Performance of Thermoplastic Starch-based Nanocomposites under Environmental Aging Conditions

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Motivation

Thermoplastic starch-based nanocomposites represent an exciting and promising alternative to conventional plastics used in food packaging, automotive, medical, pharmaceutic, and agricultural industries since they are cost-effective, renewable, abundant in nature, and biodegradable.

Introduction

Thermoplastic starch (TPS) is a plasticized nonstructured version of starch. It is usually prepared by incorporation of plasticizers into a starch matrix under heat and shear conditions. TPS-based bioplastic nanocomposites represent an exciting and promising alternative to conventional plastics since they are cost-effective, renewable, abundant in nature, and biodegradable [1,2]. Moreover, it has been widely used as an excellent candidate for partial replacement of synthetic polymers. Addition of TPS to biodegradable compostable bioplastics is a useful application of TPS aimed to a decrease of price compromising certain deterioration of physical, especially mechanical properties. However, TPS suffers from recrystallization phenomena caused by humidity. This evolution is highly detrimental, as it leads to a drastic decrease in its mechanical properties during storage [3,4]. The addition of a definite amount of nanofillers can significantly improve the physico-chemical properties of TPS.

Herein, this contribution is focused on investigating the influence of aging under exactly defined relative humidities on the mechanical properties of TPS–montmorillonite (MMT) nanocomposite.

Methodology

➢ **Cloisite Na (MMT) particles: 0.02 part (parts based on the dry weight of starch)**
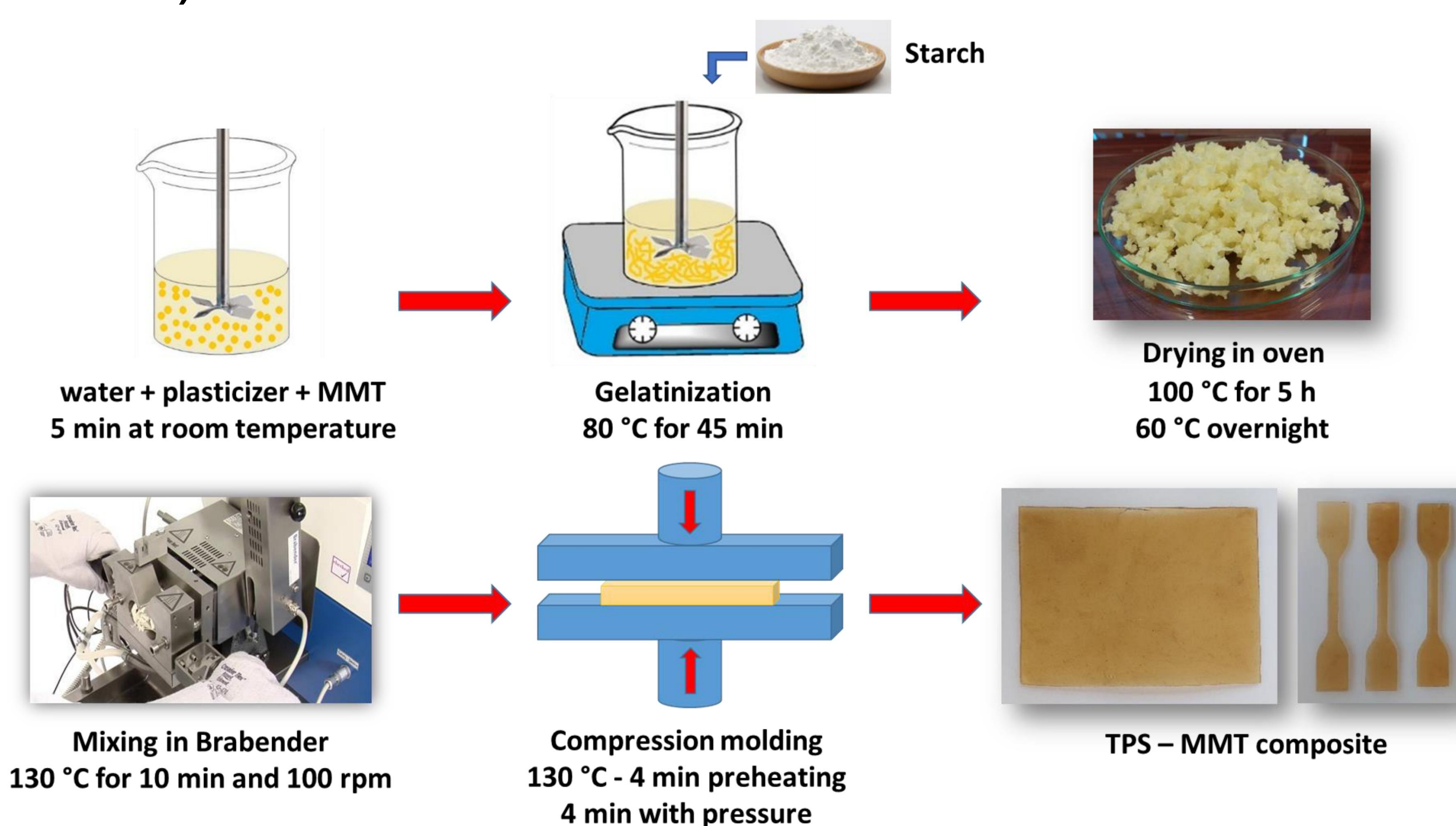

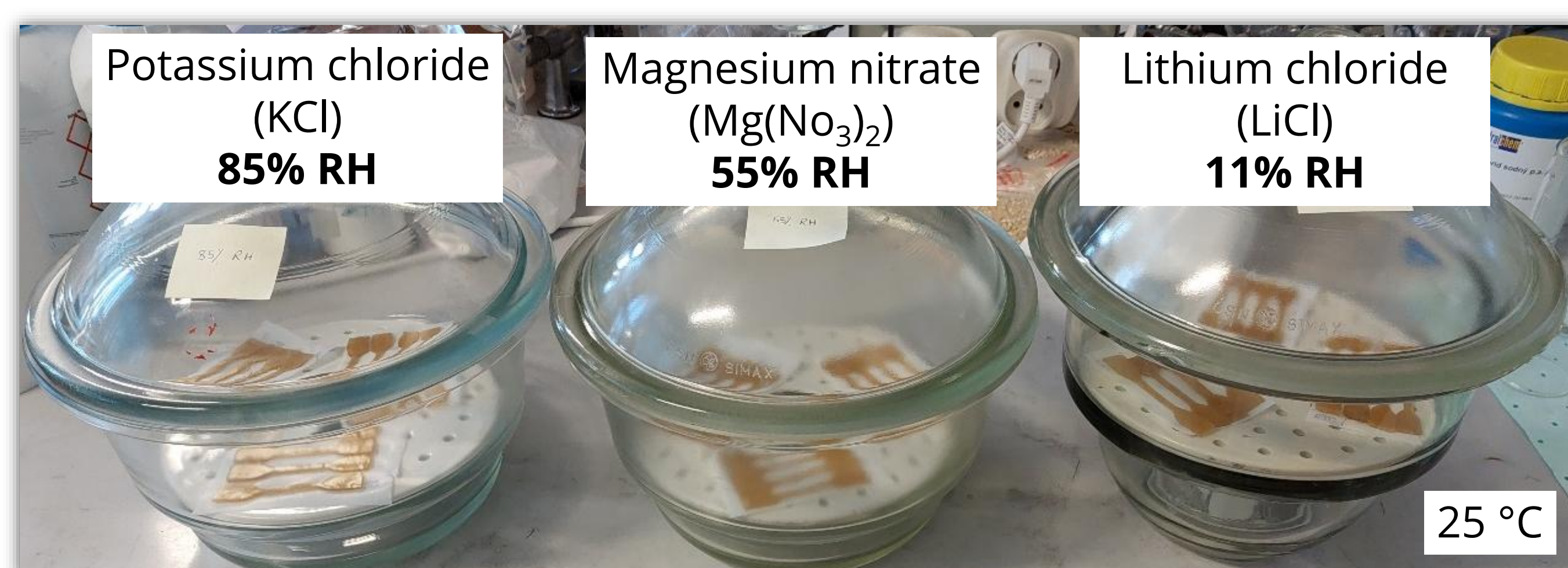**Fig. 1.** Process flow diagram for preparation of TPS–MMT composites

Fig. 2. Storage of the TPS–MMT samples in desiccators at different relative humidities (RH)

Acknowledgements

References

[1] Peidayesh H., Heydari A., Mosnáčková K., Chodák I.: Carbohydr. Polym. 118250, 269 (2021).
[2] Peidayesh H., Ahmadi Z., Khonakdar HA., Abdouss M., Chodák I.: Polym. Int. 69, 3 (2020).
[3] Šmídová N., Peidayesh H., Baran A., Fričová O., Kovaľaková M., Králiková R., Chodák I.: Materials. 16, 3 (2023).
[4] Baran A., Fričová O., Vrábel P., Popovič Ľ., Peidayesh H., Chodák I., Hutníková M., Kovaľaková M.: J. Polym. Res. 29, 7 (2022).
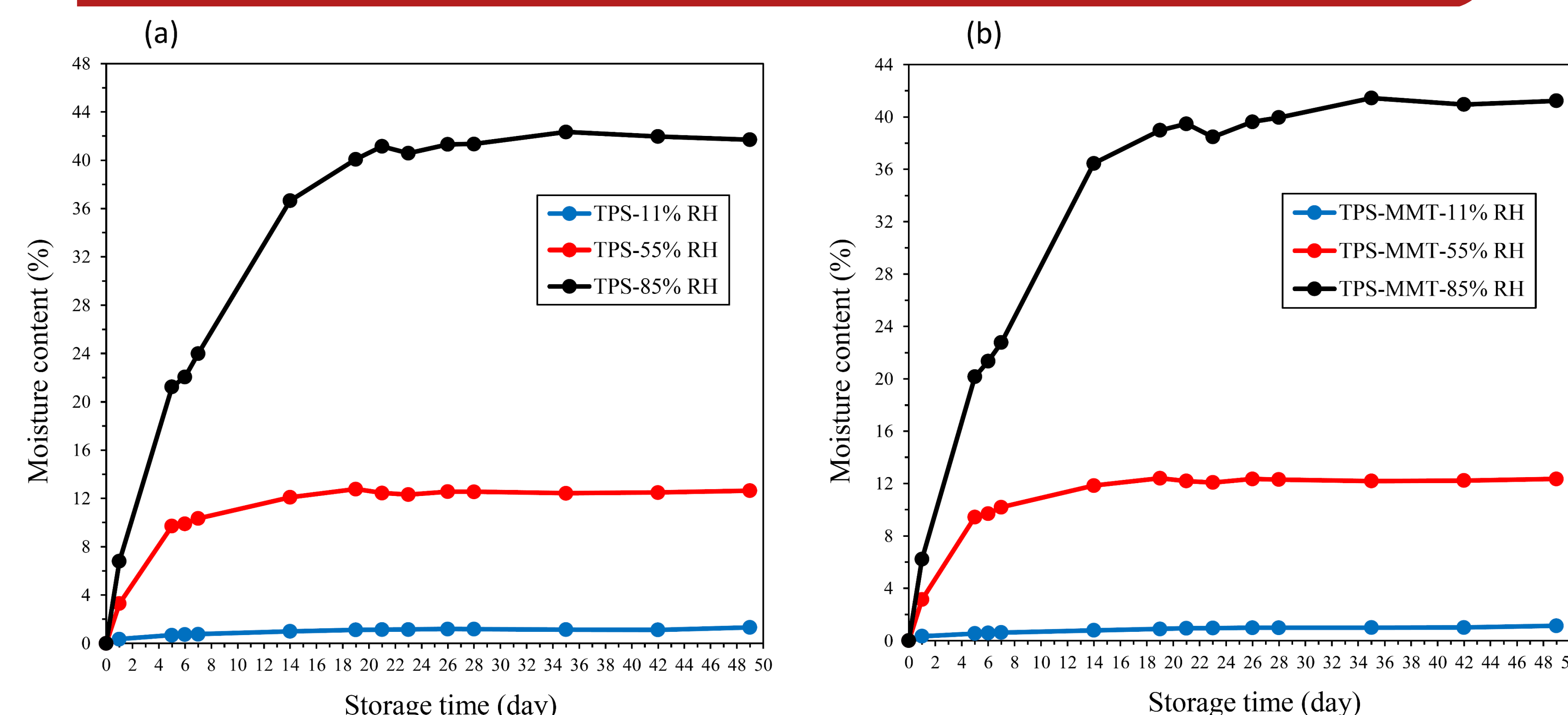
Results

Fig. 3. Moisture content curves for (a) TPS and (b) TPS–MMT samples stored at 11, 55, and 85% RHs for different storage times

❖ TPS and TPS–MMT samples reached equilibrium after one week at 11 and 55% RH, while they were absorbing moisture at 85% RH for up to five weeks to reach equilibrium.
❖ The nanocomposite samples reveal a slight lower amount of water absorption due to formation of hydrogen bonds between starch and MMT layers.

Table 1. Mechanical properties of the TPS and TPS–MMT samples stored at various humidities for one and seven weeks

	Sample Code	Dried	11% RH		55% RH		85% RH	
			1 week	7 weeks	1 week	7 weeks	1 week	7 weeks
Tensile Strength (MPa)	TPS	7.8 ± 2.7	9.3 ± 0.8	6.8 ± 0.5	1.3 ± 0.0	2.5 ± 0.1	1.3 ± 0.0	0.6 ± 0.1
	TPS–MMT	10.4 ± 1.1	11.5 ± 1.0	7.6 ± 0.2	1.4 ± 0.1	2.4 ± 0.4	1.3 ± 0.1	0.6 ± 0.1
Elongation at break (%)	TPS	1.5 ± 0.3	4.3 ± 1.6	27.1 ± 11.5	66.6 ± 2.1	34.4 ± 2.0	25.3 ± 1.2	8.2 ± 0.4
	TPS–MMT	1.7 ± 0.2	3.7 ± 0.8	31.4 ± 5.0	64.1 ± 8.9	27.8 ± 5.5	24.7 ± 1.1	7.6 ± 1.3
Young's Modulus (MPa)	TPS	970 ± 207	663 ± 75	297 ± 2.4	9.2 ± 0.5	25.2 ± 3.4	10.5 ± 0.4	9.4 ± 0.8
	TPS–MMT	1148 ± 47	703 ± 69	436 ± 4.3	10.0 ± 1.1	26.5 ± 1.3	10.9 ± 0.6	9.7 ± 0.5

❖ Tensile strength and Young's modulus of the dried samples and the samples stored at 11% RH increase with the incorporation of MMT.
❖ Tensile strength of both TPS and TPS–MMT samples is decreasing with rising RH.
❖ The higher amount of absorbed water at higher RH led to an increase in the mobility of starch chains which was caused by additional plasticizing effect.

Table 2. Temperatures of maximum values for tan δ appearance

Sample	1st Peak T (°C)				2nd Peak T (°C)			
	Dried	11% RH	55% RH	85% RH	Dried	11% RH	55% RH	85% RH
TPS	-31.3				75.5			
TPS-MMT	-28.9				86.7			
TPS- 1 week		-37.1	-54.0	n/a		71.3	8.9	n/a
TPS- 2 weeks		-37.6	-56.6	n/a		74.0	14.1	n/a
TPS- 3 weeks		-37.0	-56.0	n/a		72.4	6.1	n/a
TPS- 5 weeks		-35.6	-53.2	n/a		71.2	20.2	n/a
TPS- 7 weeks		-35.2	-58.5	n/a		69.9	11.3	n/a
TPS-MMT- 1 week		-40.2	-52.9	-61.8		70.9	13.3	-4.2
TPS-MMT- 2 weeks		-32.5	-57.5	-60.6		70.7	11.6	-22.6
TPS-MMT- 3 weeks		-20.3	-57.7	n/a		64.0	10.2	n/a
TPS-MMT- 5 weeks		-33.3	-55.4	n/a		72.7	2.8	n/a
TPS-MMT- 7 weeks		-38.5	-60.6	n/a		69.8	13.6	n/a

❖ T_g values for TPS-MMT nanocomposites are higher than for TPS samples due to the restrictions in starch chain mobility caused by a certain extent of intercalation of plasticizer molecules and starch chains into the MMT platelet galleries.
❖ The first peak, which is controlled by the plasticizer molecular motion, showed a shift to lower temperature for samples stored at higher RH.
❖ The presence of more water may decrease the intermolecular hydrogen bond density.

Conclusions

➢ **At 11% RH**, the samples did not recrystallize so that only physical ageing could take place throughout the whole period of storage.
➢ **At 55% RH**, recrystallization was happened during the first week of storage. After seven weeks of storage the samples stored at 55% RH showed improvements in mechanical properties due to newly formed interactions between starch, glycerol, and water making the structure stiffer.
➢ **At 85% RH**, the water molecules significantly reduced starch intermolecular hydrogen bonding density leading to deterioration of all mechanical properties measured.