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Nanostructuring of polymer surfaces by magnetron plasma treatment

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ABSTRACT

Stochastic nanostructured polymer surfaces exhibit superior properties like enhanced antireflective behavior and soil-resistance as well as improved adhesion to adhesives and other coatings. This paper investigates and compares the nanostructure formation on the surface of different widely used polymers by means of a roll-to-roll reactive dual magnetron plasma etching process. The etching process induces formation of stochastic nanostructures on the surfaces. Structure shapes, texture and application relevant properties depend on the composition, morphology and crystallinity of the treated polymers. The impact on optical transmission increase and hydrophobic behavior of the surfaces is discussed.

Nanostructured varnish coatings allow surface modification of inorganic surfaces that may not be etched directly in a plasma treatment. This paper therefore characterizes plasma etching of acrylic based varnish coatings on polymer webs. Structure formation is investigated in relation to surface active additive content in varnish material.

Finally, outdoor stability of a nanostructured ETFE surface is shown in a 24 month outdoor weathering test in central Europe.

1. Introduction

Nano- and micro-structured surfaces are well known from nature e.g. anti-reflection (AR) in moth eyes and water-repellence on lotus leafs [1,2,3]. Nanostructures can be applied to technical surfaces by using lithography processes, embossing or chemical and physical etching [4,5,6]. Technologies like lithography need many process steps and scaling to larger treatment areas is difficult.

Schönberger et al. described a large area plasma etching process on PET substrates to generate stochastic nanostructures with anti-reflective properties [7]. This vacuum process uses a dual magnetron system (DMS) as plasma source in a pure ionized oxygen atmosphere. Negative oxygen ions are accelerated to the polymer substrate with energies in the range of 100–300 eV and lead to an etching effect on the substrate [8]. Resulting nanostructures exhibit dimension in nanometer scale and are stochastically distributed on the surface. The process is homogenous on a large substrate surface area and can be implemented in a roll-to-roll configuration on a web-with of > 2 m [9]. *Schönberger* et al. demonstrating an anti-reflective effect leading to 99% visual light transmittance with a treatment on both sides of PET [7].

This paper investigates the transfer of the magnetron-based plasma etching process to different polymer films to create changed surface morphology with anti-reflective and/or water-repellent properties. These can be used in many fields of application like architecture, photovoltaic and automotive [10,11]. Polymer films are well used in these fields. For example ETFE is been used as roofing material in architecture [12], PEN for encapsulation of flexible electronics like OLEDs or OPV [13] and PC is a common material for car dashboards, as glass replacements and in aerospace application. Nanostructured ETFE surface with water repellent properties could result in repellence of dirt and dust, whereas nanostructured PEN with anti-reflective properties could enhance the efficiency of OPV and OLED by increasing the light transmission through the film.

This paper includes an analysis of formation and shape of nanostructures on abovementioned polymers. Previous work on ETFE showed an influence of crystallinity on the formation of nanostructures [14]. Other research groups pointed out that the used ion energy, surface roughness, crystallinity and crosslink density influences the formation of nanostructures [15,16,17]. Therefore, nanostructures are expected to show different forms and shapes in dependence of the morphology of the polymers. X-ray diffraction measurements were used to confirm the influence of crystallinity on the structure formation.

Certain application demand nanostructuring of non-polymeric surfaces like metal foils or thin glass webs. However, plasma etching of these materials requires hazardous gases or is not possible at all. Varnish coatings on these surfaces may be used to circumvent that issue and also structure surfaces of thin glass substrates or metal films. Radiation curable urethane acrylates exhibit high flexibility, good

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Table 1
Overview of the used polymer webs.

Substrate material	Trade name (supplier)	Substrate thickness [μm]
Ethylene tetrafluoroethylene (ETFE)	ET6235-Z (NOWOFOL)	50
Polyethylene terephthalate (PET)	Melinex®401 (DuPont Teijin Film)	50
Polycarbonate (PC)	Makrofol DE 1-1C (Bayer Materials)	125
Polyethylene naphthalate (PEN)	Teonex®Q51 (DuPont Teijin Films)	75
Polyether ether ketone (PEEK)	LITE (VICTREX)	25
Polymethylmethacrylate (PMMA)	PLEXIGLAS®0F014 (EVONIK)	53
Polyethylene (PE)	LA13/208/1Mc (ORBITA Films)	50

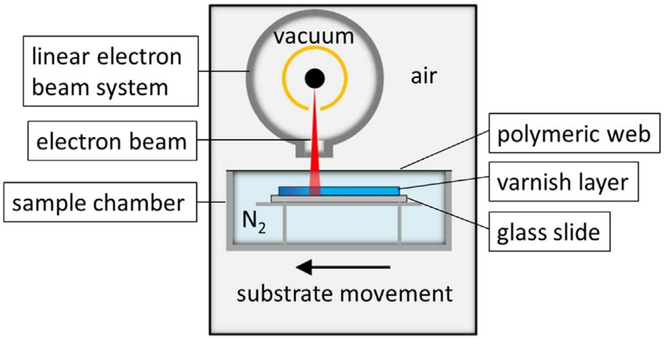

Fig. 1. scheme of atmospheric pressure electron beam unit REAMODE.

adhesion to different substrates, high scratch resistance and excellent chemical and weathering stability [18]. The use of aliphatic instead of aromatic urethane acrylates has the additional advantage that there is no yellowing during ageing, which is important for optical applications [19]. Radiation curable varnishes have the advantage of a lower energy consumption during cross-linking compared to thermal drying. Furthermore, a higher productivity and a lower thermal impact on different substrates can be ensured. In comparison to ultraviolet light (UV) curing, electron beam (EB) curing has the additional advantage of no photo-initiators being needed, which decreases the varnish costs and toxicity of varnish and final layer [20]. The varnish coating and curing by electron beam is scalable and compatible to roll-to-roll processing.

This study investigates reactive plasma etching to create nanostructures on different acrylates-based varnish coating surfaces. A polydimethylsiloxane additive was added to optimize the leveling of varnishes and to characterize the influence on the nanostructure formation. Polydimethylsiloxane is surface active and is therefore concentrated at the varnish surface [21]. The influence of additive concentration to the formation and shape of nanostructures is discussed.

2. Material and methods

2.1. Substrates

Table 1 summarizes types, thicknesses and product names of the polymer substrates used for this study. The polymers have been selected both based on their fields of application as well as their technical properties and variety in morphological properties. E.g. ETFE and PET are well known to be partially crystalline.

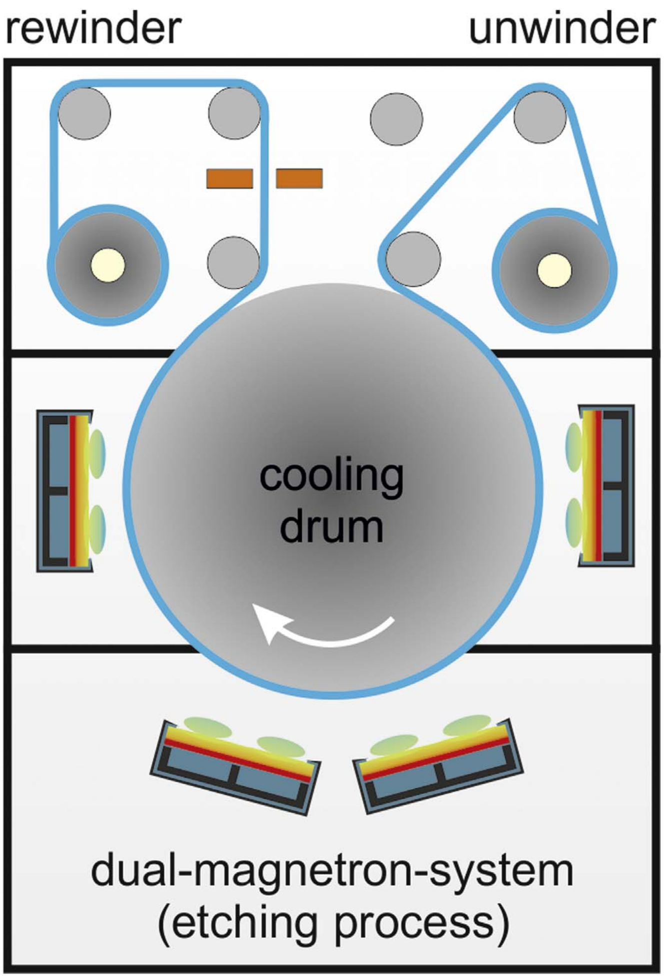

Fig. 2. scheme of the roll-to-roll coater *labFlex® 200* according to [22].

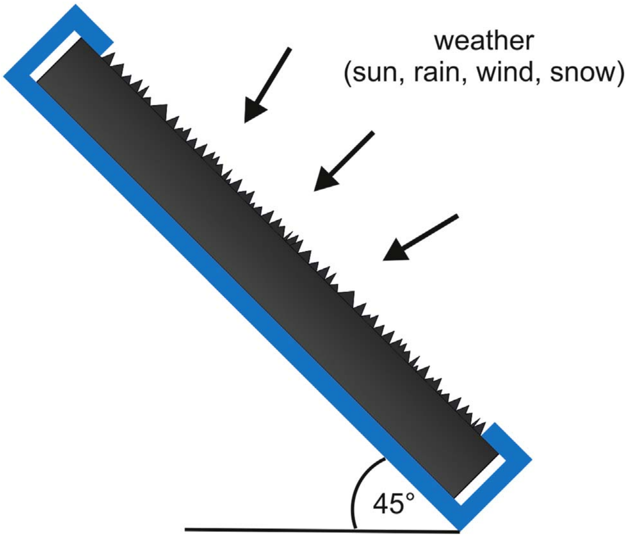

Fig. 3. scheme of the weathering test of nanostructured samples. The samples (in dark grey color) are fixed in aluminum carrier (marked blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)