

THERMAL STABILITY OF CHITOSAN NANOCOMPOSITES CONTAINING TiO₂ AND ORGANO-MODIFIED MONTMORILLONITE

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Abstract

The aim of this work was to investigate the effect of different nanoparticles (TiO₂ and organically modified montmorillonite MMT) on thermal stability of chitosan thin films (obtained by casting) and to compare with previously studied- CuO and Ag effect. Thermal degradation was carried out in air atmosphere at 140°C up to 100 hours.

Various functional groups of chitosan have a different susceptibility to degradation. The influence of nanoparticles amount on degradation of selected structural groups of chitosan was calculated. It was proved, that elongation at break of chitosan sample and its nanocomposites with TiO₂ and organically modified montmorillonite decrease rapidly after 20h of thermal degradation. Moreover, as is clear from FTIR studies, that TiO₂ nanoparticles enhance the resistant of the -C-O-C- bond responsible for chain scission of chitosan due to thermal degradation. An opposite effect is observed in a case of MMT, where the chain scission of -C-O-C- bond is higher than for pure chitosan. Another effect of nanoparticles are observed in destruction of unstable amine group (-NH₃ band at 1560 cm⁻¹) and formation of the amide group (band at 1650 cm⁻¹). In this case both nanoadditives accelerate the decomposition of amine group and the formation of amide group in higher extent in comparison to pure chitosan.

Key words: chitosan, titanium dioxide nanoparticles, organo-modified montmorillonite, thermal degradation

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1. Introduction

In the last two decades, scientist have shown significant scientific and technological interest in polymer-inorganic nanocomposites (PINCs). The incorporation of inorganic nanoparticles into polymer matrices can result in novel high-performance materials that find applications in many industrial fields. With the development of nanotechnology, there has been a tremendous growth in the application of nanoparticles (NPs) for drug delivery systems, antibacterial materials, cosmetics, sunscreens, and electronics [1,2].

Polymer nanocomposites are two-phase materials in which the polymers are reinforced by nanoscale fillers. The one of the most often used filler material is montmorillonite (MMT). MMT has been employed in many nanocomposite systems because it has a potentially high-aspect ratio and high-surface area that could lead to materials which could possibly exhibit great property enhancements. In addition, it is environmentally friendly, naturally occurring, and readily available in large quantities [3].

Over recent years, hybrid materials based on chitosan have been developed, including conducting polymers, metal nanoparticles and oxide agents due to excellent properties of individual components and outstanding synergistic effects simultaneously. Currently, TiO₂ NPs are manufactured in large quantities and widely used due to their high stability, antimicrobial, anticorrosive and catalytic properties [4].

The process of thermal degradation of chitosan in isothermal conditions was the subject of our previous studies [5-9]. In order to use nanocomposites in design-critical applications it is necessary to understand their structure, property and function relationships. Despite many reports of highly favorable properties, the behavior of polymer nanocomposites is not generally predictable. The mechanism of isothermal degradation and changes in chemical structure of chitosan during thermal degradation, confirmed by spectroscopic analysis, were described. Chitosan thermal degradation results in destruction of unstable amine group, scission of the main chain, crosslinking, oxidation and decrease of deacetylation degree.

It is necessary to point out that specimens studied in this work were obtained from acetic acid solutions of chitosan, thus, in fact chitosan acetate is present in solid state. As previously described in detail [10], it is impossible to remove completely the excess of acetic acid and to convert chitosan salt to chitosan even during long term drying at elevated temperature.

2. Materials and methods

Chitosan (Deacetylation degree 85%, Viscosity 120 mPas) were purchased from Hepepe Biomaterial GmbH i.G. Titanium (IV) oxide, TiO₂ (nanopowder, particles size: 20 nm) has been obtained from IoLiTec Nanomaterials GmbH, Germany. Organo-modified montmorillonite (Nanofil2) was purchased from Sud-Chemie.

Chitosan nanocomposites in the form of films with a thickness 10 and 35 μm containing nanoadditives of amount 1 and 2 % by weight was obtained by casting. 1% acetic acid was used as a solvent for chitosan. Nanoparticles were initially dispersed using ultrasounds in a solvent and then added to chitosan solution. Solutions were then stirred mechanically and ultrasonically.

The samples have been exposed to temperature 140°C. Maximum time of exposure was 80 h (for FTIR study).

After defined period of exposure time, the polymeric films was systematically analyzed used FTIR spectroscopy (Genesis II FTIR, Mattson, USA) and mechanical strength test (Instron 5325, according to norm EN-ISO 527-1 and EN-ISO 527-3). Dried films were tested using 5 samples for each measurement. The test was carried out at ambient temperature and at a cross-head speed of 5 mm/min.

3. Results and discussion

The aim of this work was to investigate the effect of different nanoparticles (TiO_2 and organically-modified montmorillonite) on thermal stability of chitosan thin films.

3.1. SEM micrographs

Figure 1 shows an example of SEM photos of CS+1% TiO_2 and CS+1%Nanofil2 nanocomposite. These images indicate the relatively uniform distribution of nanoparticles within polymeric films.

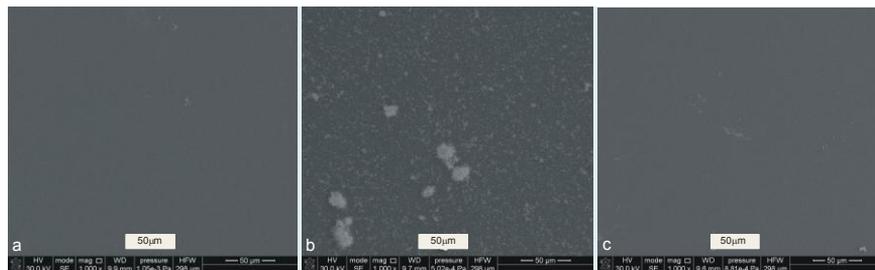


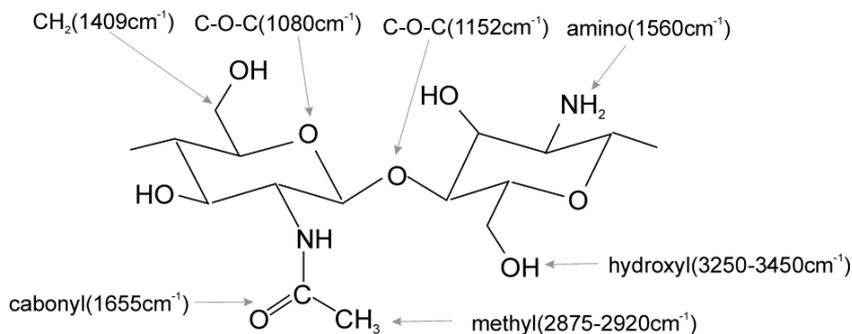
Figure 1. SEM photos of (a) chitosan, (b) chitosan/1% TiO_2 and (c) chitosan/1%Nanofil2 nanocomposites.

Some agglomerations of nanoparticles are shown in chitosan/ TiO_2 nanocomposites. Metal nanoparticles move upon drying and form aggregates. Better dispersion were obtained for chitosan/Nanofil2 films.

3.2. FTIR - structure characterization.

FTIR spectroscopic studies allowed to estimate molecular changes induced by high temperature in samples studied. The main changes observed in the chemical structure of chitosan and its composites with TiO_2 and MMT induced thermal degradation was a decrease of the amine group $-\text{NH}_2$ (1556cm^{-1}), formation of amide group (1655cm^{-1}) and scission of chitosan chains (decrease

of absorbance at 1080cm⁻¹). The films containing up to 1% of TiO₂ and MMT do not show any significant changes in FTIR spectrum compared to pure chitosan. Scheme 1 shows the structure of chitosan chain and the wavenumbers corresponding to the vibrations of chemical bonds.



Scheme 1. Chitosan chain with functional groups.

Figure 2 (a,b,c) presents the curves describing processes occurring in chitosan and its nanocomposites obtained on the base of the relative absorbance changes (A_t/A_0) of selected bands drawn versus time of thermal degradation.

As it is seen, nanoparticles presence has significant effect on thermal stability of chitosan functional groups. Destruction of C-O-C group (chain scission) increases in chitosan composites with organically modified montmorillonite. Induction time equal to about 10h is observed.

Concentration of amine groups (-NH₂) decreases upon thermal treatment by about 30% in chitosan/2% Nanofil2 and 20% in chitosan/TiO₂ nanocomposites, while in a case of pure chitosan films its drop is equal to 10%.

Increase of amide group concentration (C=O band at 1655cm⁻¹) is approximately 65% for chitosan, 80% for chitosan/TiO₂ and 100% for chitosan/Nanofil2 nanocomposites.

3.3. Mechanical properties

Improvement of elongation at break (EB) is observed in nanocomposites containing organically modified montmorillonite (Nanofil2) and nanosilver. Titanium dioxide has no pronounced effect on the initial mechanical properties of chitosan. As a result of thermal degradation, decrease of elongation at break (EB) and increase of Young's Modulus of chitosan and chitosan nanocomposites were observed due to increase of stiffness and brittleness of chitosan. Figure 3 shows comparison of elongation at break of chitosan and its nanocomposites with TiO₂ and Nanofil2 with previously studied nanosilver and copper oxide hybrid composites.

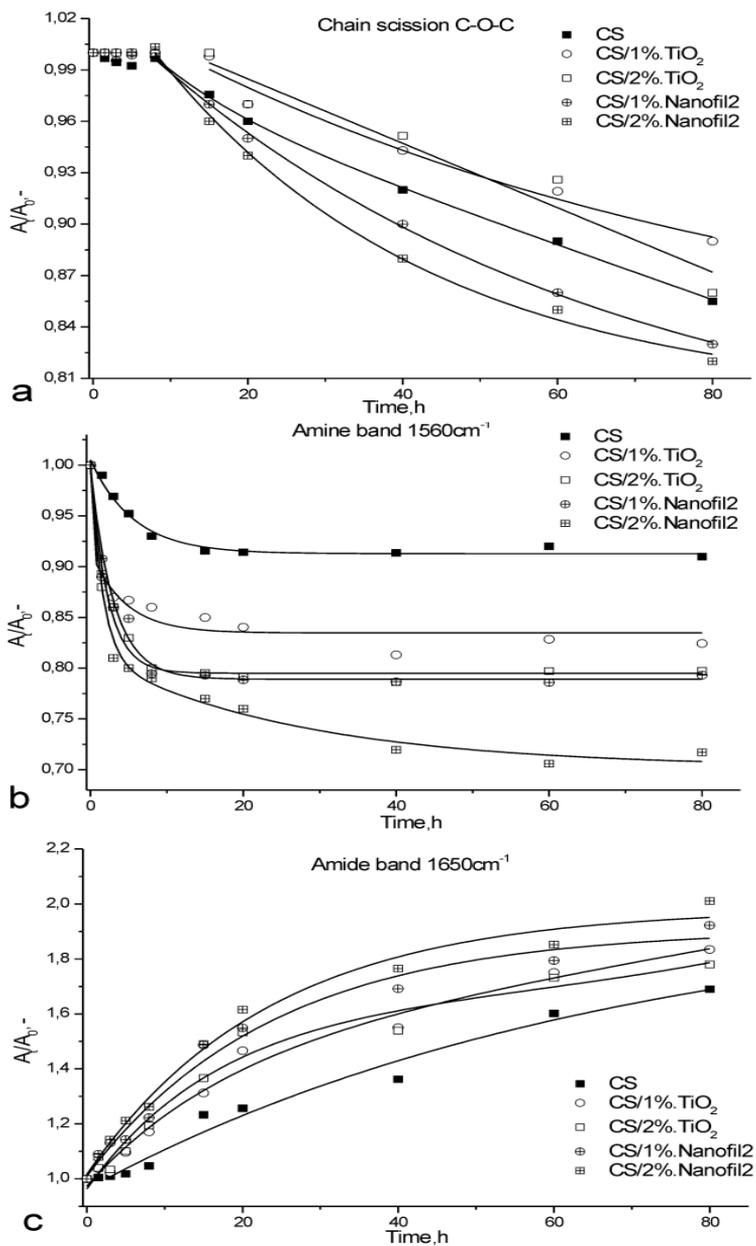


Figure 2. Relative changes of absorbance A_t/A_0 of selected bands from FTIR spectra of chitosan and its composites with 1 and 2% content of TiO_2 and Nanofil2: (a) C-O-C (1080cm^{-1}), (b) NH_2 (1577cm^{-1}), (c) C=O (1655cm^{-1}).

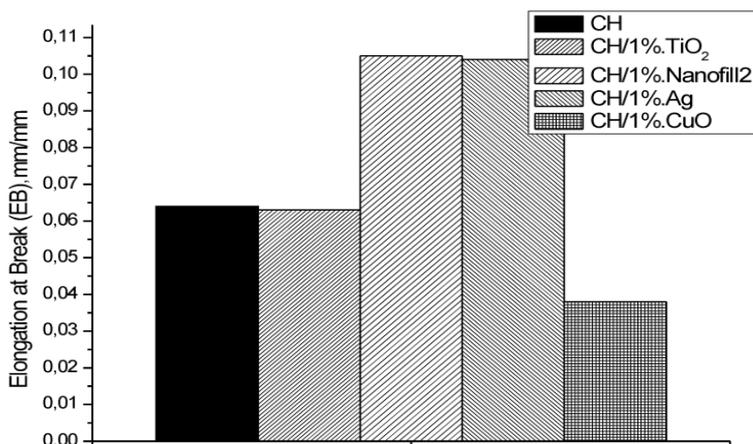


Figure 3. Elongation at break (EB) of chitosan nanocomposites before thermal treatment.

Figure 4 presents the relative changes of elongation at break of chitosan and its nanocomposites during thermal degradation.

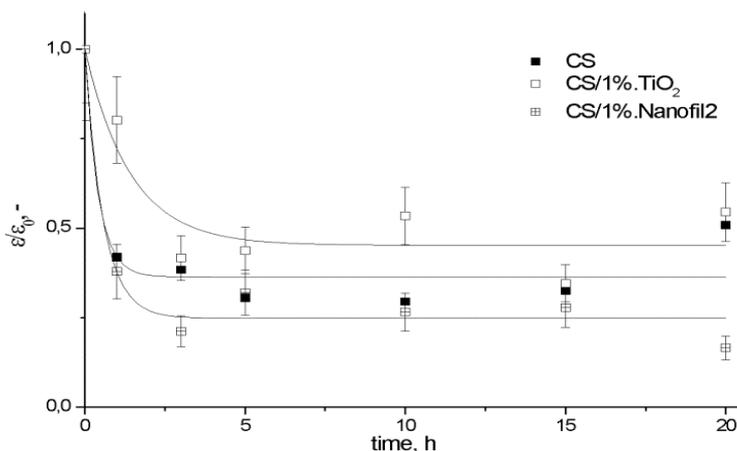


Figure 4. Effect of thermal treatment on relative elongation at break (EB) of the nanocomposites

It is seen, that samples starts to degrade immediately. After about 3h of the degradation the elongation at break is reduced by about 60% for chitosan, 50% for chitosan/ TiO_2 and 80% for chitosan/Nanofil2 nanocomposites.

4. Conclusions

In this study, the CS-TiO₂ and CS-Nanofil2 (nanoclay) thin films were prepared by solution casting method. On the basis of FTIR studies, it was found that thermal degradation extent of investigated samples depends on the presence of nanoparticles. Thermal stability of chitosan was improved by the presence of titanium dioxide. Relative EB and chain scission observed in destruction of -C-O-C- group in FTIR studies have changed weaker than in a case of pure chitosan. Opposite effect is observed in a case of nanocomposites containing organically modified montmorillonite- thermal stability is lower than of pure chitosan. It is known that organo-modified montmorillonite is unstable in thermal degradation process. The products of its decomposition can affect the degradation of chitosan molecules.

Previous studies [8,9] of chitosan thermal stability in nanocomposites with nanosilver and copper oxide have shown, that presence of the additives make worse thermal stability of chitosan.

An addition of CuO causes in deterioration of mechanical properties. During the dispersion of CS and CuO nanoparticles in acetic acid solution, CuO is changed into copper cations Cu²⁺ which are stable in neutral and mild acidic media. Copper ions can be coordinated by amine groups of chitosan [10].

5. Acknowledgements

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