflects the stiffening behavior found in DMA and quasi-static tensile test. As it could be expected, the 3D samples are softer in comparison to the corresponding compression molded materials, because of the presence of voids between extruded filaments (see FESEM micrographs in Fig. 1).

4. Conclusions

Innovative TPU with encapsulated PCM blends were developed and applied to FDM technology. In this way, dumbbell specimens were printed and thermo-mechanically characterized. A homogeneous distribution of the microcapsules inside the matrix and a good adhesion between the deposited layers in 3D printed materials were confirmed by FESEM analysis. 3D-printed samples showed melting enthalpy values up to 70 J/g for a M6D microcapsule content of 50 wt%. The glass transition temperature of the TPU was not affected by microcapsules addition.

An increase of the stiffness of the resulting materials due to the relatively high rigidity of the microcapsules shell was accompanied by an embrittlement of the samples. Moreover, both creep resistance and Shore A hardness of the samples were significantly improved upon M6D introduction. It was therefore proven the technical possibility to prepare 3D-printable TPU based filaments with thermal energy storage/ release capabilities and good dimensional stability.

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