

Encapsulation and Controlled Thermal Release of Vegetable Oils from Organic Nanoparticles for Functional Coating Applications

P. Samyn*, D. Stanssens**

*University of Freiburg, Freiburg Institute for Advanced Studies (FRIAS), Chair for Bio-based Materials Engineering, 79085 Freiburg, Germany, pieter.samyn@fobawi.uni-freiburg.de

**Topchim N.V., Wommelgem, Belgium, info@topchim.be

ABSTRACT

In this study, nanoparticles of poly(styrene-maleimide) or SMI containing different types of vegetable oil have been synthesized, which can favourably be applied as a barrier resistant coating against water and oil penetration onto paper substrates and regulate its surface hydrophobicity. First, different oils such as soy-, corn-, rapeseed-, castor-, sunflower and palm-oil were encapsulated during the imidization of poly(styrene-maleic anhydride) or SMA. The morphology of imidized SMA/oil nanoparticles changes with oil type, having homogeneous spherical shapes (20 to 60 nm) for poly-unsaturated oils, core-shell shapes for mono-unsaturated oils, or containing free oil at the surface for the most saturated oils. The vegetable oils favourable serve as a natural binder within the coating and enhance the hydrophobicity of paper substrates. Moreover, the release of vegetable oils at the paper surface during thermal treatment has been followed by spectroscopy and AFM observation, while the stability against thermal release depends on synthesis parameters.

Keywords: organic nanoparticles, vegetable oil, paper coating, release

1 INTRODUCTION

The development of protective and functional coatings for paper applications gained popularity in recent years to provide the paper surface with desirable properties while maintaining the paper bulk as a renewable substrate. In parallel, however, severe chemical treatment of the paper surface should be avoided in order to promote the sustainability and recyclability of paper products. The barrier resistance and wettability of papers is nowadays largely controlled by the application of waxes and/or fluoroderivates, as e.g. done by Stauffer et al. [1], or Schuman et al. [2]. The waxes improve the surface hydrophobicity, but they cannot be easily glued and require additional corona or plasma treatment for preserving good printing properties. The waxes also tend to migrate to the surface and thereby form a continuous layer that hold the fibers together and reduce the recyclability, as described by Hubbe et al. [3]. The extrusion of thermoplastic polyolefin films (LDPE) on one or both sides of the paper in

combination with a water resistant adhesive is industrially most relevant, but also poses implications during recycling.

Driven by innovation in papermaking and development of new products, the application of nanotechnologies provides new opportunities for creating hydrophobic and functional surfaces. The use of nanomaterials in paper coatings nowadays mainly focuses on nano-clays, inorganic pigments, minerals, ceramics, and starch [4]. The use of bio-based nanoadditives is considered since recent times including, e.g., microfibrillated cellulose [5]. A real breakthrough for bio-based nanotechnology in papermaking is lacking, mainly due to limited production and adequate processing techniques for the latter materials on industrial scale. A general problem to overcome is the equal dispersion of nanoparticles into a matrix material and processing parameters that are compatible with the paper production process. In this paper, we present an approach where renewable oils are incorporated into an aqueous dispersion of nanoparticles. The latter can be applied in parallel with traditional paper coating processes, improving the hydrophobicity of the coating. Moreover, the nanoscale pigments add further functionality to the paper coating as the mobility of the oil phase can be controlled by thermal heating and dispensing the oil at the paper surface.

2 MATERIALS AND METHODS

Hybrid organic nanoparticles were synthesized in a 1-liter autoclave, loading poly(styrene-maleic) anhydride or SMA together with vegetable oil, ammonium hydroxide and water. The styrene maleic anhydride (SMA) contains 26 mol-% maleic anhydride (MA) and has a weight-averaged molecular weight of 80,000 g/mol. Different vegetable oil types were added, such as palm-oil (PO), soy-oil (SO), sunflower-oil (ZO), corn-oil (MO), rapeseed-oil (KO), and castor-oil (CO) in a weight ratio of 50/50 relatively to the polymer phase.

The reaction mixture (850 ml) was stepwise heated to 160°C, at a rotation speed of 300 rpm, under a maximum pressure of approximately 6 bar, allowing for partial imidization of the maleic anhydride moieties into styrene maleimide (SMI) nanoparticles. After a total reaction time of 4 hours, the formation of nanoparticles was observed and characterized by a sudden drop in viscosity. After the

reaction mixture was cooled to room temperature, it was evacuated from the reaction vessel. The nanoparticle dispersions were applied by bar-coating on standard grade paper, using a K303 Multi-coater from RP-Print Coat Instruments, Ltd. The coatings were dried for 2 min at 100°C and stabilized for at least one day. Thermal release of oil was studied by heating the coated papers in a circulating hot-air oven at temperatures between 30 and 220°C. Contact angles were measured on a Digidrop equipment (GBX, France) and FTIR spectra were made on a Spectrum GX (Perkin Elmer). Raman mapping was done on a Raman Flax 400 (Perkin Elmer).

3 RESULTS AND DISCUSSION

3.1 Nanoparticles with encapsulated oil

At a fixed oil content of 50 wt.-%, the partial imidization reaction of SMA was successfully performed in presence of different types of vegetable oil. The nanoparticles were obtained in homogeneous and stable water dispersions, without further addition of surfactants or stabilizing agents. The absence of a two-phase water/oil mixture after reaction demonstrates that the oil is effectively encapsulated by the polymer phase and the partially imidized SMI polymer acts as a surfactant for stabilizing the dispersion. No oil separation from the water phase could be observed, even after more than three months standing time at room temperature. The characteristics of waterborne dispersions containing hybrid nanoparticles with encapsulated oil are given in Table 1. The pH < 7 for all dispersions indicates a small remaining fraction of carboxylic acid due to ring-opened maleic anhydride moieties. It is not surprising that CO provides highest viscosity, due to the presence of hydroxyl groups in ricinolic fatty acids that build hydrogen bonds throughout the dispersion. The morphology of imidized SMA/oil nanoparticles changes with oil type, having homogeneous spherical shapes (20 to 60 nm) for poly-unsaturated oils, core-shell shapes for mono-unsaturated oils (Figure 1).

The reaction conditions have been optimized for different precursors by evaluating the relative amounts ammonium hydroxide and maximizing the incorporated oil

up to 70 wt.-%. The interactions between the palm oil and polymer phase have been studied by TEM, IR and Raman spectroscopy and thermal analysis (TGA, (TM)DSC). From Raman spectra (Figure 2), the amounts of imide and reacted oil were quantified. The chemical imidization reaction in presence of vegetable oils resulted in a chemical esterification of the fatty acid with the ring-opened anhydride moieties. Due to concurring effects of imidization and coupling of the fatty acids, the imidization needs a slight excess of NH₃ relatively to maleic anhydride. The oxidative stability highly depends on oxidative crosslinking of free or non-reacted oil. Comparing the imide contents from spectroscopic and thermal analysis suggests that a complex rigid imide phase without strong relaxation behavior has formed in combination with oil.

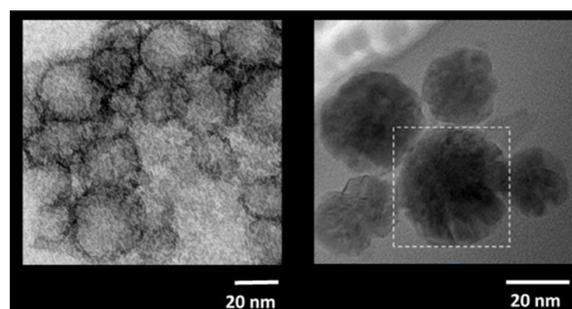


Figure 1. TEM observation of SMI/oil nanoparticles.

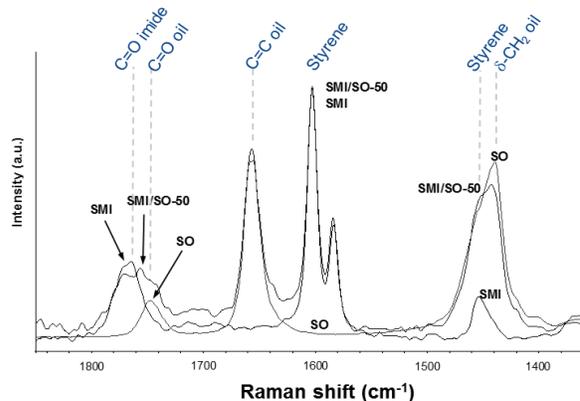


Figure 2. Raman spectra of SMI/oil nanoparticles.

Table 1. Characterisation of hybrid nanoparticles with different types of vegetable oils.

Name	pH	S.C. (%)	Viscosity (cp)	z-Average particle size, diameter by DLS (nm)	Particle size (polydispersity)
SMI/SO-50	5.48	49.8	146	149	0.163
SMI/MO-50	5.44	49.9	102	143	0.161
SMI/KO-50	5.43	49.5	91	156	0.137
SMI/CO-50	5.72	49.9	230	148	0.137
SMI/ZO-50	5.38	48.8	134	143	0.176
SMI/PO-50	5.48	50.0	104	140	0.210

3.2 Nanoparticle coatings

After application of the nanoparticle dispersions as a top-coating on a standard paper grade, the morphology was studied with AFM and SEM. The surface-adsorbed hybrid nanoparticles most likely forms an covering film (Figure 3), where the underlying cellulose fibers are not visible anymore. The physical characteristics of the hybrid nanoparticle coatings are summarized in Table 2. Some coatings offer relatively high water absorption, while SMI/PO-50 most effectively acts as a water repellent barrier coating. All of the coated surfaces behave hydrophobic and may be influenced by presence of the oil-phase around the polymer nanoparticle phase. However, the hydrophobic properties sometimes only show up after certain relaxation time of the coating, which may be attributed to more complex dynamics of oil presentation to the surface.

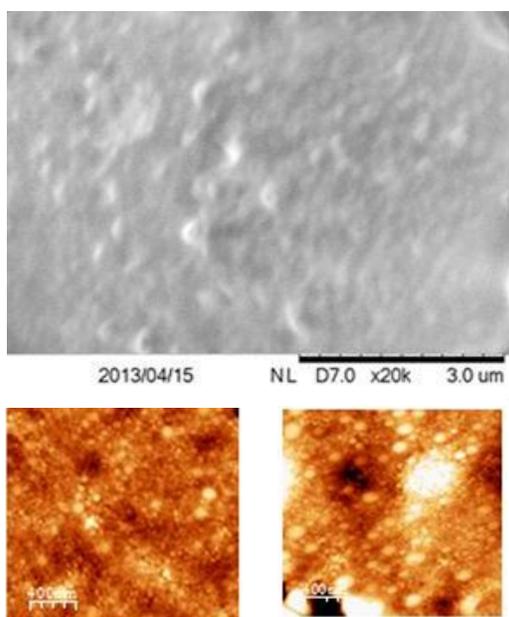


Figure 3. Morphology of absorbed nanoparticles with encapsulated oils at a paper surface, (a) SEM image of SMI/ZO-50 coating (Hitachi TM3000), (b) AFM ($2 \times 2 \mu\text{m}^2$) for SMI/SO-50, (c) AFM ($2 \times 2 \mu\text{m}^2$) for SMI/MO-50

Table 2. Physical properties of paper with coating of nanoparticles with encapsulated oil

Coating type	Coating weight (g/cm^2)	Contact angles ($^\circ$)		
		θ_{stat}	θ_{adv}	θ_{rec}
Paper	-	65	85	10
SMI/SO-50	6	103	108	38
SMI/MO-50	7	110	115	40
SMI/KO-50	7	95	98	22
SMI/CO-50	8	92	86	7*
SMI/ZO-50	6	103	99	33
SMI/PO-50	7	94	95	32

3.3 Nanoparticle coatings

The chemical imidization reaction in presence of vegetable oils resulted in a chemical esterification of the fatty acid with the ring-opened anhydride moieties. The thermal stability of the organic nanoparticles against oil release depends on the reaction conditions, especially the degree of imidization that directly relates to the molar ratio of ammoniumhydroxide to maleic anhydride. After heating of the nanoparticles above their glass transition temperature ($T_g = 170^\circ\text{C}$, which is relatively high due to the imidization reaction), progressive release of oil from the polymeric phase was observed. The thermal release of oil at the paper surface has been studied under different heating conditions. In a critical temperature range of 120 to 250°C , the oil migrates to the surface of the paper coating and further enhances the surface hydrophobicity. The progressive release of oil upon thermal heating has been demonstrated with AFM (Figure 4) and FTIR spectroscopy (Figure 5) or chemical Raman mapping (Figure 6). The progressive increase in coupled oil-related band intensities at various wavenumbers – relatively to the maleic anhydride and styrene bands – confirms the release of oil during thermal heating. At low to intermediate concentrations of ammonium hydroxide, the progressive release of oil can be followed by diminution and separation of oil-related absorption bands in Raman spectra. At high NH_3 -concentration, the better thermal stability of nanoparticles through higher imidisation degree does not allow for fluent oil release as a thermally stable chemical bond between oil and polymer are formed. Of course, the dynamics of oil release at different temperatures depends on the initial morphology of the SMI/oil nanoparticles: (i) the release from sponge-like structures in presence of soy oil occurs more gradually as a function of temperature due to diffusion processes compared with (ii) the release from core-shell type nanoparticles depends more critically on the relatively high glass transition temperature ($T_g = 176^\circ\text{C}$) of the polymer shell.

HEATING

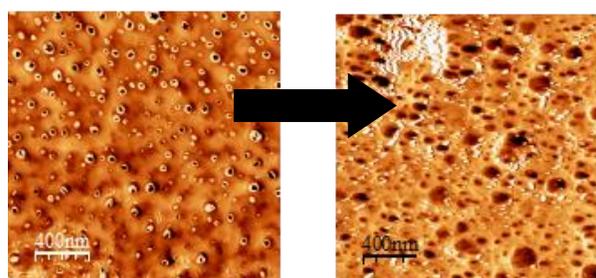


Figure 4. Thermal release of vegetable oils from papers coated with nanoparticles containing encapsulated oils: AFM ($2 \times 2 \mu\text{m}^2$) for SMI/palm oil before and after heating.

4 CONCLUSION

In conclusion, vegetable oils can be incorporated in an imidization reaction of poly(styrene) maleic anhydride, resulting in an aqueous nanoparticle dispersion with about 50 wt.-% solid content that can be applied as a paper coating. The improvement in hydrophobicity of the coated paper surface depends on the type of oil used. The functionality of the paper surface can be steered by thermal heating, resulting in progressive release of oil from the nanoparticle structures. These results have practical implications for fabrication of active papers in packaging and can be considered more general as a method for encapsulation and release of hydrophobic agents including oil-soluble inks and pigments, dyes, cosmetics, fabric treatment products, lubricants that should be deliverable in waterborne dispersion. The presented nanoparticle technology has clear industrial benefits in preparing functional coating compositions for packaging papers and active control of the surface hydrophobicity, by replacing traditional polymer coatings with renewable oils.

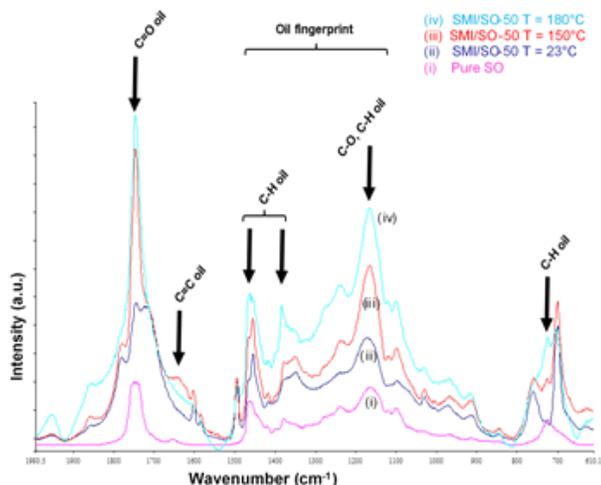
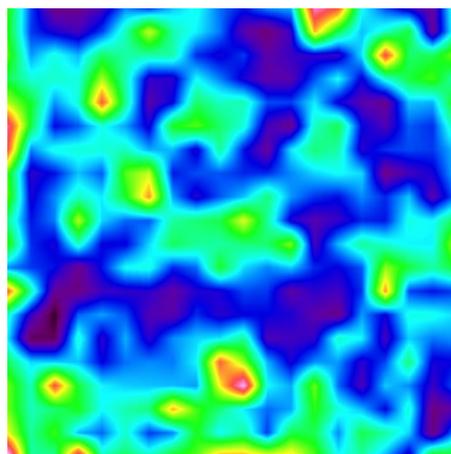
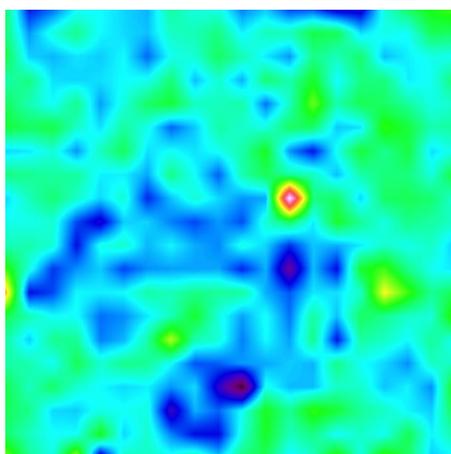


Figure 5. Thermal release of vegetable oils from papers coated with nanoparticles containing encapsulated oils: FTIR spectra for SMI/soy oil after heating at different temperatures.



23°C



180°C

Figure 6. Monitoring of the oil-coverage of a nanoparticle SMI/oil coating onto papers by Raman microscopy ($1 \times 1 \mu\text{m}^2$), illustrating the thermal release of oil at high curing temperatures (legend: blue = low intensity, green/yellow = intermediate intensity, red = high intensity).

Acknowledgements

This project is sponsored by the Robert Bosch Foundation as a Juniorprofessorship ‘Sustainable Use of Natural Materials’ and the Juniorprofessorenprogramm of the Ministry for Education of Baden-Württemberg.

REFERENCES

- [1] T. Stauffer, R.A. Venditti, R.D. Gilbert, J.F. Kadla; G.J. Montero, “Supercritical carbon dioxide dewaxing of old corrugated containers,”. *Journal of Applied Polymer Science*, 81, 1107-1114, 2001.
- [2] T. Schuman, B. Adolfson, M. Wikström, M. Rigdahl, “Surface treatment and printing properties of dispersion-coated paperboard,” *Progress in Organic coatings*, 54, 188-197, 2005.
- [3] M.A. Hubbe, R.A. Venditti, O.J. Rojas, “What happens to cellulosic fibers during papermaking and recycling? A review,” *Bioresources*, 2, 739-788, 2007.
- [4] V.S. Chauhan, S.K. Chakrabarti, “Use of nanotechnology for high performance cellulosic and papermaking products,” *Cellulose Chemistry and Technology*, 46, 389-400, 2012.
- [5] C. Aulin, M. Gällstedt, T. Lindström, “Oxygen and oil barrier properties of microfibrillated cellulose films and coatings,” *Cellulose*, 17, 559-574, 2010.