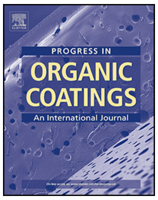
Progress in Organic Coatings 76 (2013) 1581–1585

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



Electric properties of organic thin-layers deposited by photo-polymerization on a textile substrate

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ARTICLE INFO

Article history:
Received 14 November 2012
Received in revised form 10 June 2013
Accepted 2 July 2013
Available online 24 July 2013

Keywords:
Photo-polymerized thin-layers
Organic thin-layers
Electric properties
Charge storage

ABSTRACT

The scope of the reported experiments was to study the charging behavior of photo-polymerized poly-DAP, poly-TAE and poly-PETA thin-layers, namely the remanence or storage of artificially deposited electric charges. The thin-layers were polymerized on the fibers of a technical non-woven under variation of the main parameters of the polymerization process, namely the monomer concentration in the applied precursor and the duration of UV exposure. The charging behavior of the layers was characterized by recording the charge dissipation after defined surface charging by a corona discharge. After the artificial charging, the electric field generated by residual surface charges was measured using an electric field mill as a function of time. It was found that the poly-DAP thin-layer showed no improvement in charge decay over the untreated sample. This is attributed to water absorption due to carboxylic groups. Poly-TAE and poly-PETA showed significant increases in charge remanence with increasing polymerization. It is proposed that the observed change in the electric property is related to increased cross-linking and reduced chain mobility with increasing UV exposure. Best results were achieved with poly-TAE holding, a thin-layer holding 1/e of the initial charge after more than 10 min.

1. Introduction

Compared to more conventional means of application of functional finishes or layers in the micron scale, thin-layer deposition has the interesting advantages of low deposited mass, high stability and adhesion, and extremely low use of chemicals and auxiliaries.

Organic thin-layers with defined electric properties are of increasing interest in the framework of ongoing developments in organic electronics, photo-voltaics, and energy storage [1]. Besides the development of organic thin-film transistors (OTFTs) for various applications, exemplary work can be found in [2–5], potential is also given in the design of organic thin-layers with sensoric function as, e.g., gas detector [6] or opto-thermal function [7].

In the field of textiles, surface conductivity is a long-standing topic on textured or coated textiles, but also polymer films, where antistatic properties are demanded. In more recent developments toward highly functional textiles, patterned circuits, e.g. produced by printing techniques, are increasingly evaluated in view of textiles sensors, photovoltaics on textiles (see, e.g., [8]), and heating elements [9]. On the other hand, charge storage is of interest in view of low-cost substrates for energy storage and textile filter media with electret functions, which are conventionally achieved by a finish with, e.g., carnauba wax. While the charging technique to achieve maximum charge and particle collection efficiency is the major topic in the development of filter media (see, e.g., [10]), increasingly research focuses on the degradation of electret finishes and decharging effects [11,12].

Besides plasma-based processes, photo-chemical processes are well-known for their potential for an effective and durable functionalization of polymers [13–20]. The interaction of UV light with strongly absorbing polymers allows to generate a large number of radicals at the substrate surface. If the irradiation is conducted in a reactive medium, which can be either a gaseous atmosphere or a liquid agent, four different types of reactions are possible: (I) recombination of radicals, (II) cross-linking of polymer chains, (III) addition of radicals from the reactive atmosphere, and (IV) addition of bi-functional molecules resulting in cross-linking between the functional groups. It has been shown that reactions III and IV could result in photo-induced grafting of functional groups and thus could be used to increase both wettability and fluid repellence with regard to water or oil [19,21]. In addition, the modifications are extremely durable because of covalent bonding to a certain degree. It is, therefore, possible to establish durable thin-layers following reaction schemes II and IV.

Various studies by the authors have shown the process produces homogeneous and highly stable layers from monomers such as diallylphthalate (DAP), tetraallyloxyethane (TAE), and

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http://dx.doi.org/10.1016/j.porgcoat.2013.07.001

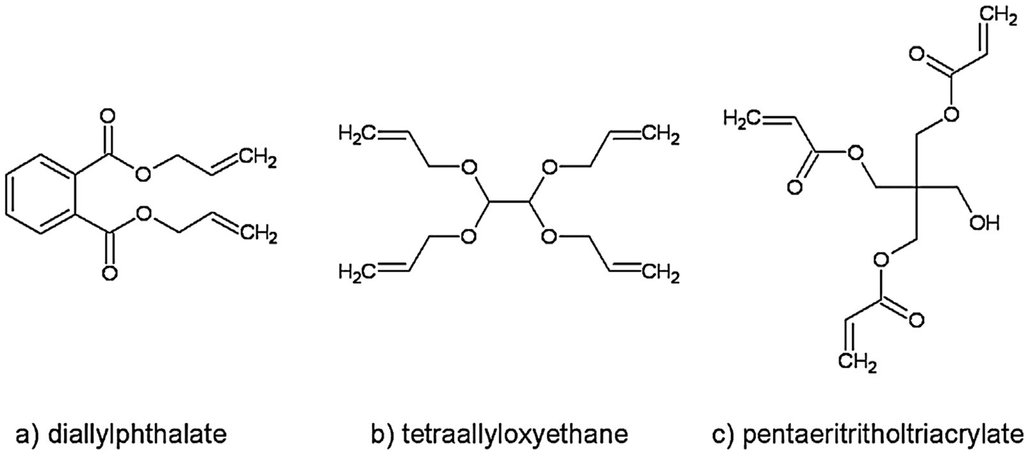

Fig. 1. Chemical structure of the reactive substances.

pentaeritritholtriacrylate (PETA). The chemical stability of thin-layers photo-polymerized from diallylphthalate (DAP) for instance could be used to significantly increase the resistance to alkaline hydrolysis of poly(ethyleneterephthalate) (PET) [22]. By means of AFM-based nanoindentation and surface-confined thermal analysis (μ-TA), photo-polymerized poly-DAP was also shown to exhibit excellent mechanical and thermal properties and was thermally stable up to 280 °C [20,23]. In another study, the abrasion resistance of polypropylene (PP) fibers could be significantly enhanced by depositing photo-polymerized layers of pentaeritritholtriacrylate (PETA) due to the high elastic modulus and thermal stability of the thin-layer [24]. Basically these effects could be attributed to either superficial cross-linking of the polymer by bridging macromolecules with multi-functional species such DAP, or a network of the multi-functional species on top of the substrate surface (thin-layer cross-linking) (cf. [20]). The various AFM-based analyses performed in the stated studies clearly indicated cross-linked thin-layers, i.e. photo-polymerization of the monomers DAP, TAE, and PETA [20,23,24]. Namely, it was found that the thermo-mechanical properties of the very surfaces – as characterized by μ-TA – were specific to the semi-crystalline poly-DAP or the polymerized aliphatic TAE and PETA, and not to the underlying substrate. The dependence of elastic modulus of poly-DAP surface layers measured by nanoindentation and the layer morphology taken from AFM phase images also showed that polymerization progressed with UV exposure time until all available monomers were cross-linked [20,23].

From their chemical structure (Fig. 1) all monomers indicate that electric conductivity of polymerized layers will be low. Although there is little scientific literature on the electric properties of DAP and TAE, these materials are used for insulating components in various applications. An interesting paper on the complex electric impendance of photo-polymerized PETA was published by Oueslati et al. [25]. The authors produced resins and studied the electric properties as a function of irradiation time. Oueslati et al. observed a decrease of conductivity with progressing polymerization which was in good correlation with the viscosity of the cross-linked polymer reported by Nixdorf and Busse [26]. Initial conductivity is explained by the abundance of monomers, which decreases with increasing cross-linking during irradiation. Oueslati et al. report constant properties from a certain irradiation time (30 min in their experiments), which they relate to the end of photo-polymerization.

The scope of the reported experiments was to study the charging behavior of photo-polymerized poly-DAP, poly-TAE and poly-PETA thin-layers, namely the remanence or storage of artificially deposited electric charges. Measured quantities were the initial charge take-up in a defined charging process, and the subsequent decay of surface charges as a function of time. This was studied in relation to the mass of the deposited thin-layers on a standard substrate, hence the thickness of the thin-layers. An industrial nonwoven produced for air filtration purposes served as case study.

2. Experimental

An industrial nonwoven made from poly(ethylene terephthalate) (PET) of 120 g/m^2 served as substrate. The material is thermally and mechanically bonded, hence without any chemical binders. For the studies, samples were cut to size of 10 cm × 10 cm.

Diallylphthalate (DAP) (Acros), tetraallyloxyethane (TAE) (Highlink TA), and pentaeritritholtriacrylate (PETA) (Aldrich) served as monomers. Besides the expected low conductivity, they were chosen also because of their hydrophobic nature and absorption properties in the 200–300 nm range (Fig. 2). The samples to be treated were dipped in the substances, which were solved in ethanol under variation of monomer concentration (3, 5, and 10%), and left to dry in air.

The irradiation was performed using a broad band UV lamp with a main emission band from 250 to 320 nm (UVACUBE 2000, Dr. Hönle, München, Germany), which was kept at a constant

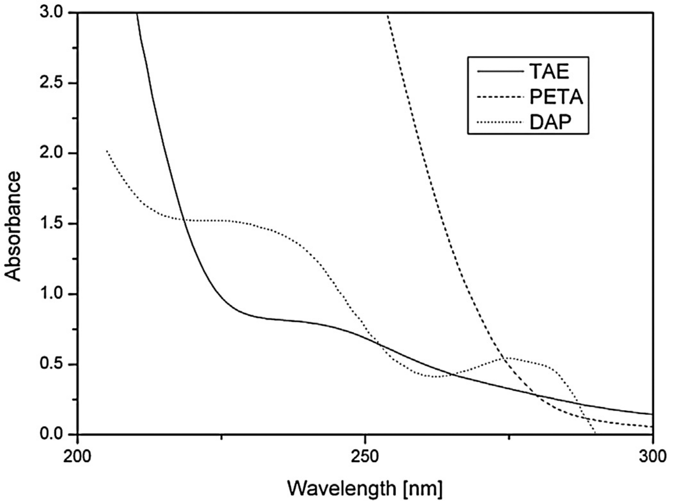

Fig. 2. UV absorption spectra of the studied reactive substances in ethanol.