Investigation of films based on hydroxypropyl methylcellulose and blends with zein as active packaging material

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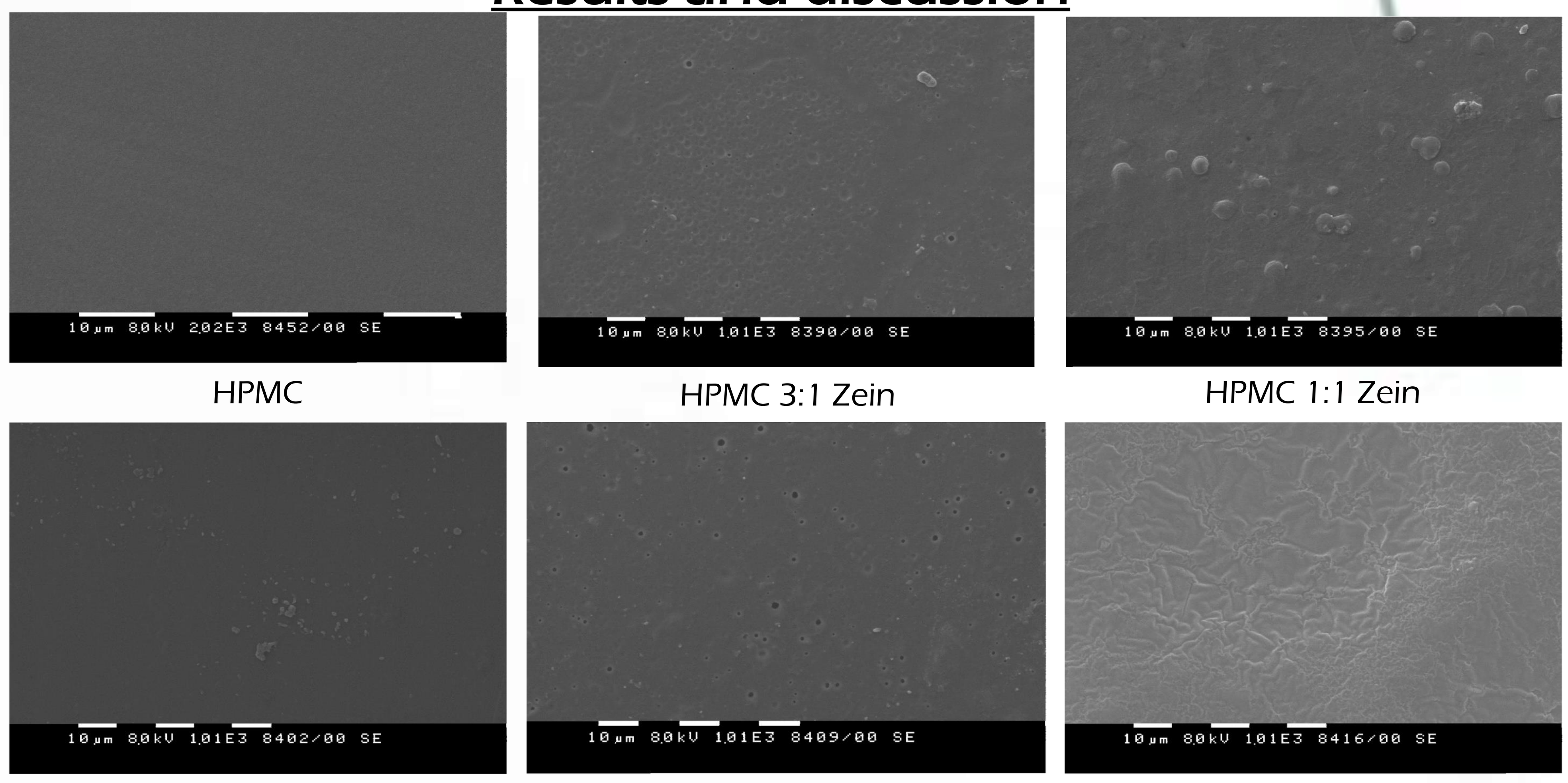
Background of this study

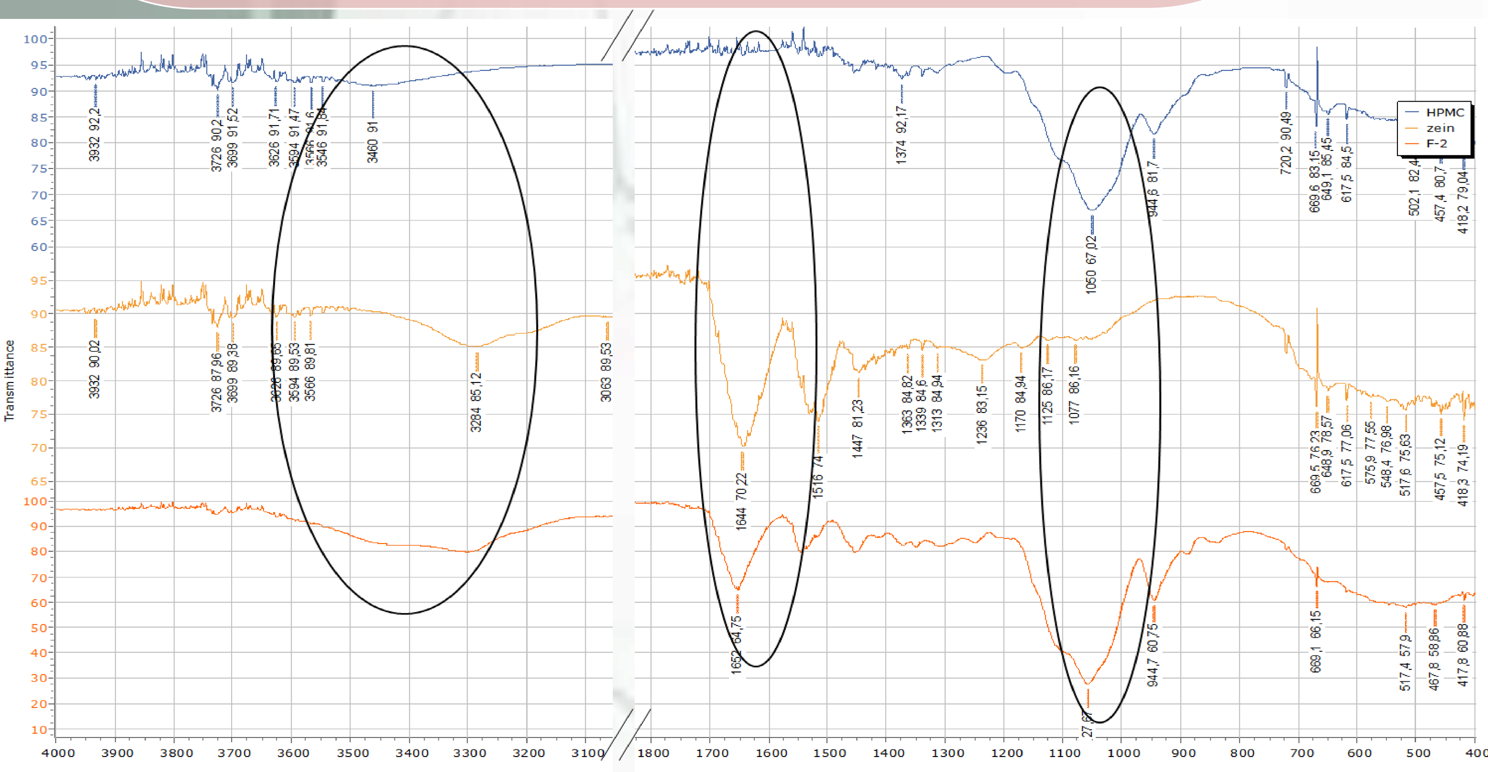
Active packaging films have gained significant attention as sustainable alternatives to conventional plastic packaging due to their biodegradability and ability to extend food shelf life by incorporating bioactive compounds. Hydroxypropyl methylcellulose (HPMC) offers quite beneficial film-forming properties, but exhibits quite high water vapour permeability and hydrophilicity. Therefore, combining it with hydrophobic biopolymers, such as zein, can be a suitable approach to obtain structures with customizable barrier, mechanical, and functional properties. The addition of compounds with bioactive properties can additionally improve these properties. Despite these advantageous outcomes, the optimal ratio between these two polymers for obtaining such a structure hasn't been examined. Also, the effect of the addition of rutin to such a structure and the overall behavior of this film haven't been reported.

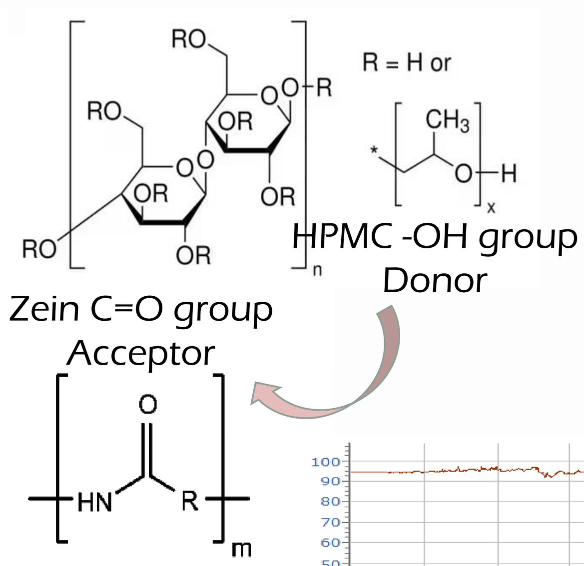
Results and discussion



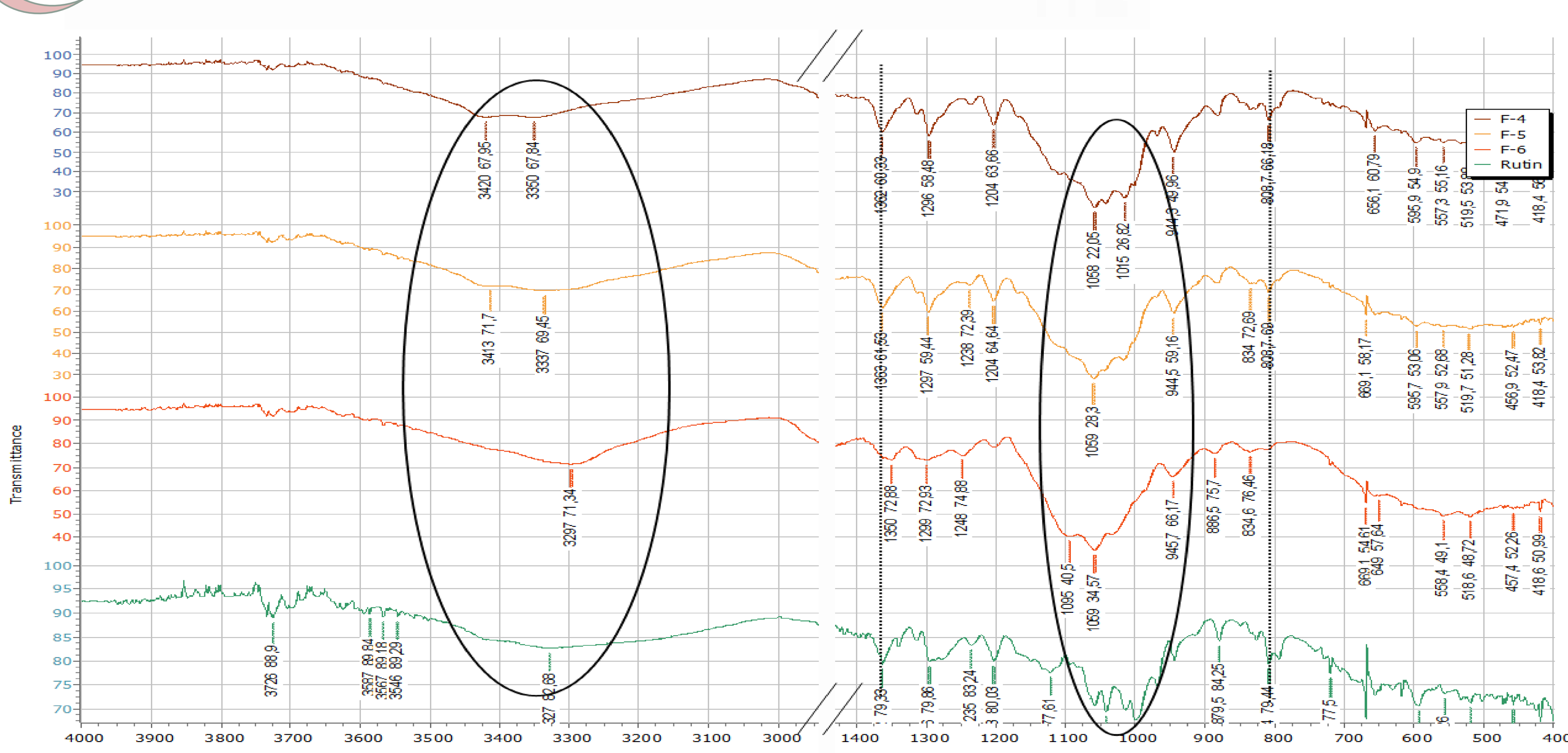
HPMC | HPMC 3:1 Zein | HPMC 1:1 Zein

HPMC + Rutin | HPMC 3:1 Zein + Rutin | HPMC 1:1 Zein + Rutin





Addition of zein leads to formation of oval shaped holes or particle-like formations, depending on the mass ratio between the two polymers. Presence of rutin had the most significant impact on the surface of the film, prepared by equal ratios of HPMC and zein, probably due to interaction with one of the polymers, namely zein.

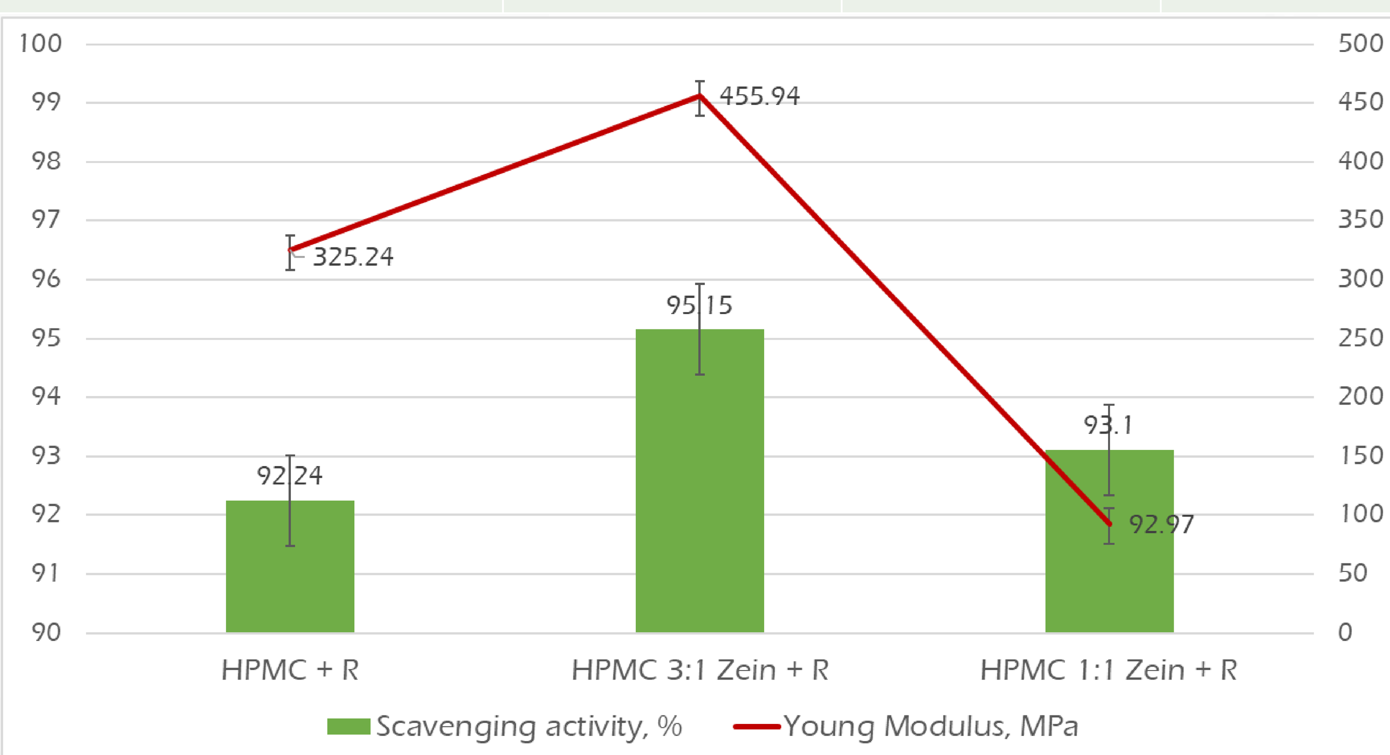


ATR-FTIR spectra of empty film compared to the native polymers (top figure) indicate change in peak intensities or shift in the wavelength number, due to possible H-bond formation between HPMCs' –OH groups and and zeins' active groups in primary and secondary amide region. Some change in ruin's characteristic bands is also noticeable (right-handise figure). More precisely, in the region of 3500-3200 cm^{-1} there is broadening of the peak and change in intensity and peak shape in the region of 1100-1000 cm^{-1}, typical again as a result of hydrogen bonds.

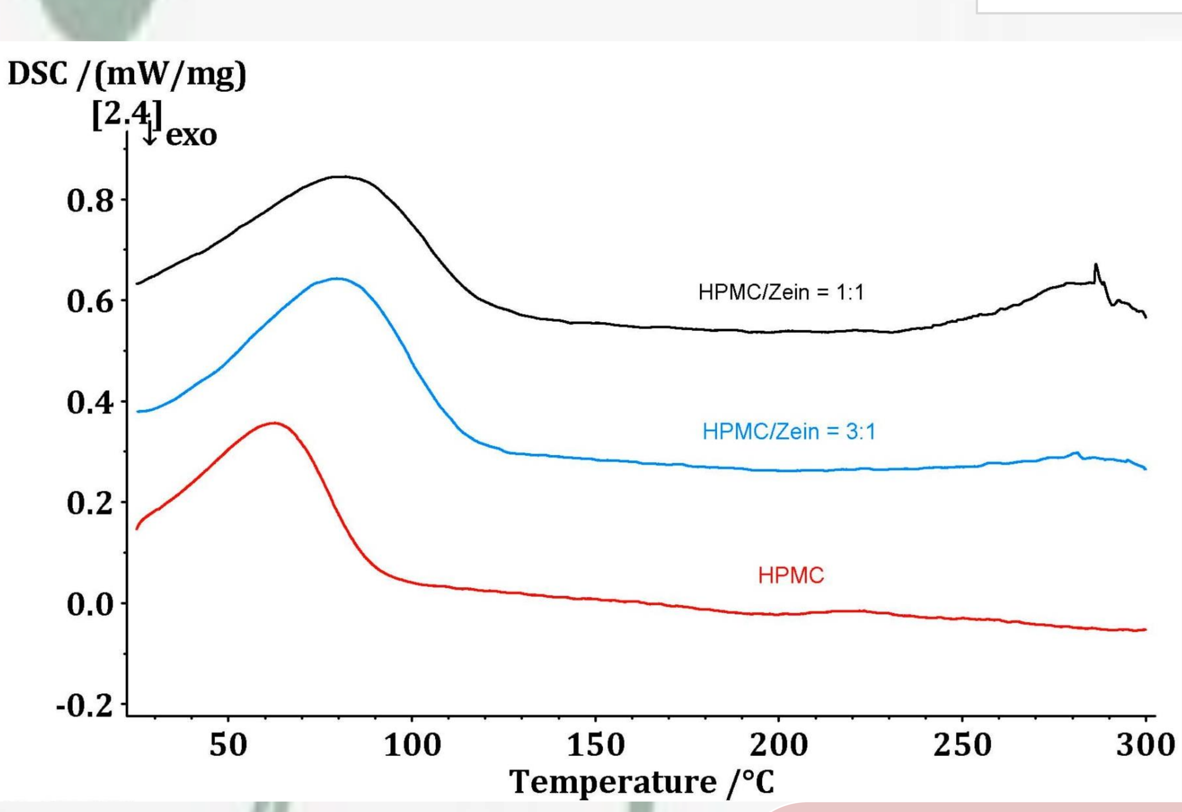
All of the obtained structures show relatively high strain at break (above 70%) prior rutin addition. A correlation between the load and stress at break and the concentration of zein in the film is evident, showing that these mechanical properties vary in accordance with the amount of zein present. This applies to the barrier properties as well. There is lowering in the permeability and transmission rate due to hydrophobicity of zein and rutin and longer diffusion path.

	HMPC	HPMC 3:1 Zein	HPMC 1:1 Zein	HPMC + Rutin	HPMC 3:1 Zein + Rutin	HPMC 1:1 Zein + Rutin
Young Modulus, MPa	276.98 ± 28.48	307.67 ± 30.73	52.17 ± 10.19	325.24 ± 69.78	455.94 ± 57	92.97 ± 15.80
Load at Break, N	54.58 ± 5.47	26.34 ± 5.36	16.76 ± 2.54	48.87 ± 9.34	35.36 ± 4.03	23.82 ± 2.80
Stress at Break, MPa	39.75 ± 3.68	20.54 ± 5.34	10.88 ± 1.87	30.39 ± 5.17	25.36 ± 3.75	13.55 ± 1.82
Strain at Break, %	86.74 ± 8.64	77.14 ± 12.20	72.44 ± 9.62	58.34 ± 9.30	16.41 ± 2.55	82.51 ± 9.61
Water vapor transmission rate, g/m^2.24h	913.07 ± 74.01	878.01 ± 6.29	873.05 ± 9.07	769.26 ± 40.85	762.70 ± 22.18	826.35 ± 33.67
Permeability, g.cm/(cm^2.s.Pa) x10^{12}	2.61 ± 0.22	3.19 ± 0.02	3.02 ± 0.08	2.58 ± 0.14	2.62 ± 0.07	3.19 ± 0.31

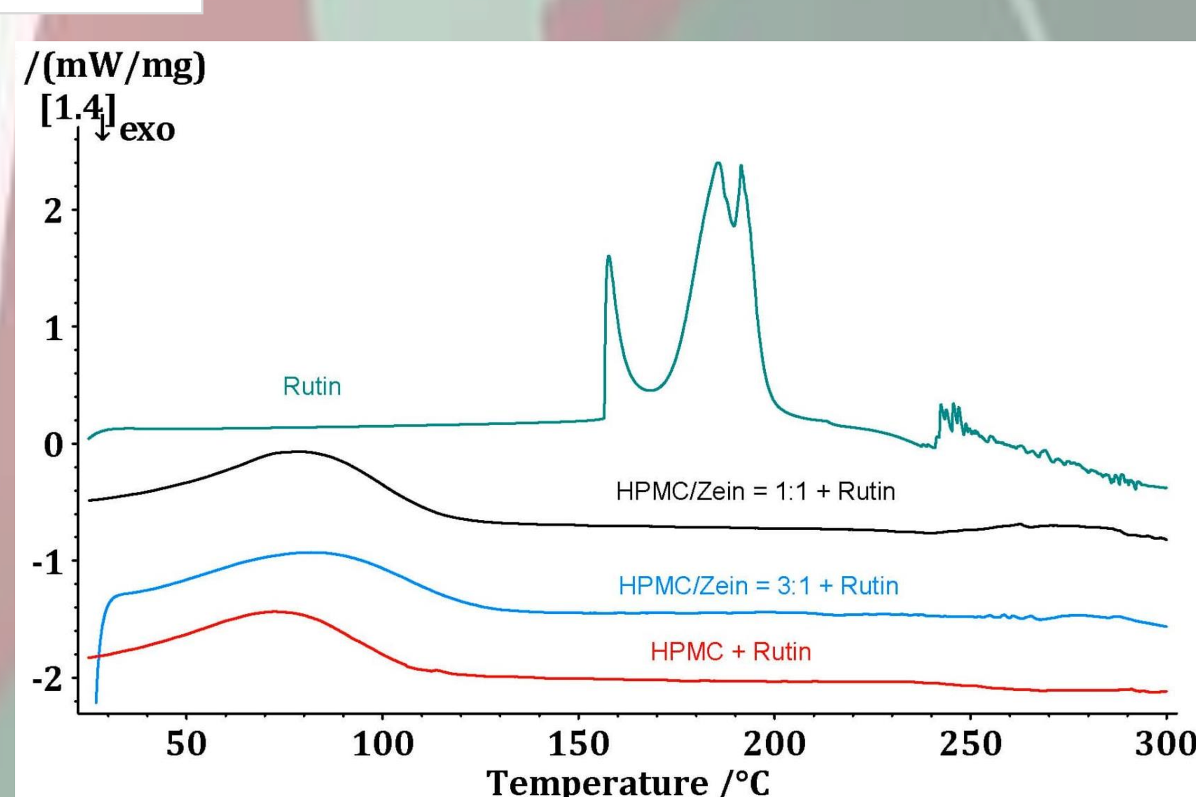
A-shaped trend line is observed for Young's Modulus of both loaded and empty films. At mass ratio 3:1 the ratio of active groups, that potentially form H-bonds, is 1,5 in favor of –OH groups and at mass ratio 1:1 this ratio shifts to 1,6, but in favor of C=O groups in zein. Consequently, there is a stronger interaction between the polymers at 3:1 and the structure becomes more compact and stiffer. Inclusion of rutin led to higher values of YM for all samples, but had the highest impact for the 1:1 mass ratio, leading to higher values.



Values of scavenging ability against DPPH free radicals followed the same tendency as the values of Young's Modulus. The highest one was at mass ratio 3:1 due to the fact that films with strong hydrogen bonds and a compact structure often show improved antioxidant properties. This is mainly because hydrogen bonding stabilizes the antioxidant molecule and facilitates the transfer of hydrogen atoms or protons to neutralize free radicals and sometimes synergistic effects.



Thermograms (left-handside) of all empty structures exhibit thermal stability up to 250 °C and wide peak from 50 °C up to above 100 °C due to evaporation of unbound water molecules. Native rutin starts (right-handside) to melt above 150 °C and decomposes above 250 °C. In rutin-loaded structures none of these peaks are to be seen. It can be concluded that, after its addition to this polymer matrix it underwent a phase transition as a result of its molecular dispersion and it was stable without inclination to recrystallization.



Conclusions

Biocompatible and biodegradable films with potential as active packages were prepared. HPMC film's structures were modified as a result of combining it with zein and rutin addition. This has led to interactions between them and alternation in the surface morphology. Mechanical and barrier properties were influenced as well, making the film structure less permeable and lowering the strain at break slightly. Young Modulus and antioxidant activity values followed A-shaped trend, due to the presence of interactions. All samples inhibited above 90% of the free DPPH radical. All samples exhibited thermal stability above 200 °C without recrystallization phenomena of the active compound.

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