ACS APPLIED MATERIALS & INTERFACES
Letter
www.acsami.org

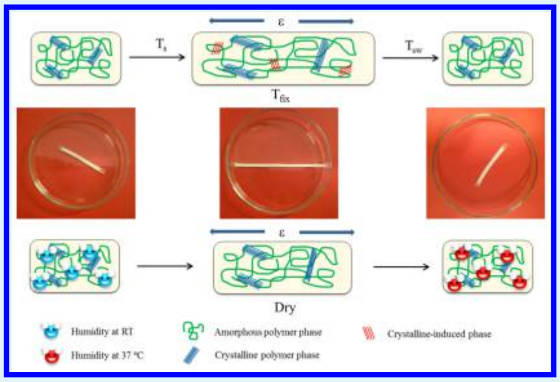
Multiresponsive Shape Memory Blends and Nanocomposites Based on Starch

Valentina Sessini,[†,‡] Jean-Marie Raquez,[*,§] Giada Lo Re,[§] Rosica Mincheva,[§] José Maria Kenny,[†,‡] Philippe Dubois,[§] and Laura Peponi[*,‡]

[†]Dipartimento di Ingegneria Civile e Ambientale, University of Perugia, Strada di Pentima 4, 05100 Terni, Italy
[§]Laboratory of Polymeric and Composite Materials, University of Mons (UMONS), Place du Parc 23, B-7000 Mons, Belgium
[‡]Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, calle Juan de la Cierva 3, 28006 Madrid, Spain

S *Supporting Information*

ABSTRACT: Smart multiresponsive bionanocomposites with both humidity- and thermally activated shape-memory effects, based on blends of ethylene-vinyl acetate (EVA) and thermoplastic starch (TPS) are designed. Thermo- and humidity-mechanical cyclic experiments are performed in order to demonstrate the humidity- as well as thermally activated shape memory properties of the starch-based materials. In particular, the induced-crystallization is used in order to thermally activate the EVA shape memory response. The shape memory results of both blends and their nanocomposites reflect the excellent ability to both humidity- and thermally activated recover of the initial shape with values higher than 80 and 90%, respectively.



KEYWORDS: *thermoplastic starch, shape memory, humidity, nanocomposite, thermomechanical cycles*

Thermally and humidity-activated shape memory properties for new-designed blends and bionanocomposites based on thermoplastic starch and ethylene-vinyl acetate were studied. The good results obtained by thermo- and humidity-mechanical cycles reveal the excellent ability to recover the original and fix the temporary shape, in both cases.

Shape-memory polymers (SMP) are stimulus-responsive materials able to change their shape by applying an external stimulus, such as temperature,[1−3] light,[4] humidity,[5] pH,[6] electric[7] or magnetic field,[8] etc. The shape-memory effect is not an intrinsic property of materials. Therefore, to show these properties, the materials require carrying out a two-stage process called "programming" and "recovery", respectively. In the first one, during the "programming", the material is deformed and fixed in a "temporary shape". In the second stage, upon the application of an external stimulus, the material recovers its initial permanent "fixed shape".[9]

In general, SMP are formed by two domains. One is the "fixity domain" and the other one acts as the "switching domain". The fixity domain maintains the shape of the polymer on actuation while the switching domain allows the occurrence of actuation. In addition, in the thermally activated SMP, the switching domain is characterized by a switching temperature (T_{sw}) correlated to a thermal transition of the polymeric segments, which enables the recovery of the permanent shape. It is well-known from the scientific literature that several molecular structures can show chemically or physically shape memory behavior such as interpenetrating polymer networks (IPN),[10] hydrogels,[6,11] semicrystalline polyurethanes,[2,12] blends,[13] etc.

In this work, a dual shape memory behavior is for the first time of our knowledge proposed on both thermoresponsive and humidity-responsive shape-memory effects.

Thanks to its biodegradability, low cost, and renewability, starch is thereby considered as a promising candidate for the development of environmentally friendly materials with multifunctional properties.[14−16] Although starch can be utilized as filler,[15,17] thermoplastic starch is preferred to be used as polymeric matrix after melt-processing native starch with plasticizers such as water and glycerol.[18] Because of its high ability to spontaneously self-assemble in function of temperature and water, starch-based materials can be considered as an interesting platform for water-responsive shape-memory performances.[19,20] To achieve the dual actuation, we melt-blended TPS with a partially miscible matrix, i.e., with EVA as a thermoresponsive. This partial miscibility has shown to be an important criterion to tune the SMP performances of miscible blends, e.g., made of PLA and PMMA with multishape SMP and temperature-memory effects.[21]

In particular, the EVA induced-crystals act as temperature-responsive switching phase responsible for fixing the temporary shape. EVA copolymers are multiphase materials exhibiting two

Received: June 2, 2016
Accepted: July 19, 2016
Published: July 19, 2016

DOI: 10.1021/acsami.6b06618
ACS Appl. Mater. Interfaces 2016, 8, 19197−19201

amorphous phases and at least two predominant crystalline phases as observed by Brogly at al.[22] Indeed, they assumed that two types of crystalline structures are involved in the melting behavior of EVA copolymers and exhibit different degrees of perfection of crystalline lamellae and morphologies. These structures are composed of a rather wide distribution of crystals both in size and morphologies. One of these has a poorly organized structure (A phase) and the other one is closer to that of pure polyethylene (B phase). In our system, a high mechanical deformation (250%) was applied in order to induce the formation of the crystal phase A. This stretch-induced crystallization is used in this work as the mechanism for studying the thermally activated shape memory effect. Indeed, mechanical stress affects the crystallization rate by modifying the entropy of activation.[23] As a polymer is stretched, the chains align and the overall entropy of the region decreases. The change in entropy associated with crystallization decreases with respect to the undeformed polymer, thus increasing the rate of crystallization. At the point that crystallization begins, the crystallization rate increases with the applied strain. Therefore, the thermally activated shape memory system was designed as follows:

- stable EVA network formed by an amorphous phase and crystalline phase B is the "fixity phase"
- crystalline phase A is the "switching phase"
- melting temperature of the crystalline phase A is considered the T_{sw}

Thermo-mechanical cycles were performed in order to study the thermally activated shape memory behavior of the materials.

In particular, two different blends with different TPS content, i.e., 40 and 50 wt %, have been tested and compared with neat EVA, as well as EVA/TPS blend-based nanocomposites reinforced with 1 wt % of natural bentonite, ($CLNa^+$). These nanofillers were considered as universal surfactant agent for blends to better control the interface between both polymeric components.[24−28]

The presence of the two different types of crystals in EVA was first confirmed by DSC analysis using the same programming condition used for the SMP activation, i.e., after stretching. In Figure 1 the DSC thermograms of the first cycle of nonstretched and stretched EVA are shown. In the inset of the figure the same is reported for the nonstretched and stretched nanocomposite, as an example of composite material. It is easy to note that while both nonstretched neat EVA and nanocomposite present only B-phase crystals, a new crystal phase is present after stretching the EVA-based samples with a T_m of about 47 °C. Thus, the desired two different crystal phases A and B were obtained in neat EVA as well as in EVA-based materials.

Therefore, the newly induced crystal phase A is the phase responsible for fixing the temporary shape of our system. When the heating is applied, the crystalline phase A melts and the system recovers its permanent shape. Knowing the role of EVA within these blends, the 3D thermomechanical stress−strain-temperature cycle and the 2D stress−strain diagram were determined for all the samples studied (Figure 2). To evaluate the repeatability of the shape-memory properties, we completed five different thermomechanical cycles for each sample.

The values obtained in every cycle for both the R_r and the R_f are summarized in Table 1.

Results show that the presence of TPS did not affect the induced thermoresponsive mechanism of EVA. The values reflect that the ability to recover the initial shape is excellent, showing R_r values higher than 90%. Moreover, the very high EVA ability to fix the temporary shape during the first cycle slightly decreases during the following thermomechanical cycles from 99 to 85%. When the TPS is added, the R_f values are maintained quite constant during all the thermomechanical cycles at about 88%. Moreover, the addition of the nanoclays did not affect the optimum results for R_r and R_f values presented by the neat blends in the heating responsiveness of these blends.

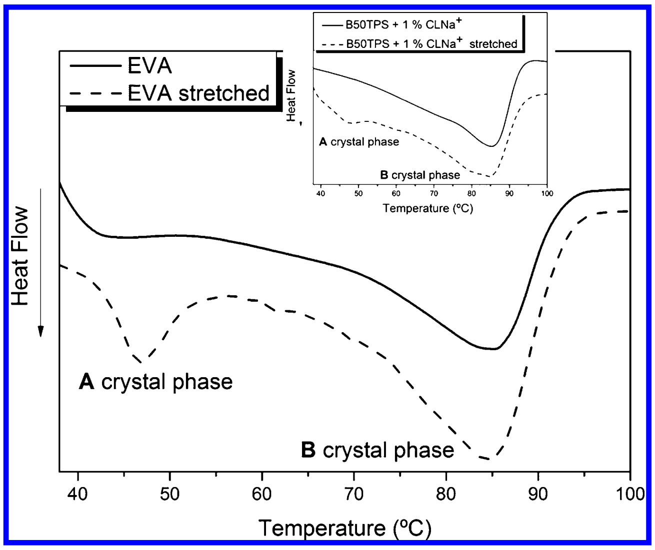


Figure 1. First cycle DSC thermogram of nonstretched and stretched EVA. In the inset the DSC thermograms for the nonstretched and stretched nanocomposite, sample B50TPS + 1% $CLNa^+$.

Furthermore, a preliminary humidity-activated shape memory test was performed. The samples were conditioned at room temperature and at 95% RH for 3 days before stretching it until 50% of elongation. Their fixation was performed at room temperature and at 50% RH and their recovery was triggered at 37 °C and 95% RH.[5,29,30] The samples were recovered in moisture saturated atmosphere instead of water immersion in order to avoid the swelling effect of the TPS phase and the migration of glycerol. In Figure 3, an example of humidity-activated shape memory recovery in an oven at 37 °C and 95% RH of the different samples is reported. In particular, L_i indicated the initial length of the sample, L_f the fixed shape. It is easy to note the stretched samples at the beginning of the test and the same samples recovered after 1 week.

Interestingly and from Table 1, the R_f and R_r values reflect that the ability to recover the initial shape is very good during the humidity-shape memory recovering, showing R_r values higher than 80%. Moreover, an increase in the R_r value in the corresponding bionanocomposites was observed probably because of the hydrophilic behavior of the nanoclay or to a certain enhancement of the miscibility within the blends.

In summary, multistimuli responsive shape memory bionanocomposites have been designed. In particular, humidity- and thermally activated shape-memory effect on bionanocomposites based on blends of EVA and TPS reinforced with 1 wt % of $CLNa^+$ was investigated. In particular, the induced-crystallization is used in order to thermally activate the EVA shape memory response. The shape memory results of both blends and their nanocomposites reflect the very good ability to both humidity- and thermally

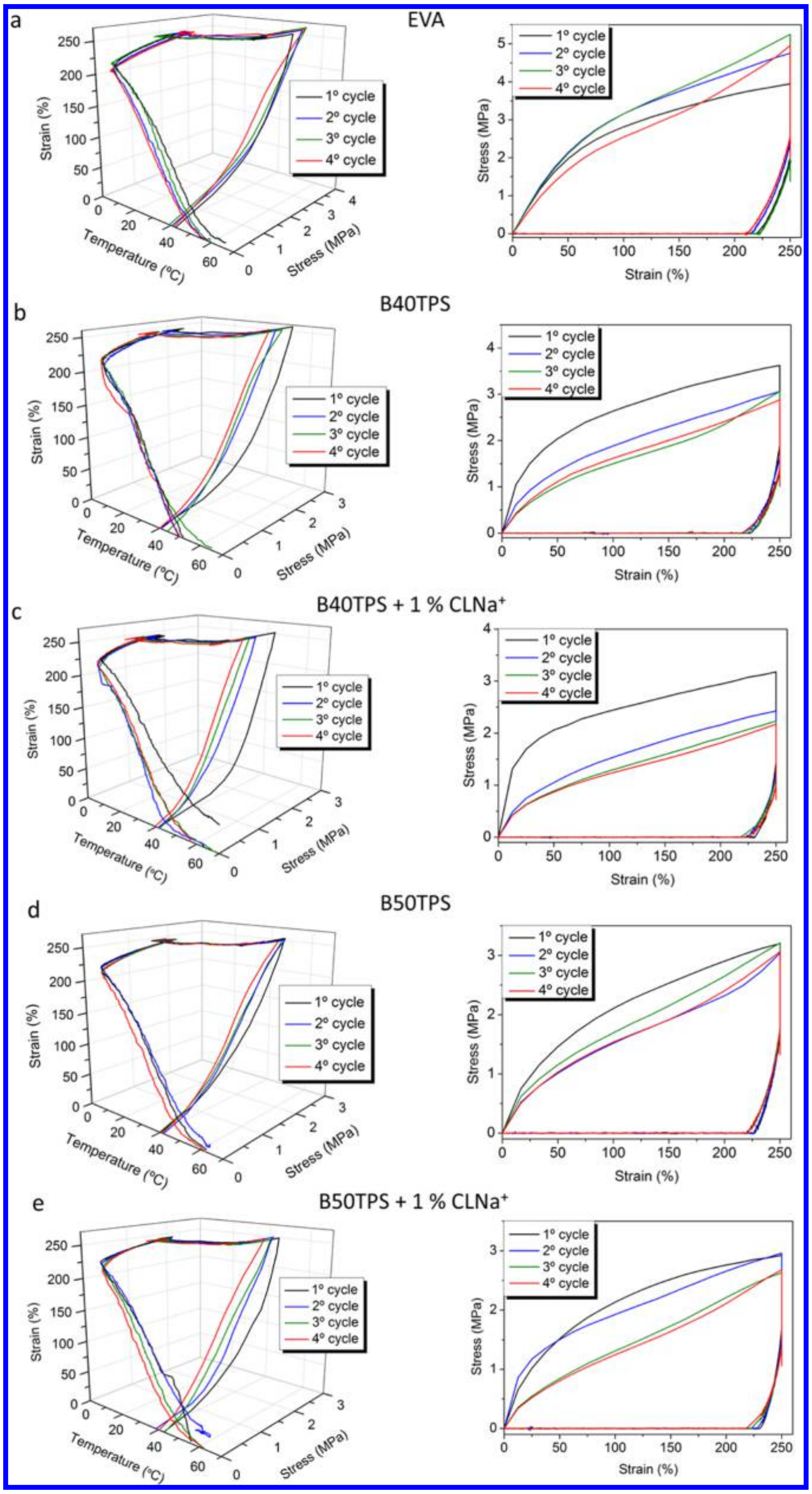


Figure 2. 3D thermomechanical stress−strain−temperature cycle and the 2D stress−strain diagram for (a) neat EVA, (b) B40TPS, (c) B40TPS + 1% CLNa$^+$, (d) B50TPS, (e) B50TPS + 1% CLNa$^+$.

activated recover of the initial shape with values higher than 80% and 90%, respectively. Moreover the ability to fix the temporary shape of these systems is very good, especially when nanofillers are added. This kind of materials could be used for biomedical applications exploiting the hydrophilic character of starch as a possibility instead of a problem. Indeed, it is possible to activate their shape memory effect by means of only humidity and the human body temperature.

Table 1. Values of R_r and R_f for Both the Thermally and Humidity-Activated Shape Memory Test for All the Samples Studied

	cycle									
	thermally activated								humidity-activated	
	R_r (%)				R_f (%)				R_r (%)	R_f (%)
sample	1	2	3	4	1	2	3	4	1	1
EVA	94	97	97	100	99	86	89	85	0	99
B40TPS	100	100	99	100	89	87	89	87	85	78
B40TPS + 1% CLNa$^+$	98	96	97	100	91	91	88	88	90	75
B50TPS	82	99	98	100	92	89	87	90	85	87
B50TPS + 1% CLNa$^+$	81	90	100	100	93	91	89	87	86	90

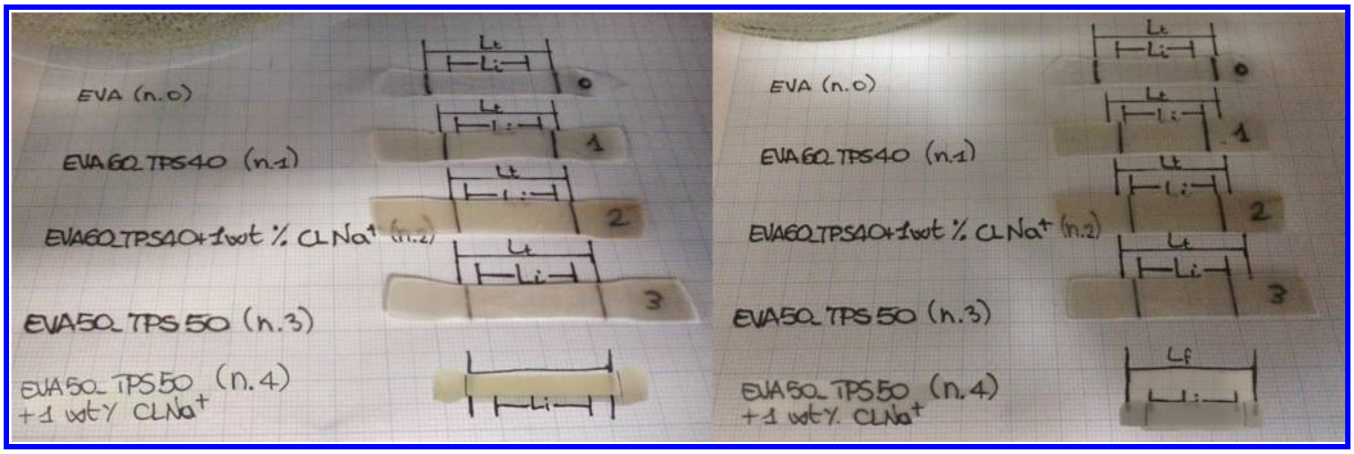


Figure 3. Humidity-shape memory recovering of different samples. Compare between neat EVA and different EVA/TPS blends and nanocomposites. On the left, the samples at the beginning of the test, and on the right, the samples after 1 week of recovering.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06618.

(S1) Materials and processing of blends and nanocomposites; (S2) characterization of the thermoactivated shape memory properties (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jean-marie.raquez@umons.ac.be.
*E-mail: lpeponi@ictp.csic.es.

Author Contributions

V.S. processed the samples with R.M. and G.L. and performed most of the measurements reported. L.P. and J.M.R. designed and guided the experimental work. V.S., L.P., and J.M.R. cowrote the paper. J.M.K. and P.D. revised the final manuscript. All authors discussed and commented the results of the paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are indebted to the Spanish Ministry of Economy and Competitiveness (MAT2013-48059-C2-1-R and MAT2014-55778-REDT) and to the Regional Government of Madrid (S2013/MIT-2862) for their economic support. L.P. acknowledges MINECO for the "Ramon y Cajal" (RYC-2014-15595) contract. UMONS authors are grateful to the "'Region Wallonne"' and European Community (FEDER, FSE) in the excellence program OPTI^{2}MAT for their financial support. UMons thanks the "Belgian Federal Government Office Policy of Science (SSTC)" for general support in the frame of the PAI-7/05. J.-M. Raquez is "'chercheur qualifié"' by the F.R.S.-FNRS (Belgium).

■ ABBREVIATIONS

EVA, ethylene-vinyl acetate
TPS, thermoplastic starch
SMP, shape memory polymer
T_{sw}, switching temperature
IPN, interpenetrating polymer network
PLA, polylactic acid
PMMA, poly(methyl methacrylate)
CLNa$^+$, sodium cloisite
T_m, melting temperature
DSC, differential scanning calorimetry
R_r, recovery ratio
R_f, fixity ratio

■ REFERENCES

(1) Lendlein, A.; Schmidt, A. M.; Langer, R. AB-Polymer Networks Based on Oligo (ε-caprolactone) Segments Showing Shape-Memory Properties. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98* (3), 842−847.

(2) Peponi, L.; Navarro-Baena, I.; Sonseca, A.; Gimenez, E.; Marcos-Fernandez, A.; Kenny, J. M. Synthesis and Characterization of PCL−PLLA Polyurethane with Shape Memory Behavior. *Eur. Polym. J.* **2013**, *49* (4), 893−903.

(3) Raquez, J. M.; Vanderstappen, S.; Meyer, F.; Verge, P.; Alexandre, M.; Thomassin, J. M.; Jérôme, C.; Dubois, P. Design of Cross-Linked Semicrystalline Poly (ε-caprolactone)-Based Networks with One-Way and Two-Way Shape-Memory Properties through Diels−Alder Reactions. *Chem. - Eur. J.* **2011**, *17* (36), 10135−10143.

(4) Ahir, S. V.; Terentjev, E. M. Photomechanical Actuation in Polymer−Nanotube Composites. *Nat. Mater.* **2005**, *4* (6), 491−495.

(5) Chen, S.; Hu, J.; Yuen, C.-w.; Chan, L. Novel Moisture-Sensitive Shape Memory Polyurethanes Containing Pyridine Moieties. *Polymer* **2009**, *50* (19), 4424−4428.

(6) Guo, W.; Lu, C. H.; Orbach, R.; Wang, F.; Qi, X. J.; Cecconello, A.; Seliktar, D.; Willner, I. pH-Stimulated DNA Hydrogels Exhibiting Shape-Memory Properties. *Adv. Mater.* **2015**, *27* (1), 73−78.

(7) Jung, Y. C.; Yoo, H. J.; Kim, Y. A.; Cho, J. W.; Endo, M. Electroactive Shape Memory Performance of Polyurethane Composite Having Homogeneously Dispersed and Covalently Crosslinked Carbon Nanotubes. *Carbon* **2010**, *48* (5), 1598−1603.

(8) Razzaq, M. Y.; Anhalt, M.; Frormann, L.; Weidenfeller, B. Thermal, Electrical and Magnetic Studies of Magnetite Filled Polyurethane Shape Memory Polymers. *Mater. Sci. Eng., A* **2007**, *444* (1), 227−235.

(9) Peponi, L.; Navarro-Baena, I.; Kenny, J. M. In *Smart Polymers and their Applications*, first ed.; Aguilar, M. R., Román, J. S., Eds.; Woodhead Publishing: Cambridge, U.K., 2014; Chapter 7, pp 204−236.

(10) Shivashankar, M.; Mandal, B. K. A Review on Interpenetrating Polymer Network. *Int. J. Pharm. Pharm. Sci.* **2012**, *4*, 1−7.

(11) Ahn, S.-k.; Kasi, R. M.; Kim, S.-C.; Sharma, N.; Zhou, Y. Stimuli-responsive Polymer Gels. *Soft Matter* **2008**, *4* (6), 1151−1157.

(12) Navarro-Baena, I.; Kenny, J. M.; Peponi, L. Thermally-Activated Shape Memory Behaviour of Bionanocomposites Reinforced with Cellulose Nanocrystals. *Cellulose* **2014**, *21* (6), 4231−4246.

(13) Navarro-Baena, I.; Sessini, V.; Dominici, F.; Torre, L.; Kenny, J. M.; Peponi, L. Design of Biodegradable Blends Based on PLA and PCL: From Morphological, Thermal and Mechanical Studies to Shape Memory Behavior. *Polym. Degrad. Stab.* **2016**, DOI: 10.1016/j.polymdegradstab.2016.03.037.

(14) Chaunier, L.; Véchambre, C.; Lourdin, D. Starch-based Foods Presenting Shape Memory Capabilities. *Food Res. Int.* **2012**, *47* (2), 194−196.

(15) Sessini, V.; Arrieta, M. P.; Kenny, J. M.; Peponi, L. Processing of Edible Films Based on Nanoreinforced Gelatinized Starch. *Polym. Degrad. Stab.* **2016**, DOI: 10.1016/j.polymdegradstab.2016.02.026.

(16) Avella, M.; De Vlieger, J. J.; Errico, M. E.; Fischer, S.; Vacca, P.; Volpe, M. G. Biodegradable Starch/Clay Nanocomposite Films for Food Packaging Applications. *Food Chem.* **2005**, *93* (3), 467−474.

(17) Angellier, H.; Molina-Boisseau, S.; Dole, P.; Dufresne, A. Thermoplastic Starch-Waxy Maize Starch Nanocrystals Nanocomposites. *Biomacromolecules* **2006**, *7* (2), 531−539.

(18) Park, H. M.; Li, X.; Jin, C. Z.; Park, C. Y.; Cho, W. J.; Ha, C. S. Preparation and Properties of Biodegradable Thermoplastic Starch/Clay Hybrids. *Macromol. Mater. Eng.* **2002**, *287* (8), 553−558.

(19) Véchambre, C.; Buléon, A.; Chaunier, L.; Gauthier, C.; Lourdin, D. Understanding the Mechanisms Involved in Shape Memory Starch: Macromolecular Orientation, Stress Recovery and Molecular Mobility. *Macromolecules* **2011**, *44* (23), 9384−9389.

(20) Véchambre, C.; Chaunier, L.; Lourdin, D. Novel Shape-Memory Materials Based on Potato Starch. *Macromol. Mater. Eng.* **2010**, *295* (2), 115−122.

(21) Samuel, C.; Barrau, S.; Lefebvre, J.-M.; Raquez, J.-M.; Dubois, P. Designing Multiple-Shape Memory Polymers with Miscible Polymer Blends: Evidence and Origins of a Triple-Shape Memory Effect for Miscible PLLA/PMMA Blends. *Macromolecules* **2014**, *47* (19), 6791−6803.

(22) Brogly, M.; Nardin, M.; Schultz, J. Effect of Vinylacetate Content on Crystallinity and Second-Order Transitions in Ethylene—Vinylacetate Copolymers. *J. Appl. Polym. Sci.* **1997**, *64* (10), 1903−1912.

(23) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-Induced Chemical Changes in Polymeric Materials. *Chem. Rev.* **2009**, *109* (11), 5755−5798.

(24) Ali, Z.; Le, H. H.; Ilisch, S.; Thurn-Albrecht, T.; Radusch, H.-J. Morphology Development and Compatibilization Effect in Nanoclay Filled Rubber Blends. *Polymer* **2010**, *51* (20), 4580−4588.

(25) Das, A.; Mahaling, R. N.; Stöckelhuber, K. W.; Heinrich, G. Reinforcement and Migration of Nanoclay in Polychloroprene/Ethylene−Propylene−Diene-Monomer Rubber Blends. *Compos. Sci. Technol.* **2011**, *71* (3), 276−281.

(26) Persenaire, O.; Raquez, J. M.; Bonnaud, L.; Dubois, P. Tailoring of Co-continuous Polymer Blend Morphology: Joint Action of Nanoclays and Compatibilizers. *Macromol. Chem. Phys.* **2010**, *211* (13), 1433−1440.

(27) Vo, L. T.; Giannelis, E. P. Compatibilizing Poly(vinylidene fluoride)/Nylon-6 Blends with Nanoclay. *Macromolecules* **2007**, *40* (23), 8271−8276.

(28) Peponi, L.; Puglia, D.; Torre, L.; Valentini, L.; Kenny, J. M. Processing of Nanostructured Polymers and Advanced Polymeric Based Nanocomposites. *Mater. Sci. Eng., R* **2014**, *85* (1), 1−46.

(29) Beilvert, A.; Chaubet, F.; Chaunier, L.; Guilois, S.; Pavon-Djavid, G.; Letourneur, D.; Meddahi-Pellé, A.; Lourdin, D. Shape-Memory Starch for Resorbable Biomedical Devices. *Carbohydr. Polym.* **2014**, *99*, 242−248.

(30) Mendez, J.; Annamalai, P. K.; Eichhorn, S. J.; Rusli, R.; Rowan, S. J.; Foster, E. J.; Weder, C. Bioinspired Mechanically Adaptive Polymer Nanocomposites with Water-Activated Shape-Memory Effect. *Macromolecules* **2011**, *44* (17), 6827−6835.