Biobased UV-blocking Composites Mediated by Nanoparticle Assembly

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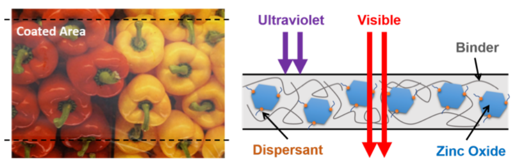
ABSTRACT

- A thin, biobased nanocomposite with exceptional UV-blocking (95%) and visible transparency (>70%) was synthesized from cellulose derivatives and ZnO nanoparticles.
- Choice of polymer binder mediates nanoparticle assembly, with the formation of assembly networks promoting high levels of UV-blocking.
- A new methodology which differentiates optical behaviors (scattering, absorption, transmission, reflection) is introduced and applied.
- With the new method, wavelength dependent scattering and absorption behaviors were identified.
- The polymer mediated assembly is shown across various nanoparticle identities including TiO_2, SiO_2, and polystyrene.

GRAPHICAL ABSTRACT



INTRODUCTION

- Light filtering coatings have great potential to alleviate the effects of light induced degradation of sensitive products such as food and dyes.
- Here, we suggest a biobased, thin, highly transparent plastic coating for application on common packaging materials.[1]
- The coating has three key components: light-blocking nanoparticle, polymeric binder, and chemical dispersant.
- It was shown that hydroxyethyl cellulose (HEC) and hydroxyethyl starch (HES) polymer matrices form distinctly different nanoparticle assembly structures.
- The assemblies formed by HEC provide improved UV-blocking whilst maintaining visible transparency.
- The optics of the coating follows a mixed mechanism of absorption and scattering behaviors, quantified with a new analytical instrument which measures apparent absorption as a function of distance.
- The biobased character of the coating provides functionality with reduced environmental impact.
- The use of other nanoparticles to form similar structures provides opportunities in coating application.

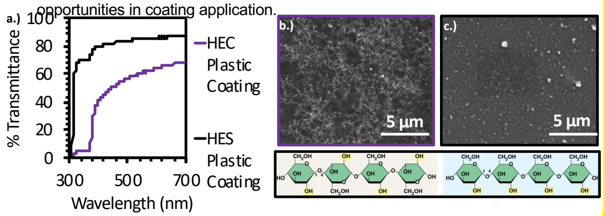


Figure 1. a.) UV-Vis spectra of the HES and HEC plastic coatings with ZnO nanoparticles. b.) SEM of HEC coating. c.) SEM of HES coating. It is found that the nanostructure in the plastic coatings occurs at the expense of binder selection.

RESULTS AND DISCUSSION

- Two polymers were explored in this study: hydroxyethyl starch and hydroxyethyl cellulose, both with ZnO nanoparticles and Tween20 surfactant formulated into coatings.
- Differences in the mesostructure are observed in these coating films due to the persistence length of the binder, which impacts assembly mechanism (Figure 1).
- The assembly structures alter the optical properties of the films, with more open network structures promoting larger degrees of UV-blocking.
- The optical capacity of the films was identified via the introduction of a new technique which uses distance to probe scattering and absorption behaviors (Figure 2).

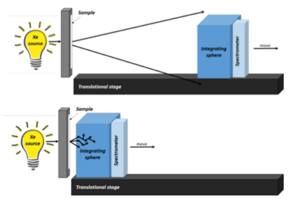


Figure 2. Light scattering instrument composed of a spectrophotometer and translation stage to differentiate optical behaviors as a function of distance.

- The method was validated with reflecting and diffusing standards (***Figure 3***) according to the ratio identified in ***Equation 1***.
- Measurement of the two coating systems shows a mixed mechanism of scattering in the UVB and UVA and absorption in the UVC (***Figure 3***).
- HEC coating films show higher levels of scattering in the UVA at the expense of the nanoparticle assembly structures.
- Similar structures were formed with different nanoparticles including TiO_2, SiO_2, and ZnO nanopowder (all 30 nm) (***Figure 4***).

$$Apparent\ Absorbance = {}^{Absorbance_{Distance}}/_{Absorbance_0} \qquad \textbf{Equation 1}$$

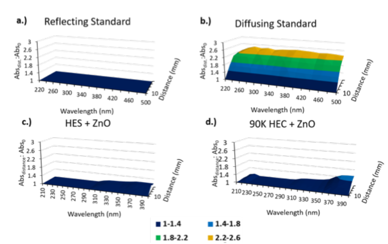


Figure 3. Validation of the light scattering instrument with a.) reflecting and b.) diffusing standards and measurement of c.) HES and d.) HEC coating films with ZnO nanoparticles. HEC polymer matrices appear to promote higher degrees of scattering.

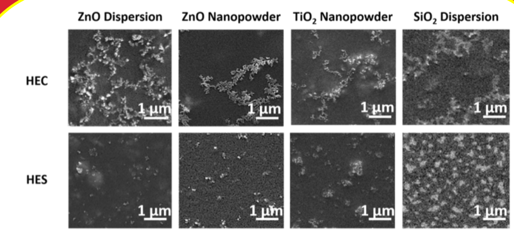


Figure 4. Various nanoparticle identities in HEC and HES matrices. Choice of polymer matrix continues to dictate nanoparticle assembly.

CONCLUSIONS

- Nanoparticle assembly can be controlled with the choice of polymer matrix, with HEC initiating the formation of branched structures and HES initiating typical dispersion behavior.
- Differing assembly patterns allow for different capabilities in the coating film (i.e. UV-blocking with ZnO and HEC).
- Optical mechanism (and wavelength dependence) can be identified with the use of a new analytical instrument which measures apparent absorption as a function of wavelength and distance.

NEXT STEPS

- To better understand the drivers for polymer mediated assembly, the wet drying process will be tracked with fluorescent polystyrene particles (***Figure 5***).
- The impact of particle size and surface chemistry, as well as the polymer molecular weight, and loading will be assessed in this system.
- The structures will be quantified for fractal dimension and lacunarity.

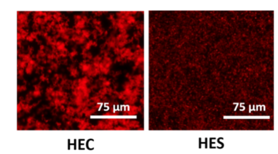


Figure 5. Rhodamine isothiocyanate (RITC) labelled polystyrene beads (2 µm) in HEC and HES matrices.

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REFERENCES

[1] 2018. Olson, E., Jiang, S. UV Absorbing Coating Including Zinc Oxide Nanoparticles. ISURF #04777.