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Multi-responsive shape memory blends and nanocomposites based on starch

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KEYWORDS: thermoplastic starch, shape memory, humidity, nanocomposite, thermo-mechanical cycles.

ABSTRACT. Smart multi-responsive bio-nanocomposites 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 the 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.

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 electric⁷ or magnetic field,⁸ etc. The shape-memory effect is not an intrinsic property of materials. Therefore, in order 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 behaviour such as interpenetrating polymer networks (IPN),¹⁰ hydrogels,^{6, 11} semi-crystalline 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 thermo-responsive 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 Due to 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, TPS was melt-blended with a partially miscible matrix, i.e., with EVA as a thermo-responsive. 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 amorphous phases and at least two predominant crystalline phases as observed by Brogly et 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”;
- The crystalline phase A is the “switching phase”;
- The 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 non-stretched and stretched EVA are shown. In the inset of the figure the same is reported for the non-stretched and stretched nanocomposite, as an example of composite material. It is easy to note that while both non-stretched 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.

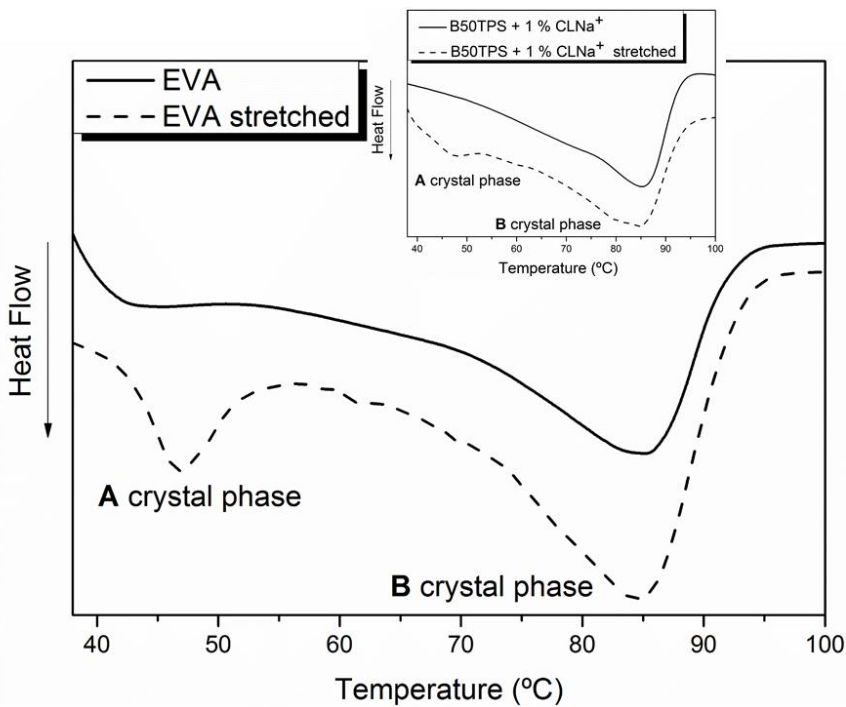
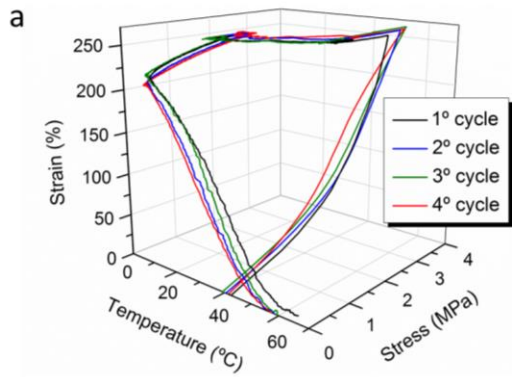
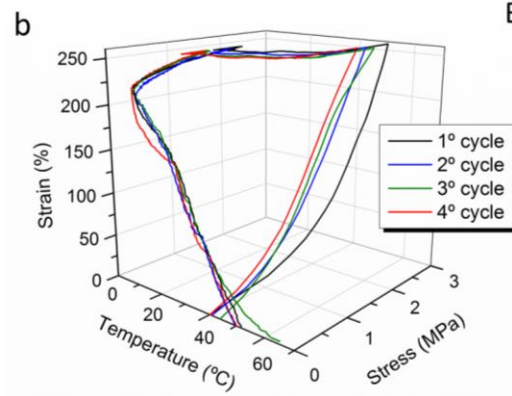
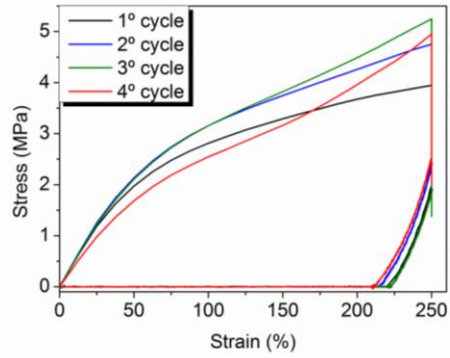


Figure 1. First cycle DSC thermogram of non-stretched and stretched EVA. In the inset the DSC thermograms for the non-stretched and stretched nanocomposite, sample B50TPS + 1 % CLNa⁺.

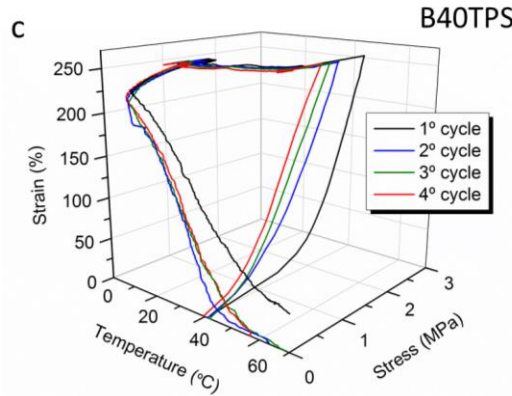
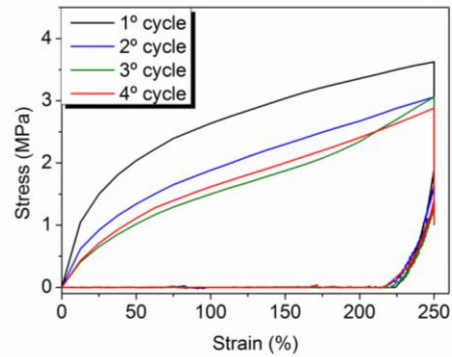
Therefore, the newly induced-crystal phase A is the phase responsible for fixing the temporary shape of our system. When the heating is applied, the crystalline phase A melts and the system recovers its permanent shape. Knowing the role of EVA within these blends, the 3D thermo-mechanical stress-strain-temperature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



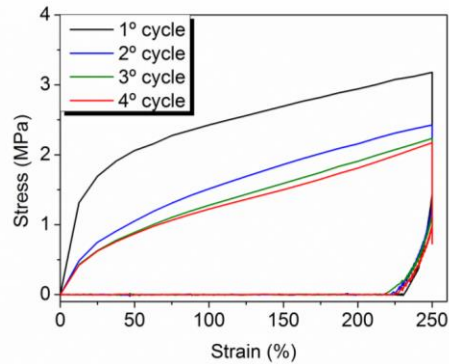
EVA



B40TPS



B40TPS + 1 % CLNa⁺



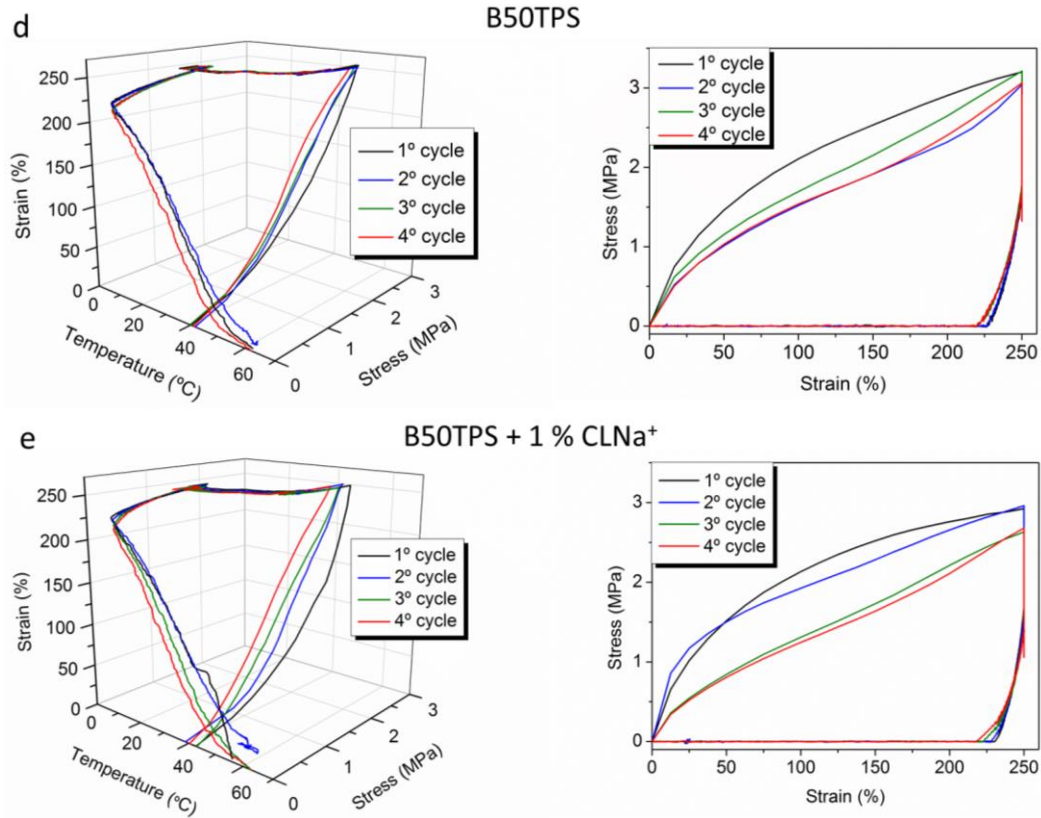


Figure 2. 3D thermo-mechanical stress-strain-temperature cycle and the 2D stress-strain diagram for (a) Neat EVA, (b) B40TPS, (c) B40TPS + 1 % CLNa⁺, (d) B50TPS, (e) B50TPS + 1 % CLNa⁺.

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

Table 1. Values of R_r and R_f for both the thermally and humidity-activated shape memory test for all the samples studied.

Sample	Thermally-activated								Humidity-activated		
	R_r [%]				R_f [%]				R_r [%]	R_f [%]	
	Cycle	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

Results show that the presence of TPS did not affect the induced thermo-responsive mechanism of EVA. The values reflect that the ability to recover the initial shape is excellent, showing R_f values higher than 90 %. Moreover, the very high EVA ability to fix the temporary shape during the first cycle slightly decreases during the following thermo-mechanical cycles from 99 % to 85 %. When the TPS is added, the R_f values are maintained quite constant during all the thermo-mechanical 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.

Furthermore, a preliminary humidity-activated shape memory test was performed. The samples were conditioned at room temperature and at 95 % RH for three 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 one week.

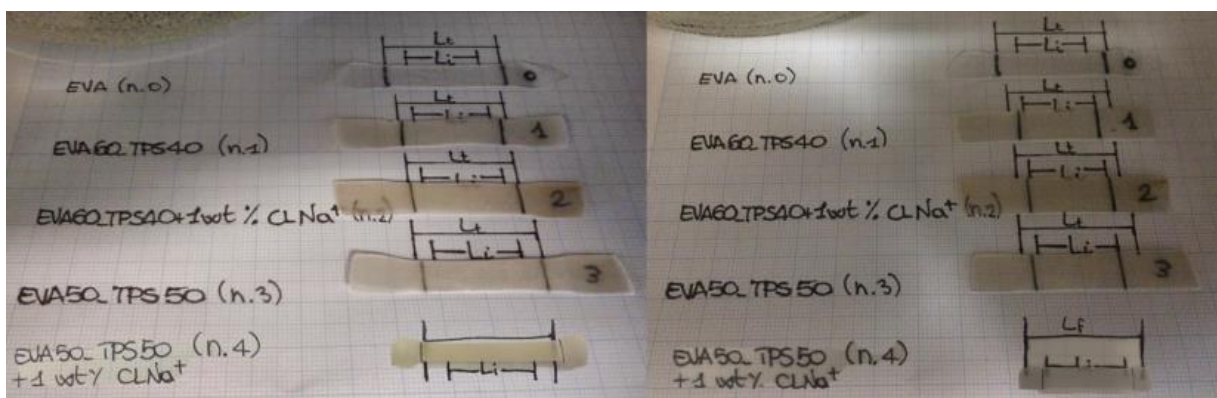


Figure 3. Humidity-shape memory recovering of different samples. Compare between neat EVA and different EVA/TPS blends and nanocomposites. On the left, the samples at the beginning of the test and on the right, the samples after one week of recovering.

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 of the R_r value in the corresponding bionanocomposites was observed probably due to the hydrophilic behaviour of the nanoclay or to a certain enhancement of the miscibility within the blends.

In summary, multi-stimuli 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-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 mean of only humidity and the human body temperature.

ASSOCIATED CONTENT

Supporting Information. (S1) Materials and processing of blends and nanocomposites. (S2) Characterization of the thermo-activated shape memory properties.

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Author Contributions

VS processed the samples with RM and GL and performed most of the measurements reported. LP and JMR designed and guided the experimental work. VS, LP and JMR co-wrote the paper. JMK and PD revised the final manuscript. All authors discussed and commented the results of the paper.

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2014-15595) contract. UMONS authors are grateful to the “Region Wallonne” and European Community (FEDER, FSE) in the excellence program OPTI²MAT 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.

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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.

