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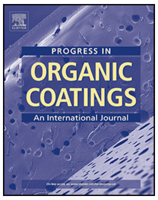

New printing inks with barrier performance for packaging applications: Design and investigation

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ABSTRACT

Barrier properties of packaging materials against moisture and oxygen penetration are of high relevance. Enhanced protection of existing materials against weather conditions can be achieved by application of printed coatings. To improve barrier performance of packaging materials, new inks for obtaining printed coatings with a layered structure were developed and investigated. The proposed ink compositions for flexographic printing on paper substrates are based on an environmentally friendly acrylic binder and contain inorganic fillers with platelet particles incorporated in the polymer matrix. Coatings based on the developed printing inks demonstrate significantly decreased water vapour permeability compared to traditional polymer inks. The effect of decreased permeability was investigated considering inks rheological behaviour, the coating structure, mechanical properties, surface energy and water uptake for different ink formulations. The developed inks provide variable optical properties including coatings with a relatively high transparency. The development of the functional barrier inks contributes to saving natural resources by prolonging life performance of packaging materials and goods.

1. Introduction

The concept of improving the quality of paper packaging materials by enhancing their barrier performance is of high interest in research, technology and application [1–5]. Enhancement of the barrier properties of paper and board packaging materials is relevant for prolonging the life cycle of the materials and packed goods thus bringing economic impact and contributing to saving natural resources. In addition to their barrier performance, packaging materials are expected to be environmentally friendly, resistant to mechanical impact, to be of a relatively low cost [1,2], and in several cases to provide desired optical characteristics.

Examples of packaging materials with improved barrier performance include materials based on polymer films, aluminium foils and multi-layered polymer composite materials. Filled and unfilled polymer materials for packaging are usually based on polyvinyl chloride, polystyrene, polypropylene, polyacrylonitrile and others [3]. Inorganic fillers with a platelet particle shape can be introduced in polymer materials for providing barrier effect against water vapour and gases. The barrier effect is given by increasing the tortuous path for water vapour and gas during their penetration through the material [6]. Fillers with high aspect ratio and with a relatively high specific surface area contribute to an enhanced reinforcement effect [7]. Most commonly used inorganic fillers with platelet particles are layered clays, such as montmorillonite nanoclays and silicates in general, known for their barrier performance, low cost and easy processability [3,7,8].

Paper and board materials have been widely used in packaging. Traditionally used paper and board have, however, a disadvantage of a relatively poor resistance to moisture and gases [9]. Application of polymer coatings with enhanced barrier performance is one of the possibilities to improve the quality of paper packaging materials. Application of polymer materials for coatings by printing has benefits in technological and economic aspects. The existing materials for printing providing the barrier effect against moisture are based mainly on polymer compositions containing waxes or other organic components for decreasing coating water vapour permeability [10,11]. However, application of wax in a polymer composition in an amount sufficient for providing the barrier effect of the coatings can be disadvantageous due to a possibility for decreasing printability and the quality of the printed coatings. This can be due to the drawbacks in the ink transfer and adhesion leading to ink refusal, print mottle and smearing of water-borne inks containing wax [12]. Decreasing permeability of water vapour and gases through materials with polymer coatings still remains a challenge.

Development of new polymer ink compositions for packaging with enhanced barrier performance and other improved characteristics of the printed coatings, such as desired mechanical strength

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and optical properties, is supposed to be beneficial for different packaging applications. Incorporation of inorganic fillers with a platelet particle shape was expected to enhance the barrier effect of the printed coatings to water vapour and to provide other desired functions to the coatings obtained by flexographic printing.

Development of such materials for flexographic printing is an alternative approach to improve the quality of packaging materials. Application of filled water-borne coatings with enhanced barrier performance allows for creating new packaging materials based on paper and board with beneficial functional performance, sustainability and environmentally friendly nature.

The goal of the study was to develop new ink compositions for flexographic printing on paper with improved barrier effect and other functional characteristics. The developed ink compositions were investigated with regard to their coating structure, rheological behaviour, water vapour permeability performance, mechanical properties, surface energy of the coatings, water uptake by free films and wetting of paper by the developed compositions. The developed compositions were applied on the selected paper substrate by flexographic printing and water vapour permeability of the paper substrates covered by the printed coatings was evaluated.

2. Materials and methods

A water-based acrylic dispersion (pH 7.9 at 23 °C) used in the study was provided by BASF SE. Three types of fillers (aluminium, borosilicate glass and talc) with platelet particles were selected. Aluminium flake paste and borosilicate glass powder were provided by Eckart Effect Pigments GmbH and talc powder was provided by Mondo Minerals B.V. To prevent foam formation during dispersion, an anti-foaming agent was used during preparation of the printing ink compositions. A dispersion of the anti-foaming agent was provided by BASF SE. Each of the fillers was introduced in acrylic polymer dispersion separately to obtain printing inks with different filler volume contents (6 vol.%, 8 vol.%, 9 vol.% or 10 vol.%, 17 vol.% or 19 vol.% and 26 vol.%) to investigate the effect of type and content of fillers on the coating properties.

For incorporation of borosilicate glass and talc particles, aqueous slurries of each of them were prepared using an ammonia based dispersion agent provided by BASF SE and a pH buffer solution for modifying pH during the preparation of the slurries. Dispersion was performed using a high speed dissolver.

The prepared slurries were incorporated in the water-based polymer dispersion containing an anti-foaming agent to obtain ink compositions for each of the fillers with different filler volume contents ranged from 8–10 vol.% to 26 vol.%. Critical pigment volume concentration (CPVC) was calculated considering oil absorption [13] and density of the fillers [14]. Filler content in the prepared compositions did not approach CPVC. Aluminium paste was introduced in the polymer binder composition as received using a high speed dissolver to obtain ink compositions with different aluminium particle content ranged from 6 vol.% to 26 vol.%.

The prepared ink compositions were applied by a Doctor Blade applicator to obtain coatings and by flexographic printing. The coatings prepared using a Doctor Blade applicator served as a model for investigation of the properties of flexographic printed coatings.

In order to obtain the coatings, the prepared ink compositions were applied on glass, Tedlar® polyvinyl fluoride film and on selected paper substrates, and underwent drying at ambient conditions. A white top coated Kraft liner paper was used as a substrate for the application of the developed compositions by a blade applicator and by the laboratory flexographic printing process. The coatings on glass and paper substrates with thicknesses of 10 μm and 30 μm were analysed as prepared.

Free films with thickness of 35–40 μm were obtained by pulling off the coatings from Tedlar® polyvinyl fluoride film substrates due to a lower adhesion of the filled polymer films to the Tedlar® substrates. The prepared free films served as a model of coatings to investigate the effect of type and content of the fillers on the structure and mechanical properties of the printed coatings.

The laboratory flexographic printing was performed using a flexographic printing test machine Nissha (model S.15) equipped with a Harper XLT-technology anilox roller with the 60° cell geometry, cell volume of 33.80 cm^3/m^2 and a 70 L/cm line screen (Harper Graphics GmbH). A full-tone printing plate Cyrel TDR 112 with thickness of 2.84 mm and hardness of 38 Sh A used in the printing tests was provided by DuPont GmbH.

The coatings prepared by a blade applicator and by flexographic printing as well as free films were kept in a temperature and humidity controlled environment at standard conditions (23 °C, 50% RH) for at least 24 h before investigations.

Rheology analysis of the ink compositions was performed using a Physica MCR 501 rheometer (Anton Paar GmbH) with cone-plate geometry (1° angle) at a constant temperature of 23 °C. The rheological behaviour was evaluated for at least 3 samples of each composition to prove reproducibility of the measured tendencies.

Light transmittance of the coatings with the thickness of 30 μm applied on glass substrates was determined using Perkin-Elmer UV–vis spectrophotometer in the visible wavelength region of 400–750 nm. The calibration of the spectrophotometer was performed using a glass substrate as a reference.

The structure of the coatings with the thickness of 10 μm on glass substrates was investigated by light and polarised light microscopy using an upright and inverted light microscope (Carl Zeiss AG) containing a digital camera to obtain images at different magnifications. The structure of a cryogenic fracture at a cross-section of free standing films was evaluated using scanning electron microscopy (SEM) (FEI Helios Nanolab).

Water vapour barrier performance of the coatings was evaluated by analysing the water vapour transmission rate (WVTR) of free standing films of similar thickness using a permeability tester (Lyssy AG). The permeability at the steady stage was determined by the following equation:

$$P = \frac{\Delta W \cdot x}{\Delta t \cdot A \cdot \Delta p} \qquad (1)$$

where ΔW is the weight of the permeate passing through a film with the thickness x, mm, and area A, mm^2, during time t, s; Δp is the differential partial pressure across the film.

Water uptake ratio (WUR) of the prepared free films was determined gravimetrically after their immersion in water at standard conditions for specified time intervals. Water uptake ratio of each film was calculated as an average of the measurements for 3 samples. The WUR (%) was calculated as follows [15]:

$$WUR = 100 \cdot \frac{m_t - m_0}{m_0} \qquad (2)$$

where m_t and m_0 correspond to the weight of samples before and after their immersion in water during time intervals t.

Surface energy analysis was made at the standard conditions by the sessile drop method using an OCA-series contact angle device (DataPhysics Instruments GmbH) containing a digital camera. Four liquids (water, diiodomethane, thiodiglycol and ethylene glycol) were used for the surface energy analysis. The surface energy of the liquids used for the analysis is shown in Table 1 [16–18]. The measurements were repeated at least 5 times for each liquid. The relative standard deviation of each measurement did not exceed 5%. The surface free energy was calculated by the Owens–Wendt–Kaelble method [19,20].