Elastocaloric properties of thermoplastic polyurethane

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11 Abstract

12 Very few studies have explored the elastocaloric effect of elastomers other than natural rubber
13 (NR). The aim of the present article is thus to evalute the elastocaloric properties of a
14 thermoplastic polyurethane (TPU) in terms of microstructural characteristics and thermoelastic
15 coupling. Calorimetric measurements showed two successive peaks at 240 K and 282 K,
16 attributed to respectively the crystallization and melting of soft segments. X-ray diffraction
17 indicated that TPU exhibited a fully reversible strain-induced crystallization (SIC) at room
18 temperature. Thermomechanical experiments performed at different elongations revealed a
19 minimum adiabatic temperature variation of about -8 K after retraction of a sample initially
20 elongated at $\lambda=5$. This is comparable to NR performances. However, for cycles carried out
21 between $\lambda=1$ and $\lambda=5$, tensile stress/elongation curves showed a non-elastic behavior of TPU.
22 A pseudo-elastic response was obtained for cyclic elongation when unloading was incomplete,
23 in our case when λ was between 3 and 5. The recorded peak-to-peak temperature variation
24 decreased from 4.5 K to 3.3 K when the number of cycles was increased to 5000. Despite that
25 the issue of fatigue resistance for TPU needs to be adressed, this work opens new perspectives
26 for studying the elastocaloric properties of various polyurethanes (whether crosslinked or
27 thermoplastic) as well as other materials with a tendency for strain-induced crystallization, such
28 as polychloroprene, hydrogenated acrylonitrile butadiene rubber and others.

29

32 The development of caloric materials is an active research area dedicated to replacing coolants

33 used in cooling systems.[1,2] Basically, caloric materials can become structurally

34 ordered/disordered upon the application/removal of an electric or magnetic field or a

35 mechanical stress.[1,3–5] The resulting order/disorder transitions are responsible of entropy

36 variations. When these transitions are faster than the time needed for the material to exchange

37 heat with its surroundings, there occurs a positive or negative temperature variation of the

38 material.[1] Among elastocaloric materials, elastomers are of interest due to their elastocaloric

39 effect being triggered by small stress values (a few MPa) and the associated significant

40 temperature variations which can reach 14 K.[6–9] In addition, they are cheap materials. For these

41 reasons, the use of elastomers in solid-state cooling systems is gaining widespread interest in

42 several scientific communities,[9,10] and strongly motivates studying the elastocaloric effect of

43 various elastomers.

44 The elastocaloric effect is mainly attributed to two contributions:[6–8,11,12] the first is a reversible

45 orientation/disorientation of macromolecules in the strain direction (entropic elasticity),[11]

46 which can be observed in all amorphous elastomers. The second contribution is strain-induced

47 crystallization (SIC) that corresponds to a partial crystallization of the elastomer as a result of

48 the deformation.

49 Depending on the initial structure of the elastomer (crosslink density, crosslink distribution…)

50 and the mechanical stress program that is applied, the elastocaloric effect can be either

51 reversible or irreversible. For instance, the stretching of natural rubber (NR) with a low

52 crosslink density can lead to the formation of crystals that are stable at room temperature

53 whereas with an intermediate crosslink density, the formed crystals are unstable and melt when

54 the stress is released.[13–16] The elastocaloric effect of NR has been well documented and it has

55 been revealed that the dominant caloric effect is the reversible SIC.[6,7] However, although SIC

56 is observed in other elastomers such as polyurethane, hydrogenated acrylonitrile butadiene

57 rubber (HNBR) and polychloroprene[17–24], the elastocaloric effect of these materials has yet to

58 be investigated.

59 The motivation for the work presented here is to display an elastocaloric effect in thermoplastic

60 elastomers (TPE). These heteropolymers are made of hard segments (HS) (with a melting

61 temperature T_m or a glass transition temperature T_g above room temperature T_{room}) and soft

62 segments (SS) that are in the rubbery state at T_{room}.[25] These HS and SS are covalently bonded,

63 but their partial or total immiscibility is responsible for a phase-separated structure made of HS-

64 and SS-rich domains. The HS-rich domains play the role of physical crosslinks at T_{room}

permitting the elastomeric behavior of SS in TPE, while above T_m, the TPE can be melt processed due to the melting of the HS-rich domains. This melt processability can be advantageous for making complex hermetic systems at lab scale for testing elastocaloric devices such as regenerative systems incorporating a fluid.[10]

Previous investigations have brought to light the strain-induced crystallization (SIC) of crosslinked and thermoplastic polyurethanes (TPU) using calorimetry and X-ray diffraction (XRD).[20–24] The main objective of this work is to evidence the reversible SIC of the TPU chosen for this study by the aforementioned techniques and the second aim is to study the elastocaloric effect of TPU by stretching the samples rapidly at $1600\%.s^{-1}$ and measuring the temperature variation. The final goal is to explore the cyclic elastocaloric behavior of TPU over 5000 cycles.
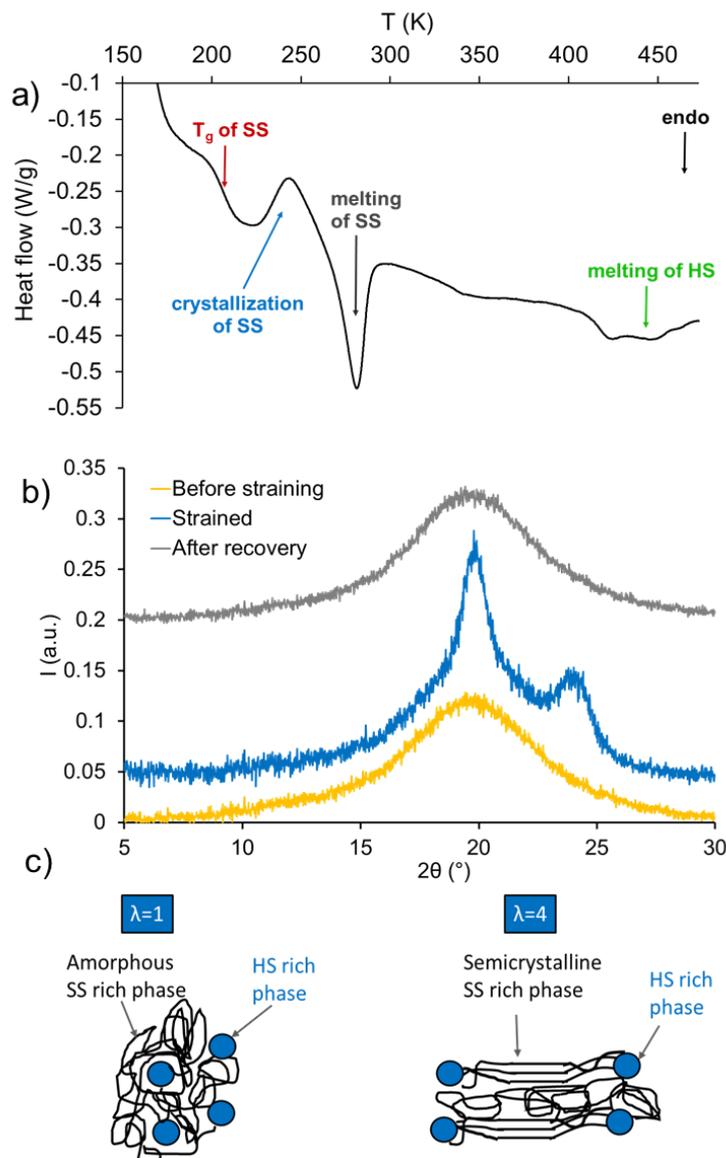
The investigated material is an aromatic polyether-based thermoplastic polyurethane Estane® X4977 NAT 039 grade from Lubrizol. TPU is composed of poly(tetramethylene-oxide) (PTMO) with a molecular weight of 2000 g/mol as soft segments (SS) and 4,4'-methylene-bis-(phenyl-isocyanate) (MDI) and 1,4-butanediol (BDO) as hard segments (HS). Due to phase separation, the HS formed highly polar and stiff microdomains embedded in a soft poorly polar matrix. [26] The same procedure as the one described by Jomaa et al. was used to prepare a TPU film by solvent casting.[26] In short, TPU granules were dissolved in dimethylformamide (DMF) at a ratio of 25wt%. After being heated up to 353 K for 4h, the solution was cast onto a glass plate with an Elcometer 3700 film applicator. The films were then dried at 333 K for 24h and annealed at 398 K for 3 hours. Their final thickness is about 200 µm.

X-ray diffraction measurements were carried out at room temperature with an XPert Pro MPD Panalytical diffractometer equipped with a graphite monochromator (CuKα1 radiation) and a X'Celerator detector. For the measurement under strain, the samples were manually stretched and fixed to the sample holder during their deformation. The calorimetric analysis was performed by Differential Scanning Calorimetry (Setaram, DSC 131 evo) under nitrogen atmosphere. The samples (about 20 mg) were placed in closed aluminum crucibles and cooled from ambient temperature down to 153 K, then heated to 488 K and finally cooled. The heating and cooling ramps were carried out at 10 K.min^{-1}.The elastocaloric coupling of TPU samples ($20*20*0.2$ mm^3) was investigated via a tensile test bench combined with an infrared camera similar to the one used by Yoshida et al.[27] The tensile test bench was composed of a single axis robot RSDG212 (MISUMI Corporation, Japan) with an analog force sensor XFTC300-200N (Measurement Specialties, France). The displacement was measured with a laser optical displacement sensor ILD1420-200 (micro-epsilon, France) and the corresponding elongation

98 $\lambda = \frac{l(t)}{l_o}$ was defined as the ratio between the length l at time t and the initial length l_0=20 mm.

99 In parallel, the material's surface temperature was measured using a thermal camera Optris

100 PI450 (Optris, Germany).

101 Figure 1(a) presents the thermogram of TPU after processing. The glass transition temperature

102 of the soft segments T_{gSS} is visible at 205 K. The peaks observed at 240 K and at 282 K (just

103 below room temperature) could be attributed to the partial crystallization and the melting of SS,

104 respectively.[26,28] The enthalpy of melting is about 17 kJ/kg. The double peaks at 424 K and 445

105 K could either correspond to the melting of the semicrystalline HS with two different chain

106 lengths, or be related to rearrangements within SS and HS followed by the fusion of crystalline

107 HS. [26] In summary, below the glass transition temperature of the soft segments (T_{gss}=205 K),

108 the material is mainly made up of amorphous SS-rich phases and semicrystalline HS-rich

109 phases, whereas above T_{gss}, the SS phase crystallizes partially around 240 K until reaching 273

110 K and melts just below room temperature (at around 282 K), thus reverting to the initial stucture

111 made of amorphous SS domains and semicrystalline HS-rich phases.

FIG. 1. (a) DSC thermogram of TPU. (b) X-ray diffractograms of TPU before, during and after straining at λ=4. (c) Schematic of strain-induced crystallization of TPU
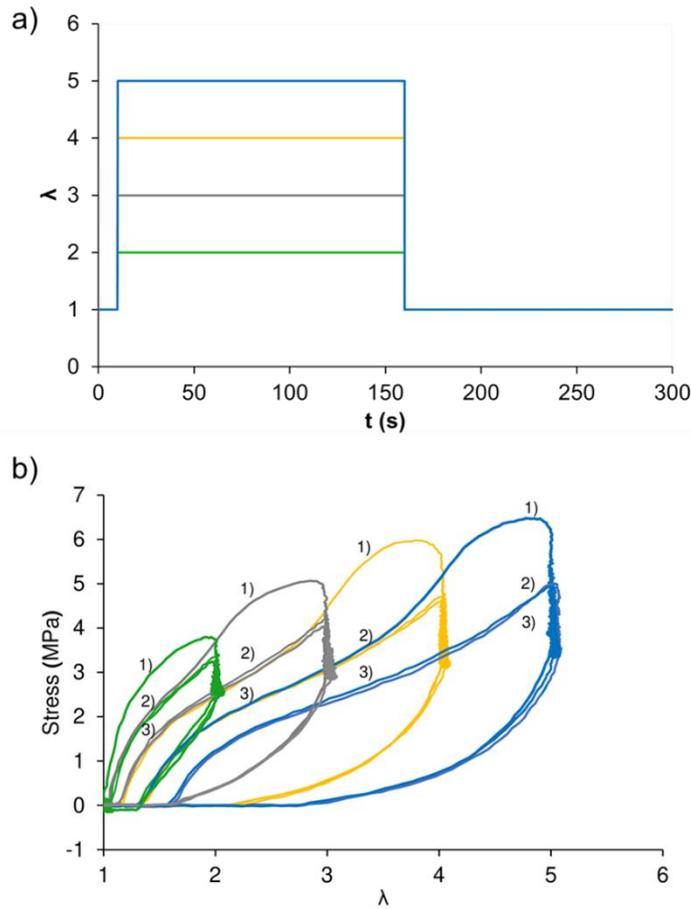
This experiment suggests that the soft segments, not subjected to any strain, are amorphous at room temperature. X-ray diffraction was performed on the TPU before, during and after stretching at λ=4 (Fig. 1(b)). Although the hard domains were not melted, an amorphous halo was observed at λ=1 for the unstretched sample. It was centered at $2\theta=20°$ and had a shoulder at $2\theta=12°$. When the material was stretched up to λ=4, two diffraction peaks appeared at $2\theta=19.8°$ and $2\theta=24.1°$. According to Ren et al, this is evidence of strain-induced crystallization (SIC) of the PTMO soft segments as depicted in Fig. 1(c).[23] These results are in good agreement with the X-ray diffraction pattern of pure PTMO.[29] Furthermore, when the stress was released, the X-ray pattern exhibited an amorphous halo once again thus demonstrating the reversibility of the SIC at room temperature.

It is worth mentioning that the presence of a melting peak at a temperature between 273 K and 283 K and the ability of the elastomer to crystallize under strain at room temperature has also been observed in other elastomers such as natural rubber (NR), hydrogenated acrylonitrile butadiene rubber (HNBR) or polychloroprene.[17–19,30,31] The presence of such a melting peak could be an indicator of a reversible SIC in the elastomers. In the case of SIC, the orientation of the macromolecules in the strain direction causes an entropy reduction of the macromolecules conformation which shifts the crystallization and melting temperatures towards a higher value.[15] However, after releasing the stress completely, the melting temperature drops, leading to the complete melting of the crystals.

The occurrence of SIC in TPU suggests a strong elastocaloric effect. In order to estimate the adiabatic temperature variation, TPU was strained adiabatically at different elongations from $\lambda=1$ to λ_f (Fig. 2(a)) according to the following:

The first step consisted in stretching the TPU at 320 mm.s^{-1} (1600%.s^{-1}), after which the material was maintained at constant elongation during 150 s. When thermal equilibrium was reached, the elongation was decreased back to $\lambda=1$ at 320 mm.s^{-1}, and kept there until reaching thermal equilibrium again.

TPU exhibited fatigue during the first cycles as evidenced in Fig. 2(b) which displays the stress/elongation curves of the first three mechanical cycles of TPU elongated to various final elongations, i.e., $\lambda_f = 2, 3, 4$ and 5.
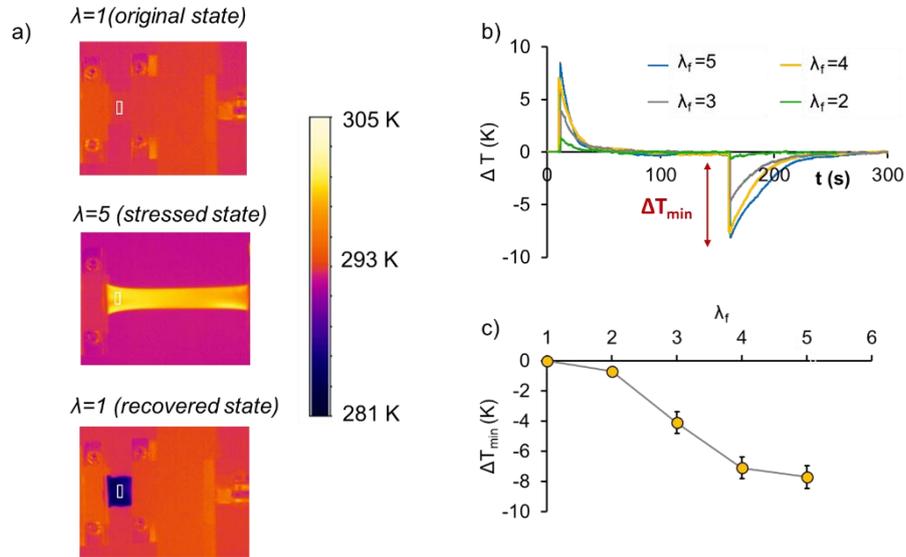
FIG. 2. Mechanical testing of TPU. (a) The mechanical stress program. (b) The evolution of the stress as a function of elongation (first 3 cycles).

For each mechanical test, the first cycle differs from the second and third cycles in that it presents a higher stress but the same remanent elongation. This is probably due to the structural modification of the HS structure.[32] Indeed, it can be noted that the mechanical response exhibits both elastic and inelastic parts and when the elongation increases, so does the inelastic part. The third cycle is similar to the second, suggesting that the mechanical behavior becomes stabilized. The maximum stress of the third cycle ranges from 3 MPa to 5 MPa, for a maximum elongation varying between 2 and 5.

155 Moreover, during the third mechanical cycle, the temperature of the sample surface was

156 measured with an IR camera in the white rectangle represented in Fig. 3(a). The resulting

157 temperature variation ΔT as a function of time is reported in Fig. 3(b).
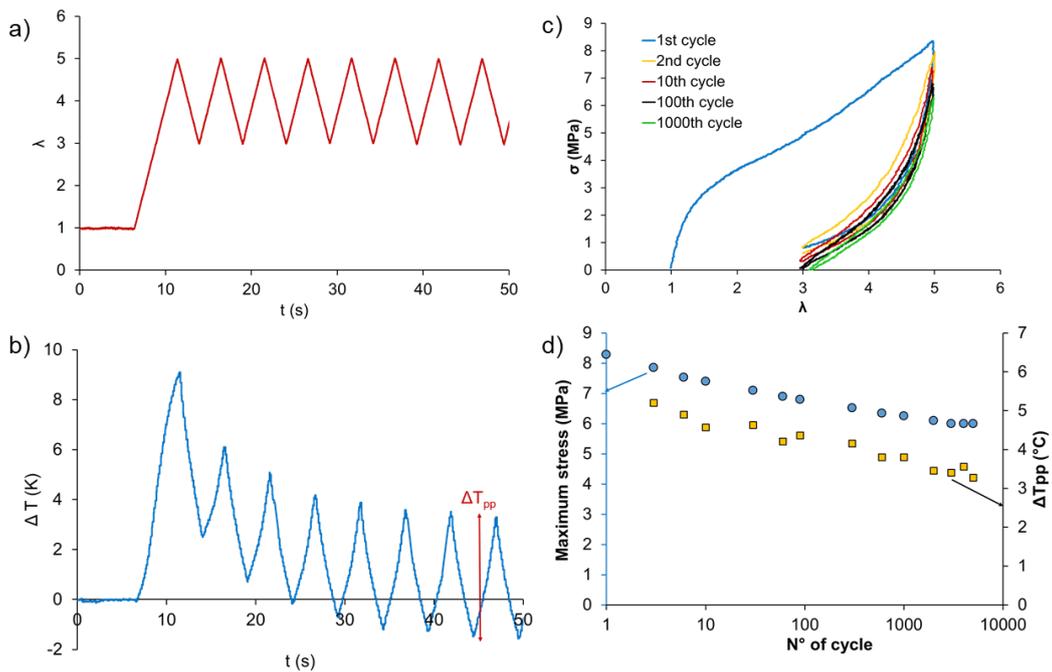
158

159 FIG. 3. Elastocaloric properties of polyurethane. (a) IR images for three states: $\lambda=1$ (original

160 state), $\lambda=5$ (stressed state) and $\lambda=1$ (recovered state) of TPU (b) Temperature variation as a

161 function of time ($\Delta T = T(t) - T_{room}$). (c) The minimum temperature variation ΔT_{min} as a function

162 of the final elongation λ_f..

163 The fast stretching of the material induces a positive temperature variation ΔT caused by SS

164 orientation and crystallization. At constant elongation the temperature drops until reaching

165 thermal equilibrium. Then, a return to the initial elongation at $\lambda=1$ leads to a decrease of ΔT

166 induced by disorientation of the soft segments and melting of the crystals. Moreover, the width

167 of these two peaks varies. It becomes narrower after elongation than after retraction due to the

168 stretched sample becoming thinner in comparison with the initial thickness at $\lambda=1$. The

169 thickness reduction of the sample favors heat transfer.[32]

170 Regarding the elastocaloric effect, $|\Delta T_{min}|$ increases significantly (from 1 K to 7.1 K) for a

171 final elongation λ_f between 2 and 4 and slightly (from 7.1 K to 7.7 K) when λ_f varies between

172 4 and 5 (Fig. 3(c)). This onset of saturation could be explained by a higher inelastic mechanical

173 response when λ_f increases. Finally, the temperature variation is within the same range as that

174 of natural rubber (NR) at $\lambda_f=5$ whereas for lower elongations, the adiabatic temperature

175 variation is higher for TPU.[7,8]

8

176 Cyclic elastocaloric properties were studied by imposing a triangular cyclic elongation between
177 λ=3 and λ=5 (Fig. 4(a)). With a chosen frequency f=0.2 Hz, 5000 cycles could be applied
178 without the sample breaking. The resulting temperature variation is presented in Fig. 4(b). The
179 peak-to-peak temperature variation ΔT_{pp} varies between 4.5 K and 3.3 K (Fig. 4(d)) when the
180 number of cycle increases from 10 to 5000. It corresponds to a decrease of about 10% per
181 decade. It can be noted that ΔT_{pp} for TPU is in the same range as for NR when the latter is
182 cycled between λ=3 and λ=6 [33], but with a lower stability.

183

184
185 FIG. 4. Elastocaloric effect of polyurethane during triangular solicitation when λ was varied
186 between 3 and 5 at f=0.2Hz. (a) Elongation program. (b) Temperature variation as a function
187 of time. (c) Stress/elongation curves of TPU for a varying number of cycles. (d) Maximum
188 stress and peak-to-peak temperature variation as a function of the number of cycles.

189 Figure 4(c) shows the stress/elongation curves of TPU for a varying number of cycles. With the
190 exception of the first cycle, the hysteresis loss is about 1 kJ/kg per cycle. The maximum stress
191 and the peak-to-peak temperature variation ΔT_{pp} decrease when the number of cycles increases
192 (Fig. 4(d)). After the hundredth cycle, the stress at λ=3 is equal to 0 MPa, indicating an inelastic
193 response. Besides, an estimation of heat exchange can be obtained according to Q≈c ΔT_{pp}= 8
194 kJ/kg (where c is the specific heat capacity of TPU). This is 8 times larger than the mechanical
195 losses in a single cycle. An indicator of material performance of a cooling device using a caloric

196   material is the coefficient of performance COP, defined roughly as $COP_{mat}=Q/W_{losses}$. The COP
197   value of 8 obtained here is in the normal range of caloric materials, i.e., between 5 and 20. [34,35]

198   To sum up, this work investigated the elastocaloric properties of thermoplastic polyurethane. A
199   strain-induced crystallization was revealed via X-ray diffraction, and it was verified that the
200   crystals melted after complete unloading, indicating a fully reversible strain-induced phase
201   transition. Consequently, the latent heat of this phase transformation contributed fully to the
202   elastocaloric effect after complete unloading. The adiabatic mechanical tests exhibited a
203   temperature variation in the same range as that found for natural rubber when tested under
204   identical conditions.

205   The mechanical and elastocaloric fatigue tests demonstrated that a large elastocaloric effect
206   ($\Delta T_{pp}>3K$) could be maintained for 5000 cycles. From a system point of view, it should be
207   noted that thermoplastic polyurethane can be melt processed or potentially 3D printed, opening
208   great perspectives in terms of fabrication and optimization of cooling devices at a lab scale.
209   Such cooling systems could also be advantageous for testing analytical or numerical models of
210   elastocaloric devices with a variety of complex shapes that can be practically produced.
211   However, from an applicative viewpoint, the continuous decrease of elastocaloric properties
212   and the inelastic response of TPU are limiting factors for solid state cooling applications. To
213   address these issues and increase the panel of elastocaloric polymers, other polyurethanes, such
214   as crosslinked polyurethane with varying HS/SS ratios, or other elastomers, such as HNBR or
215   polychloroprene, should be studied. [17–24]

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224   Data availability
225   The data that support the findings of this study are available from the corresponding authors
226   upon reasonable request.

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