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Bio-Inspired, Self-Toughening Polymers enabled by Plasticizer-Releasing Microcapsules

*Worarin Meesorn[1], Céline Calvino[1], Jens C. Natterodt[1,2], Justin O. Zoppe[1,3], Christoph Weder[1,]**

W. Meesorn, C. Calvino, Prof. C. Weder
Adolphe Merkle Institute, University of Fribourg
Chemin des Verdiers 4, CH-1700, Fribourg, Switzerland
E-mail: christoph.weder@unifr.ch

Dr. J. C. Natterodt
Current address: Dow Silicones Deutschland GmbH
Rheingaustrasse 34, 65201 Wiesbaden, Germany

Dr. J. O. Zoppe
Current address: Omya International AG
Baslerstrasse 42, CH-4665, Oftringen, Switzerland

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Abstract

A new concept for the design of self-toughening thermoplastic polymers is presented. The approach involves the incorporation of plasticizer-filled microcapsules in an intrinsically rigid and brittle matrix polymer. The intriguing adaptability that this simple tactic enables is demonstrated with composites composed of a poly(lactic acid) (PLA) matrix and 5-20% w/w poly(urea-formaldehyde) (PUF) microcapsules (MC) that contained hexyl acetate as plasticizer. At low strain (<1.5%) the glassy PLA/MC composites remain rigid, although the intact microcapsules reduce the Young's modulus and tensile strength by up to 50%. While the neat PLA shows brittle failure at a strain of around 2.5%, the composites yield in this regime, because the microcapsules rupture and release their plasticizing cargo. This effect leads to an up to 25-fold increase of the elongation at break and 20-fold increase of the toughness *vis-à-vis* the neat PLA, while the impact on modulus and ultimate stress is much smaller. Ballistic impact tests show that the self-toughening mechanism also works at much higher strain rates than applied in tensile tests and the operating mechanism was corroborated through systematic thermomechanical studies that involved dynamic mechanical testing and thermal analysis.

Main Text

Bio-inspired materials design approaches are increasingly used to develop new technologies in domains that have *à priori* little connection to biology.[1] A particularly useful and fascinating capability of many biological materials systems is their ability to change certain physical properties on command, *i.e.*, either upon exposure to an external stimulus or as a result of an internally created signal. Many of the underlying concepts have been applied to create artificial stimuli-responsive or adaptive materials, whose properties can be altered in a similar manner.[2-4] Polymeric materials whose mechanical properties can be switched on demand embody an intriguing and important subset of this materials family.[5, 6] Such materials are useful in applications such as biomedical implants, soft robotics, and active dampening systems and are thus attracting considerable attention.[7-9] Several operating principles found in biological materials have inspired artificial polymers with similar mechanical morphing capabilities, including changing the cross-link density of polymer networks,[10] altering the connectivity of reinforcing fillers in composites,[11-13] and simple plasticization. The latter effect is at play in hemicelluloses, in which a change from dry to humid conditions can cause the Young's modulus to drop by as much as three orders of magnitude.[14] Plasticization is also well established in polymer technology and used to increase the flexibility of rigid polymers.[15] Usually, plasticization is exploited in a permanent manner, *i.e.*, by incorporating plasticizers with the intent to serve during the lifetime of a product. However, the framework has also been used to modulate the mechanical properties of mechanically adaptive composites by way of plasticization upon exposure to appropriate solvents.[16, 17] Such external plasticization requires the transport of the plasticizer into the polymer and the switching speed is thus limited by diffusion. We show here that self-toughening, *i.e.*, an autonomous and rapid mechanical change, can be achieved by releasing the plasticizer from reservoirs embedded within the material, akin to locally releasing a specific protein in sea cucumber to rapidly and reversibly alter the stiffness of their skin when threatened.[18-20] To achieve this we adopted a concept that was previously exploited to mechanically release functional agents from microcapsules embedded in a matrix polymer. This framework has been used to impart polymers with several interesting functions,[21] including drug delivery,[22, 23] fragrance release,[24] damage-sensing,[25-29] and self-healing.[30-32] In the context of the latter, Braun and co-workers incorporated an encapsulated plasticizer as a healing agent in a poly(methyl methacrylate) matrix;[33] however, the mechanical properties of the temporarily plasticized material generated when the capsules ruptured due to mechanical force were not further explored. We show here that the combination of this framework with judiciously chosen components permits creating composite materials that exhibit mechanically induced mechanical morphing that manifests itself in the form of a rapid and pronounced *self-toughening* effect. Poly(lactic acid) (PLA) was selected as the matrix based on the facts that this thermoplastic, bio-based polymer[34-36] is attractive for a wide range of applications,[37, 38] the notion that the low impact resistance and brittleness of PLA limit its usefulness,[39] and that a significant body of work has been devoted to enhancing the flexibility and the toughness of PLA by plasticization.[40-44] It is well established that plasticizers increase the flexibility of PLA by reducing PLA-PLA interactions and thereby decreasing the glass transition temperature (T_g). In a systematic study, we explored the (mechano-responsive) mechanical properties of composites featuring a PLA as polymer matrix and 5-20% w/w poly(urea-formaldehyde) (PUF) microcapsules (MC) filled with hexyl acetate as plasticizer. At low strains the glassy PLA/MC composites remain rigid, although the intact microcapsules reduce the Young's modulus and tensile strength by up to 50%. Upon further deformation, but *before* the samples fail, the plasticizer is released from the capsules, and the extensibility and toughness of the PLA/MC composites are increased 20-25 fold *vis-à-vis* the neat PLA.

Based on the expectation that an ester structure should be a good plasticizer for PLA, hexyl acetate, which offers a conveniently high boiling point of 182 °C and an appropriately low melting temperature of -80 °C, was selected as the plasticizer, although we acknowledge that for practical uses a less volatile plasticizer must be employed (*vide infra*). Hexyl acetate was incorporated into poly(urea formaldehyde) (PUF) microcapsules (herein referred to as MCs) by an emulsion polycondensation reaction of urea, resorcinol, formaldehyde, and poly(ethylene-*alt*-maleic anhydride). The encapsulation process was carried out at 55 °C in the presence of 1-octanol, as previously reported.[27, 29, 45] The analysis of optical microscopy images (**Figure 1a and 1b**) reveals that the MCs have diameter of 67 ± 22 μm and a shell thickness of 15 ± 8 μm.[29] Optical micrographs reveal that most of the MCs are intact after isolation (Supporting **Figure S1**) and thermal analysis suggests an encapsulation of 66 ± 1% hexyl acetate based on the weight loss of the microcapsules in thermogravimetric analysis experiments (Supporting **Figure S2**).

The PLA used in this study is poly-DL-lactide (**PDLLA**), which is fully amorphous and has a T_g at 55°C (Supporting **Figure S3**). In order to explore how the properties of the PLA/MC composites could maximally change, we first studied the swelling of neat PLA films with hexyl acetate at room temperature. A time-dependent gravimetric swelling experiment (Supporting **Figure S4**) revealed that films of a thickness of 0.2 mm have reached an equilibrium hexyl acetate content of 15% w/w after two days of immersion in the solvent, although substantial plasticization was already evident after 5 min. Next, PLA/MC composite films containing 5, 10, or 20% w/w MCs were prepared by solution-casting mixtures of the polymer and the MCs from acetone and drying under ambient conditions. The optical microscopy image shown in **Figure 1c** reveals that even at a MC content of 20% w/w, the microcapsules are well dispersed in the PLA matrix and their appearance remains spherical and intact after drying. It is noted that the present PUF microcapsules were easily dispersed in PLA matrix without the need for surface functionalization, unlike previously reported PMMA composites, where the microcapsules had to be surface-modified to achieve good dispersion and prevent microcapsule rupture during processing.[33] As a (weak) vacuum was applied to dry the films after processing (See Experimental Details in the Supporting Information), it appeared appropriate to investigate what fraction of hexylacetate actually remains encapsulated in the processed films. Thermogravimetric analysis of the PLA/MC composite films containing 5, 10, or 20% w/w MCs suggests that hexyl acetate content in these materials is ≈2.8, 3.6 and 4.1% w/w, respectively, *i.e.*, considerably lower than the theoretical amount originally introduced by the MCs (≈3-13%) (Supporting **Figure S5**). The fact that this is related to vacuum-drying the samples is supported by the TGA trace of PUF microcapsules exposed to composite film processing conditions (Supporting **Figure S2**), which reflects a reduction of the hexyl acetate content from ca. 66 to 16% w/w.

The mechanical properties of neat PLA, hexyl acetate-swollen PLA (prepared by immersion in hexyl acetate as reported above), and PLA/MC composite films were studied using tensile tests, dynamic mechanical analyses (DMA), and impact testing. The stress-strain curve of the neat PLA (**Figure 2**), recorded at ambient temperature and with a strain rate of $10\%\cdot\text{min}^{-1}$, shows brittle fracture at a strain of ca. 2.4% (**Table 1**). By contrast, the hexyl acetate-swollen PLA film displays plastic deformation and the elongation at break is increased to ca. 125%. At the same time, the elastic modulus is reduced from 670 MPa (neat PLA) to 25 MPa (hexyl acetate-swollen PLA), the stress at break drops from 12 to 6.3 MPa, while the toughness is increased by more than an order of magnitude from 175 to 4470 $\text{kJ}\cdot\text{m}^{-3}$. Thus, the data reflect unequivocally that the introduction of hexyl acetate plasticizes the PLA significantly.

The corresponding tensile tests of the PLA/MC composite films reveal that in the low-strain regime (<1.5%) the introduction of the hexyl acetate-containing MCs does not change the rigid glassy nature of the material, although the Young’s modulus is reduced *vis-à-vis* the neat PLA and varies between 325 and 455 MPa (**Figure 2**, **Table 1**). While there is no statistically significant trend, it appears that the introduction of the MCs reduces the stiffness of the matrix a bit. Intriguingly, the stress-strain curves reveal that the composites, as intended, do not exhibit brittle failure; instead, ductile behavior is observed. In the case of the PLA/MCs containing 5% or 10% w/w microcapsules, yield points are observed at 3 and 5% strain and at stresses (9.5 and 9.1 MPa) that are not much lower than the maximum stress (12 MPa) of the neat PLA. At the same time, the elongation at break is increased to ca. 9% and 23%, respectively (**Table 1**). In the case of the PLA/MC composite containing 20% w/w microcapsules, the maximum stress is reduced to 7.5 MPa, while the ductile regime is further extended and the elongation at break increases to ca. 60%. The toughness increases steadily with the MC content from 175 (neat PLA) to 3825 kJ·m^{-3} (20% w/w MCs) and approaches that of the hexyl acetate swollen PLA reference. Thus, the mechanical behavior of the MC-containing samples is consistent with plasticization of the PLA by hexyl acetate, which is released from rupturing microcapsules upon deformation. The fact that for all composites the onset of plastic deformation is observed around 3-5% strain suggests that the initially rigid materials display a similar mechanical behavior and irrespective of the composition, the MCs rupture and release their cargo at a similar strain.

In order to investigate the influence of the mechanically induced plasticizer release on the thermal behavior of the PLA/MC composites, differential scanning calorimetry (DSC) experiments were conducted with the as-prepared films, as well as samples that had been freshly (*i.e.*, just before the DSC measurements were conducted) deformed to a strain of 5%. The as-prepared PLA and PLA/MC films all exhibit a T_g in the range of 52-55 °C, which is consistent with the commonly reported range of 52–57 °C for PLA[46-48] (**Figure 3a**). The DSC of the hexyl acetate-swollen PLA does not show a glass transition, perhaps on account of broadening, but DMA (*vide infra*) suggest that the T_g is reduced to 22°C (note that the T_g values established by DMA are usually somewhat higher than those measured by DSC[49, 50]). As expected, the T_g of the deformed PLA/MC composite films also decreased, although in a less pronounced manner, to 52, 51, and 46 °C (for composites with 5, 10, or 20% w/w MCs) (**Figure 3b**).

In order to corroborate the above interpretation, the composites were further investigated by dynamic mechanical analysis (DMA). Measurements were again carried out on as-prepared samples as well as on films that had been deformed to a strain of 5% (**Figure 4**). The DMA traces of the as-prepared films closely mirror each other and confirm that the incorporation of the MCs only has a relatively small influence. They show a glassy regime that is characterized by a storage modulus (E') of 1.3-1.4 GPa (measured at 25 °C), which extends to ca. 75 °C. Above this temperature the modulus drops on account of passing through the glass transition. The analysis of the $\tan\delta$ peaks (Supporting **Figure S6**) reveals a T_g of 80 °C for the neat PLA and the composites with 5 or 10% w/w MCs, and a value of 79 °C for the composite with 20% w/w MCs (**Table 2**). An inspection of the DMA traces of the 5% strained PLA/MC composite films shows a shift of the curves to lower temperatures and a slight reduction of E' in the glassy regime. The analysis of the $\tan\delta$ peaks shows strikingly that the T_g reduction increases with the MC content to a value of 61 °C for the 20% w/w composite. At the same time, the E' at 55 °C (*i.e.*, at the T_g of the neat PLA) decreases from ~1240 MPa (neat PLA) to ~720, 500, and 220 MPa upon incorporation of 5, 10, and 20% w/w MCs, respectively. While the DMA trace of the hexyl acetate swollen PLA reference shows a much more pronounced plasticization (with a significant broadening of the glass transition and a $\tan\delta$ maximum of 22 °C), the data show that in the deformed composites the PLA is plasticized by the hexyl acetate released from the MCs. Samples of the 20% w/w composite were also strained to 10% and 30% and tested by DMA and DSC (Supporting **Figure S7** and **Figure S8**). No further T_g reduction or mechanical change can be observed, which suggests that a strain of 5% is sufficient to rupture most of the capsules. The fact that T_g slightly increased when the strain was increased beyond 5% may suggest evaporation of the plasticizer. This is corroborated by the observation that testing stretched samples after different time intervals (Supporting **Figure S7**) displayed a gradual increase of T_g, also reflecting plasticizer evaporation. To confirm that plasticization is indeed caused by hexyl acetate, control experiments were carried out with PLA/20% MC composite films that were dried to remove the hexyl acetate from the microcapsules. The stress-strain curve of this material (Supporting **Figure S9a**) mirrors the one of neat PLA and shows brittle failure at a slightly reduced stress. The samples were deformed to failure and DSC and DMA tests were carried out. The DSC trace of the dried composite film shows a T_g at 55 °C, matching the value of the neat PLA and never-dried un-deformed PLA/20% MC (Supporting **Figure S9b**). The DMA trace is in between those of PLA/20% MC and the neat PLA (Supporting **Figure S9c**). It shows storage moduli of 1440 MPa at 25 °C and 1285 MPa at 55 °C (these values are comparable to those of the neat PLA) while the modulus drop occurs at the same temperature as observed for the never-dried unstretched PLA/20% MC. Thus, these results demonstrate that the toughening effect is clearly related to the plasticization of PLA by hexyl acetate.

To investigate the impact strength of the PLA/MC films, and demonstrate that the toughening mechanism also occurs at much higher strain rates than applied for tensile testing, free-falling dart impact test experiments were carried out at ambient temperature with an experimental setup that is shown in supporting **Figure S10**.[51] While the neat PLA film fractured in all cases after the metal projectile was dropped, due to its high brittleness (**Table 3, Figure 5a**), the composites do indeed display a better impact resistance, and the toughening effect clearly scales with the content of MCs, with the 20% w/w composite being able to withstand the projectile impact at all impact energies (**Table 3, Figure 5b-c**).

In summary, we have demonstrated a simple but seemingly powerful concept for the design of self-toughening polymers that merely involves the incorporation of plasticizer-filled microcapsules in an intrinsically rigid and brittle matrix polymer. The PLA/MC composites investigated show that it permits creating materials which, at low strain, largely preserve the mechanical characteristics of the matrix polymer employed, notably high stiffness and strength. However, instead of brittle failure, the mechanical properties morph upon application of extensive force, and the materials adopt a ductile deformation behavior and exhibit a significant increase of the elongation at break and toughness, on account of the release of the built-in plasticizer. Importantly, the mechanism also functions at high strain rates, as are experienced for example upon ballistic impact. The approach can thus be used to bestow brittle and rigid polymers with built-in fail-safes against catastrophic impact, without the need for chemical modification of the polymer. The framework appears to be general, but the results shown here clearly reflect that plasticizer volatility is an issue that must be addressed for practical applications. This is particularly relevant if melt-processing of thermoplastic polymers is targeted. On the other hand, curing of capsule-containing thermosets may be the best way to incorporate plasticizer-filled microcapsules into polymers without prematurely extracting the capsule's payload. One caveat is that the microcapsules employed here cause substantial light scattering, at least in PLA, and thus render the composites opaque. Further studies will be needed to investigate if a (substantial) reduction of the microcapsule diameter and refractive index matching can render the concept applicable to transparent materials. Furthermore, it appears that if a less volatile plasticizer is used, so that partial evaporation during processing and possible use time can be avoided, even larger mechanical switching effects are possible.

Experimental Section

Materials: An amorphous PLA with a density of 1.24 g/cm^3 and a glass transition temperature of 55-60 °C was supplied from NatureWorks LLC, USA under the tradename Ingeo biopolymer 4060D. Poly(ethylene-*alt*-maleic anhydride), urea, resorcinol, ammonium chloride, hexyl acetate, sodium hydroxide, 1-octanol, formaldehyde in solution (37% w/w in H_2O), acetone, and dichloromethane were purchased in analytical grade quality from Sigma-Aldrich. All chemicals were used without further purification.

Preparation of Hexyl Acetate-Containing Microcapsules: Poly(urea-formaldehyde) (PUF) microcapsules filled with hexyl acetate, having an average diameter of 67 ± 22 μm and a shell thickness of 15 ± 8 μm, were prepared *via* an oil-in-water emulsion technique following a previously reported protocol,[29] which in turn is an adaptation of the technique reported by Brown *et al*.[45] An aqueous solution (125 mL deionized water) of poly(ethylene-*alt*-maleic anhydride) (0.67 g), urea (2.5 g), resorcinol (0.25 g), and ammonium chloride (0.25 g) was placed in a 500 mL round-bottom flask, an 1 M aqueous sodium hydroxide solution was drop-wise added to adjust the pH to 4. One drop of 1-octanol and hexyl acetate (60 mL) were added, the mixture was stirred for 10 min, before formaldehyde (6.3 g) was added to the reaction mixture, and the temperature was raised to 55 °C. The mixture was then mechanically stirred at 450 rpm for 4 h. The agitation was stopped, the mixture was cooled to ambient and left to stand overnight, before the microcapsules were filtered off using a Büchner funnel. The hexyl acetate-containing microcapsules (referred to as MC) were thoroughly washed with water, acetone, and dichloromethane, and dried for 24 h under ambient conditions to yield colorless microcapsules (23 g).

Preparation of neat PLA Reference Film and PLA/MC Films: PLA (1.825 g) was dissolved in acetone (36.5 mL) at a concentration of 50 mg/mL. A portion (10.0 mL) of this solution was cast into a round Teflon® Petri-dish having a diameter of 7.5 cm, which was left to stand in a well-ventilated hood at ambient temperature for 24 h. It was then placed in a vacuum oven at ambient temperature under 270 mbar for 24 h to completely remove the acetone and afford the neat PLA reference film with a thickness of ca. 0.20 mm. The microcapsules were separately dispersed in acetone and amounts of 25, 50, or 100 mg were combined with aliquots (9.5, 9, 8 mL) of the PLA solution to create composites containing 5, 10, or 20% w/w microcapsules. The mixtures were stirred with a magnetic stirrer for 5 min and processed into PLA/MC films using the same procedure as for the neat PLA.

Swelling Studies: The dried neat PLA reference films were used to study the swelling of this polymer with hexyl acetate. Films with a length of 10 mm, a width of 5.3 mm and a thickness of ca. 0.20 mm were weighted and immersed at room temperature in hexyl acetate. The films were removed from the solvent after periodic time intervals, their surface was carefully wicked with tissue paper, the weight was recorded, and the films were returned to the hexyl acetate bath. On the basis of the data thus collected (Supporting **Figure S4**), all samples referred to as "hexyl acetate swollen PLA" were conditioned by immersion in hexyl acetate for 48 h at room temperature.

Thermal and Mechanical Characterization: Differential scanning calorimetry (DSC) experiments were carried out under N_2 atmosphere on a Mettler-Toledo STAR DSC instrument. Samples having a weight of ∼10 mg were heated from 0 to 120 °C and cooled back to 0 °C with heating and cooling rates of 10 °C/min. Thermogravimetric analyses were also carried out under N_2 atmosphere on a Mettler-Toledo STAR thermogravimetric analyzer. Samples were first heated from 25 to 160 °C with a rate of 5 °C/min, kept isothermal at 160 °C for 4 h, and then heated from 160 to 400 °C, also with a rate of 5 °C/min. The mechanical properties of the neat PLA and PLA/MC films were studied using a TA instruments Model Q800 dynamic mechanical analyzer (DMA). The tests were performed on films with a length of ca. 10 x 5.3 x 0.20 mm in tensile mode. A strain amplitude of 15 µm and a frequency of 1 Hz were applied, the temperature range was -50 to 100 °C, and a heating rate of 5 °C/min was chosen. The mechanical data quoted in the text and Table 2 represent average values of 3 – 5 individual measurements ± standard deviation. Tensile tests were performed at ambient temperature on the above-described DMA applying a strain rate of 10%·min^{-1}. These measurements were also performed with 3 – 5 samples per composition and averages are reported. Impact tests were conducted by a free-falling dart method according to a previously published procedure[29] with an instrumental setup that is shown in Supporting **Figure S10**. In brief, a 50 g metal projectile was attached to a string that permitted adjusting the desired falling height (7, 18, 29, or 40 cm, which is translated to impact energy of 34, 88, 142, or 196 mJ respectively) and the projectile was dropped through a guiding tube onto films with dimensions of 25 x 25 x 0.2 mm that were placed underneath. The tests were performed with 3 samples per composition and each falling height. The films' fracture behavior was observed with the help of an Olympus BX51 optical microscope.

Microscopy: Scanning electron microscopy (SEM) was used to study the morphology of hexyl acetate-containing microcapsules. The MCs were directly placed on a carbon adhesive tape on top of a metallic SEM sample holder. SEM images were acquired with a TE Scan Mira 3 microscope operated between 5–10 kV. Images of the MCs and the PLA/MC composites were recorded using an Olympus BX51 microscope equipped with a DP72 digital camera. Size and shell thickness measurements of the microcapsules were carried out using the Stream Basic software suite. The capsule size average was determined based on data from 200 capsules measured in 6 micrographs. The shell thickness was determined based on data from 200 capsules. These were embedded in PDMS according to the method reported by Calvino et al.,[29] and sliced with a razor blade (approximately 15 slices were made) before the composite was imaged.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Supplementary Figures S1–S10 and a comprehensive account of all experimental details.

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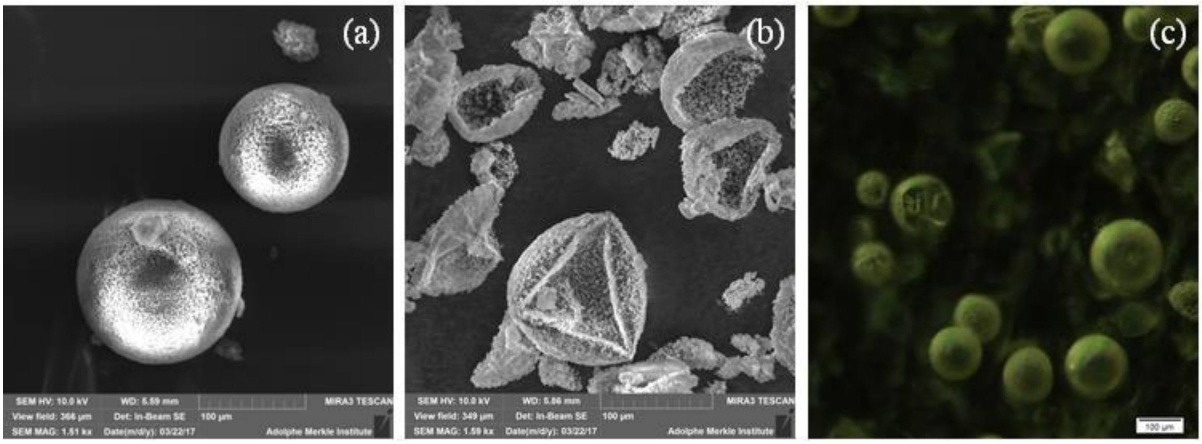


Figure 1. Scanning electron microscope images of PUF microcapsules filled with hexyl acetate (a) and ruptured microcapsules (b), and an optical microscopy image of a PLA/MC composite film containing intact hexyl-acetate filled microcapsules (c).

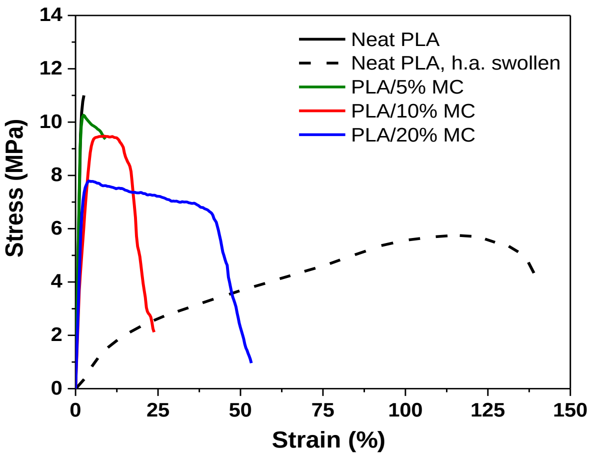


Figure 2. Representative stress-strain curves of neat PLA, hexyl acetate-swollen PLA, and PLA/MC composite films containing 5, 10, or 20% w/w MCs. The experiments were conducted at ambient temperature and at a strain rate of 10%·min^{-1}.

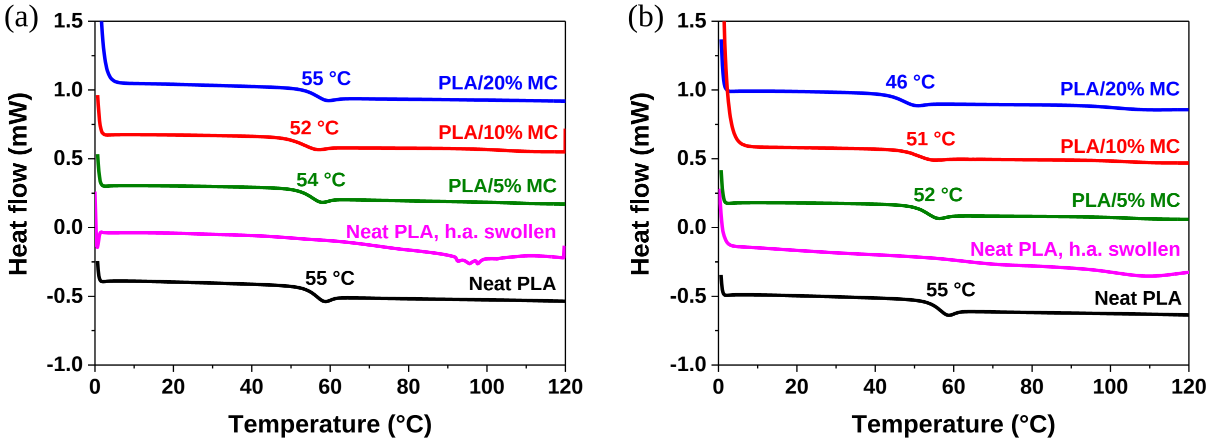


Figure 3. DSC traces of neat PLA, hexyl-acetate swollen PLA, and PLA/MC films with 5, 10, or 20% w/w MCs before (a) and after (b) uniaxial deformation to a strain of 5% (in the case of neat PLA to 2.4%).

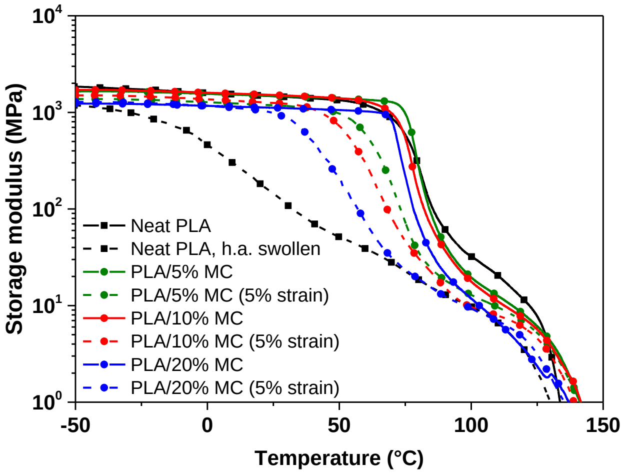


Figure 4. Dynamic mechanical analysis traces of neat PLA and PLA/MC composite films with 5, 10, or 20% w/w MCs before (solid lines) and immediately after (dashed lines) uniaxial deformation to a strain of 5%. The trace of a hexyl-acetate swollen PLA film is also shown.

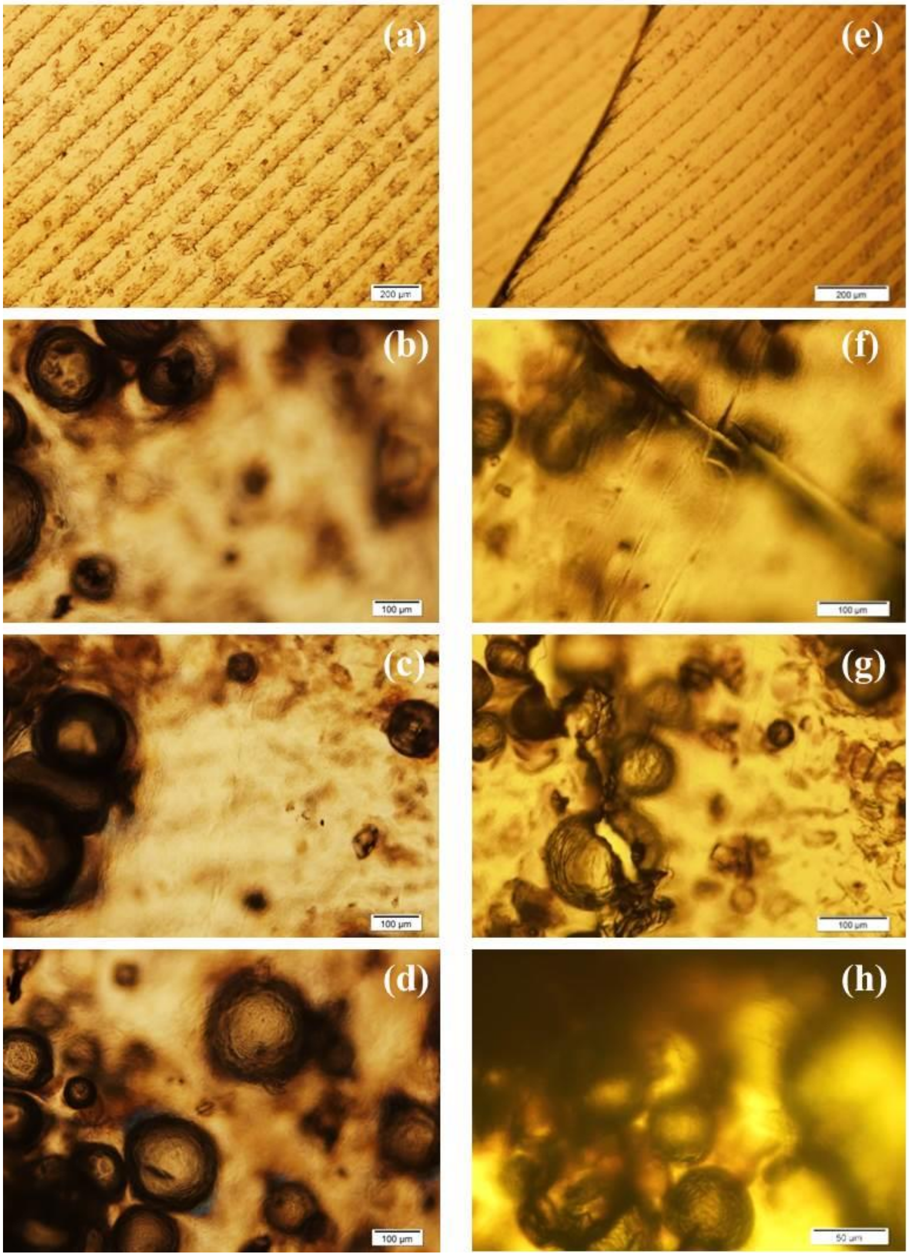


Figure 5. Optical microscopy images of samples before (a-d) and after (e-h) impact testing with a projectile dropped from a height of 40 cm (corresponding to an impact energy 196 mJ) (a, e) neat PLA, (b-h) PLA/MC composites with 5 (b, f), 10 (c, g), or 20% w/w MCs (d, h).

Table 1. Tensile Properties of Neat PLA, Hexyl Acetate-Swollen PLA, and PLA/MC Composite Films[a]

Composition	Young's modulus[b] (MPa)	Maximum stress[c] (MPa)	Elongation at break[d] (%)	Toughness[e] ($kJ\cdot m^{-3}$)
Neat PLA	670 ± 60	12 ± 1	2.4 ± 0.2	175 ± 10
Neat PLA, h.a. swollen	25 ± 13	6.3 ± 1.1	125 ± 20	4470 ± 1070
PLA/5% MC	455 ± 140	9.5 ± 1.1	8.9 ± 0.9	710 ± 160
PLA/10% MC	325 ± 60	9.1 ± 0.7	23 ± 7	1620 ± 535
PLA/20% MC	340 ± 20	7.5 ± 0.9	61 ± 25	3825 ± 410

[a] The measurements were conducted by tensile testing at 25 °C applying a strain rate of $10\%\cdot min^{-1}$. Data shown represent averages (number of individual measurement, $N = 3$) ± standard error measurements. [b] Determined in the strain (engineering strain $\varepsilon=\Delta l/l_0$) range of 0.5-1.5%. [c] Maximum stress (engineering stress, $\sigma=P/A_0$) and [d] maximum strain ε measured before failure occurred. [e] Determined by integration of the stress-strain curves.

Table 2. Storage Moduli and Glass Transition Temperature of Neat PLA, Hexyl Acetate-Swollen PLA, and PLA/MC Composite Films

Composition	Storage Modulus (MPa)[a]			Glass transition temperature (°C)	
	At -40 °C	At 25 °C	At 55 °C	DMA[a,b]	DSC
Neat PLA	1645 ± 565	1410 ± 490	1240 ± 420	80 ± 1	55
PLA/5% MC	1480 ± 210	1320 ± 200	1220 ± 175	80 ± 4	54
PLA/10% MC	1595 ± 100	1400 ± 105	1265 ± 85	80 ± 2	52
PLA/20% MC	1380 ± 360	1245 ± 330	1165 ± 295	79 ± 2	55
Neat PLA, h.a. swollen	1210 ± 80	120 ± 25	40 ± 7	22 ± 3	-
PLA/5% MC (5% strain)	1255 ± 245	1085 ± 205	720 ± 90	72 ± 4	52
PLA/10% MC (5% strain)	1300 ± 185	1100 ± 145	505 ± 65	70 ± 2	51
PLA/20% MC (5% strain)	1070 ± 185	800 ± 175	220 ± 95	61 ± 4	46

[a]Determined by DMA. Data represent average (number of individual measurement, $N = 3–5$) ± standard error measurements. [b]Maximum of the *tan δ* peaks.

Table 3. Impact Tests of Neat PLA and PLA/MC Films with 5, 10, and 20% w/w of Microcapsules by Free-falling Dart Method[a]

Composition	Falling Height(cm) / Impact energy (mJ)			
	7/34	18/88	29/142	40/196
Neat PLA	✓	✓	✓	✓
PLA/5%MC	✗	✓	✓	✓
PLA/10%MC	✗	✓	✓	✓
PLA/20%MC	✗	✗	✗	✗

[a]Experiments were performed at ambient temperature with 3 samples per composition for each falling height / impact energy. The symbol ✓ indicates that all samples were observed to fracture, whereas the symbol ✗ reflects that no fracturing was observed in any of the samples.

Summary

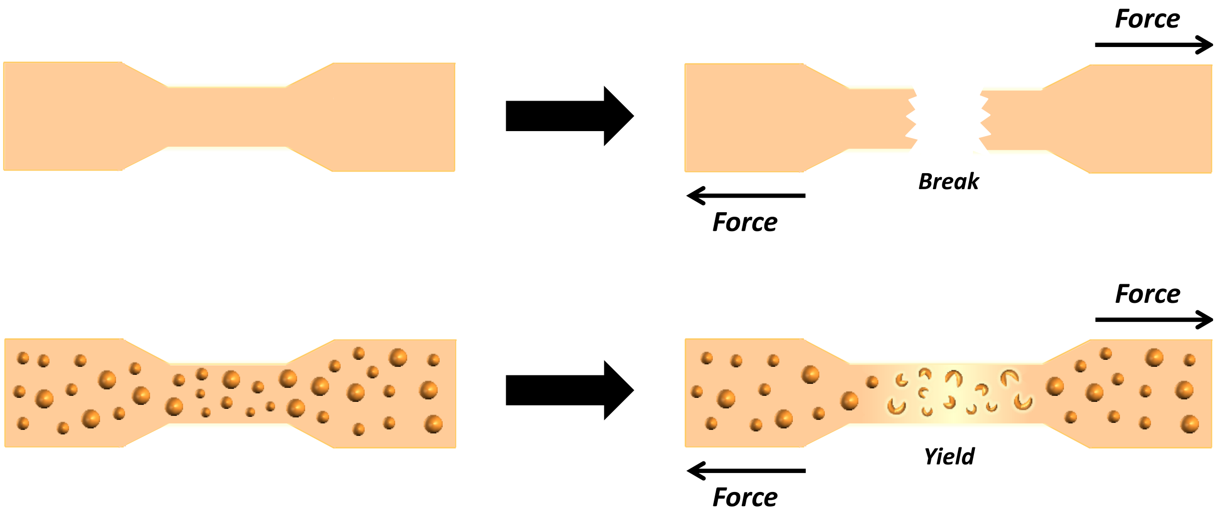
Self-toughening polymers composed of a rigid poly(lactic acid) matrix and poly(urea-formaldehyde) microcapsules containing a plasticizer are presented. At low strain, the composites retain the stiffness of the matrix polymer. However, while the latter eventually shows brittle failure, the composites yield, because the microcapsules rupture and release their plasticizing cargo. This effect substantially increases the elongation at break and the toughness.

Keywords: bio-inspired, self-toughening, PLA, plasticizer, microcapsules

Worarin Meesorn[1], Céline Calvino[1], Jens C. Natterodt[1,2], Justin O. Zoppe[1,3], Christoph Weder[1,]*

Bio-Inspired, Self-Toughening Polymers enabled by Plasticizer-Releasing Microcapsules

ToC Figure



Supporting Information

Bio-Inspired, Self-Toughening Polymers enabled by Plasticizer-Releasing Microcapsules

Worarin Meesorn[1], *Céline Calvino*[1], *Jens C. Natterodt*[1,2], *Justin O. Zoppe*[1,3], *Christoph Weder*[1,*]

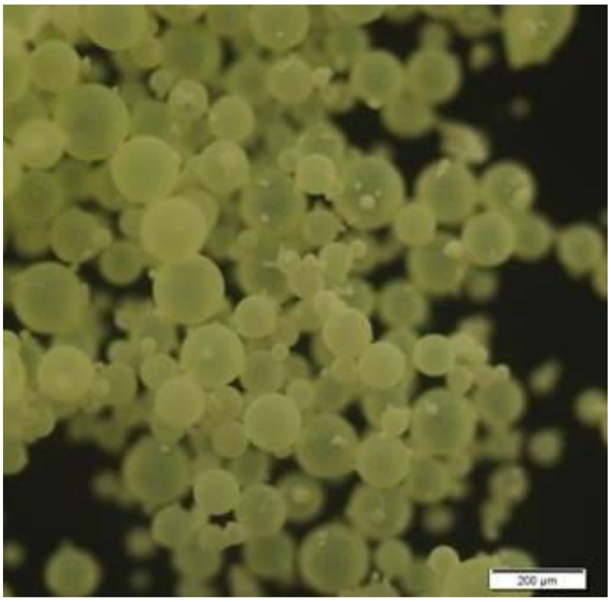


Figure S1. Optical microscopy image of PUF microcapsules filled with hexyl acetate.

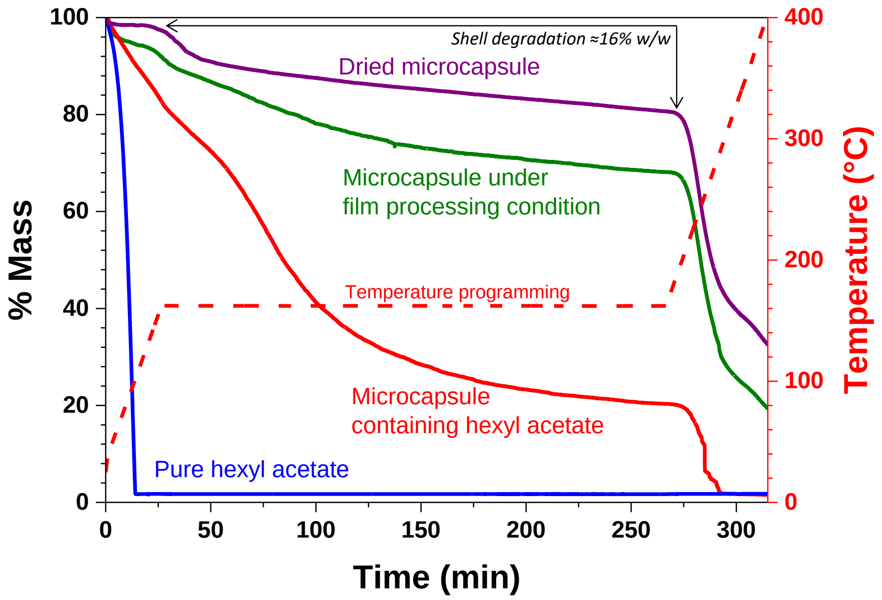


Figure S2. Thermogravimetric analysis traces of pure hexyl acetate, PUF microcapsules filled with hexyl acetate, dried microcapsules, and hexyl acetate filled microcapsules exposed to film processing conditions, all measured under N_2 atmosphere. The samples were first heated from ambient temperature to 160 °C with a heating rate of 5 °C/min. The temperature was then kept constant at 160 °C for 4 h, before it was increased to 400 °C with a heating rate of 5 °C/min. The weight loss observed for dried microcapsules that were heated and kept at 160 °C for 4 h was ca. 16% w/w. The hexyl acetate content in the hexyl acetate filled microcapsules was determined by their mass loss after 4 h at 160 °C minus the weight loss observed for dried microcapsules; the encapsulation efficiency was thus calculated to be 66 ± 1%. The hexyl acetate content in the microcapsules after film processing conditions (kept in a vacuum oven at ambient temperature under 270 mbar for 24 h) was determined in a similar manner to be ca. 16% w/w.

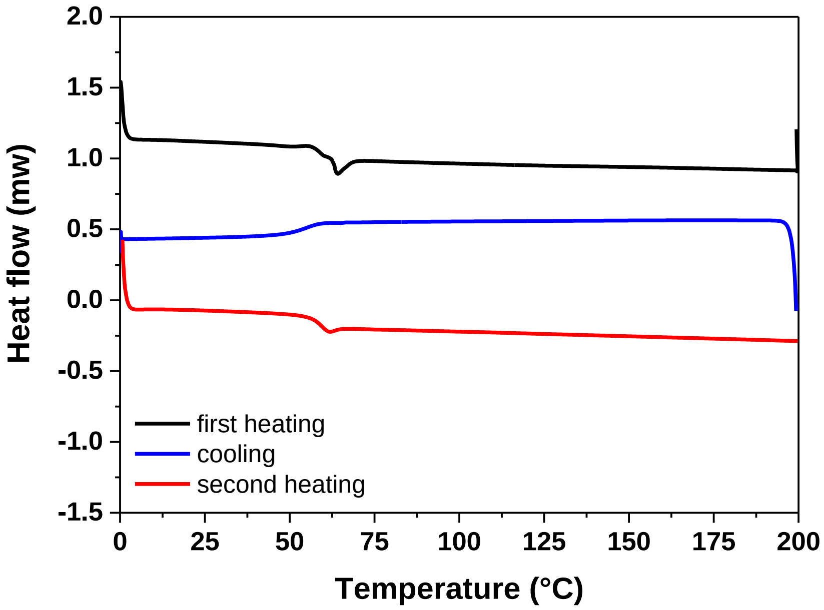


Figure S3. DSC trace of neat PLA with a heating and cooling rate of 10 °C/min.

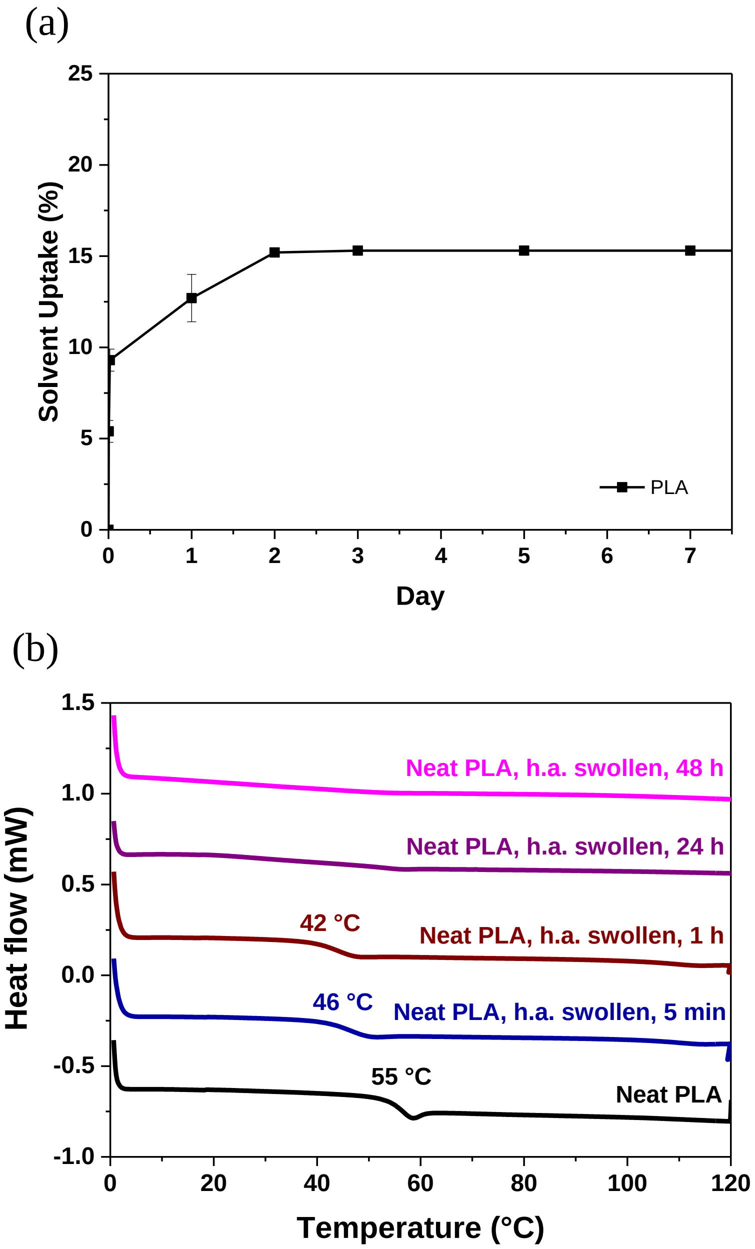


Figure S4. (a) Solvent uptake of neat PLA films upon immersion in hexyl acetate at room temperature. Data points represent averages of three measurements. (b) DSC traces of neat PLA films after immersion in hexyl acetate at various time intervals.

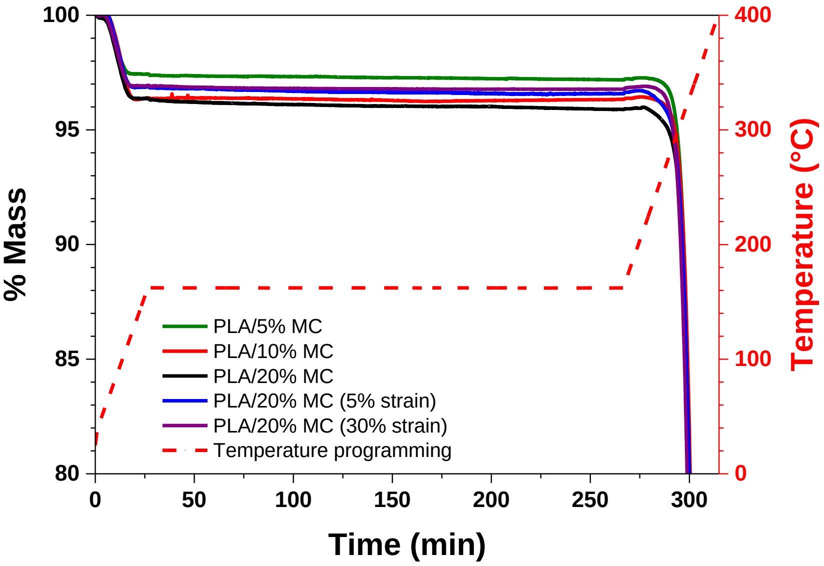


Figure S5. Thermogravimetric analysis traces of PLA/MC composite films with 5, 10, or 20% w/w MCs performed under N_2 atmosphere. In the case of the 20% w/w composite TGAs were also carried out on films that had ben uniaxially stretched to strains of 5 or 30%. The films were first heated from ambient temperature to 160°C with a heating rate of 5 °C/min. The temperature was then kept constant at 160 °C for 4 h, before it was increased to 400 °C with a heating rate of 5 °C/min. The amount of hexyl acetate was determined by the mass loss of the film before the PLA degraded at 160 °C, which was calculated to be 2.8, 3.6 and 4.1% for the undeformed film with 5, 10 and 20% w/w MCs, and 3.4%, or 3.2% for the films deformed to strains of 5% or 10%, respectively.

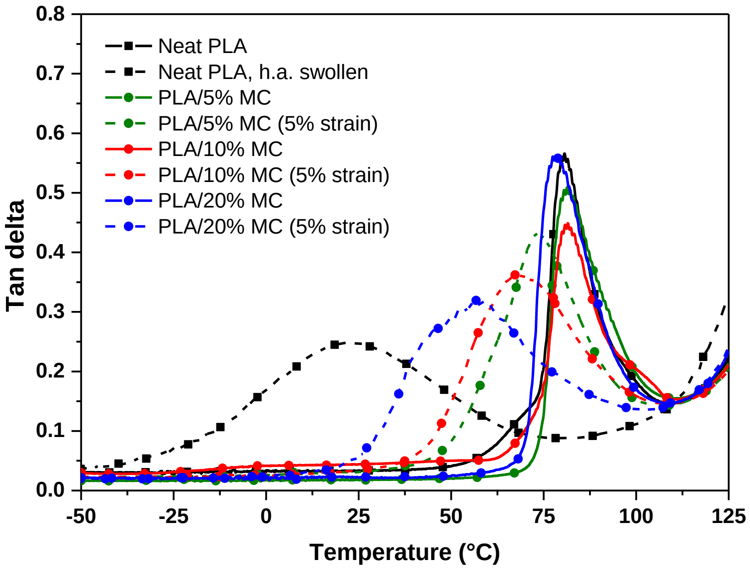


Figure S6. *Tan δ*-graph of neat PLA and PLA/MC composite films with 5, 10, or 20% w/w MCs before (solid lines) and immediately after (dashed lines) uniaxial deformation to a strain of 5%. The graph of a hexyl-acetate swollen PLA film is also shown.

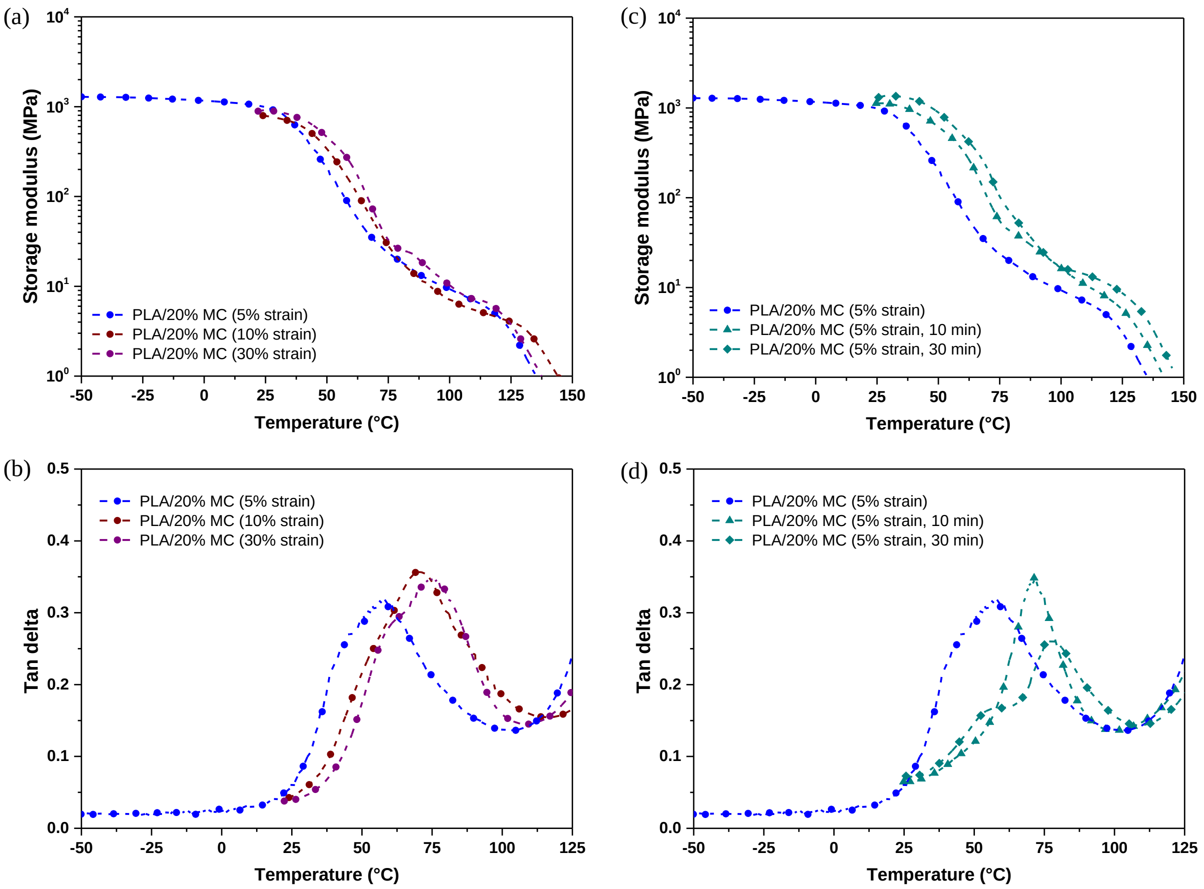


Figure S7. DMA traces (a) and *tan δ* graph (b) of PLA/MC composite film with 20% w/w MCs immediately after uniaxial deformation to a strain of 5%, 10%, or 30%, and in the case of 5% strain as a function of time before measuring(c, d).

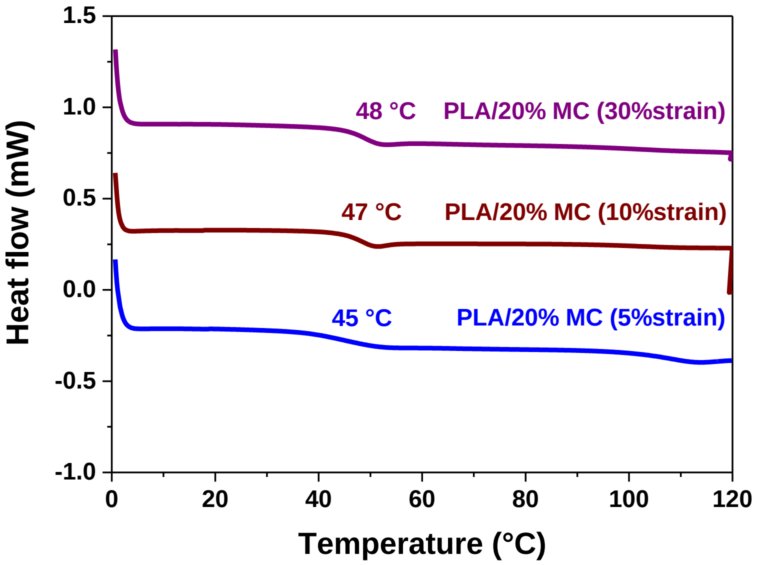


Figure S8. DSC traces of PLA/MC film with 20% w/w MCs immediately after uniaxial deformation to a strain of 5%, 10%, or 30%.

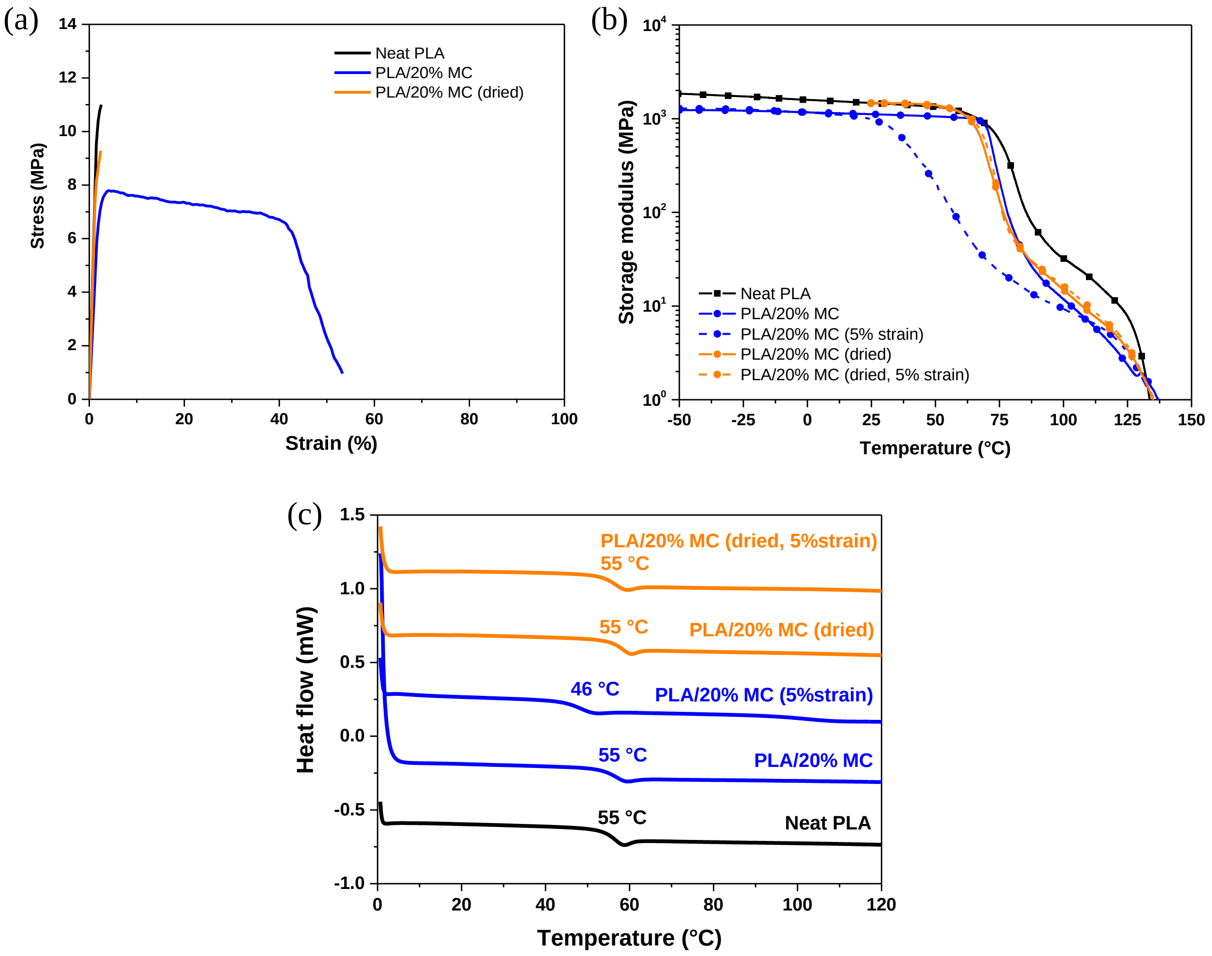


Figure S9. (a) Stress-strain curve, (b) DMA trace, and (c) DSC trace of dried PLA/20%MC compare to the neat PLA and the never-dried PLA/20%MC.

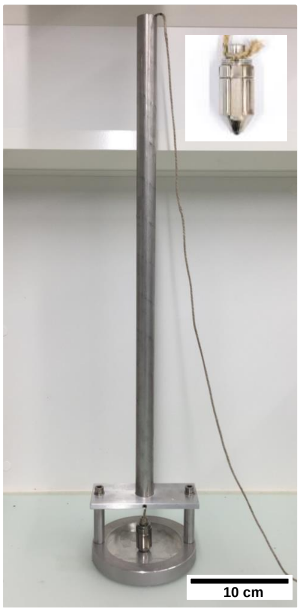


Figure S10. Picture of the instrumental setup used for impact tests.