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Plasma based ion implantation of engineering polymers

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ABSTRACT

An overview of the rapidly developing field of modification of engineering polymers by plasma based ion implantation (PBII) and plasma based ion implantation and deposition (PBII&D) is presented. Furthermore, the applicability and usefulness of the approach of "design of experiments" is demonstrated by the nitrogen PBII treatments of polyamide 6 (PA) and poly(bisphenol A carbonate) (PC). Alterations in surface chemical composition and bonding were studied by XPS. Modifications in surface mechanical and tribological properties were followed by dynamic depth-sensitive nanoindentation and multiple nanoscratch measurements. Changes in wettability, surface energy and its components were evaluated by contact angle studies. Alterations in surface electrical resistance were also determined.

Surface compositional changes reflected a relative decrease in the C-content and increase in the N-content for both polymers, while alterations in the peak shapes suggested degradation of the amide group with the formation of imine, protonated amine and urethane-like moieties for PA, and degradation of surface carbonate groups with the formation of imine, tertiary amine and amide-like groups for PC. The hydrophilicity of the surface increased and the surface electrical resistance decreased significantly for both polymers. The volume loss, obtained by the multi-pass scratch test, decreased from the original value expressed as $V_0 = 100\%$, down to $V = 11\%$ and 59% for PA and PC, respectively. For PA the incorporation of some N had a favorable effect on the resistance to abrasive wear, but an excessive amount of N decreased this effect. Similarly, for PC a significant increase of the wear resistance could not be reached by the mere increase of the total N-content, but the surface concentration of tertiary amine type N should be maximized. The latter showed positive correlations with the fluence and the fluence rate applied.

1. Introduction

Engineering polymers are characterized by favorable properties like machinability, dimensional stability, nonflammability, resistance to corrosion, most acids, solvents and heat. However, some of their surface properties including wear resistance, wettability, surface conductivity, etc., have to be improved in several applications. A possible way of modifying advantageously their surface layers and improving their surface properties, is plasma based ion implantation (PBII) and its deposition variant (PBII&D).

The scope of this work is twofold: firstly, it intends to give a short overview of the title topic; secondly, the applicability and usefulness of the approach of "design of experiments," applied in the authors' laboratory to perform and evaluate PBII treatments, will be demonstrated on two selected engineering polymers — polyamide and polycarbonate. In particular, the main objective was to study the effect of nitrogen PBII treatment on the evolution of the chemical structure and wear properties, wettability and electrical resistance as functions of acceleration voltage, particle fluence and fluence rate as the main processing parameters.

2. Literature overview

The goal of this overview is to examine the dynamics of development in the field of the PBII of polymers and to show the main trends of development, regarding the materials modified and the essential properties studied. When searching the databases, the terms plasma source ion implantation (PSII), plasma immersion ion implantation (PIII) and plasma based ion implantation (PBII) were considered synonymous (although sometimes distinction is made between them, e.g., between PSII and PIII, based on the fact that the pioneers of the method historically applied different ways of plasma generation). Many useful information can be found in the related books like in the handbook of Anders [1] and in the recent books on ion beam treatment of polymers edited by Fink [2] and written by Kondyurin and Bilek [3]. In addition, we found more than 150 publications on PBII and PBII&D of polymers [4–157]. The majority of them deal with real engineering polymers. However, a number of articles dealing mainly with bioengineering/biomedical aspects are also considered here, since a part of information included can be of relevance also in the engineering field.

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Fig. 1 demonstrates a rapid increase in the cumulative number of publications appearing in the last 13 years. (Obviously, the value for year 2009 is not yet final). As a subset, the evolution of the number of publications dealing with the deposition variant of the method is also shown in this figure. Starting from 2004, the share of publications describing deposition type treatments is about one fourth of the total number of related papers.

Fig. 2 shows the distribution of publications according to the polymers studied. Clearly, the most intensely studied polymers are poly(ethylene terephthalate) (PET) [13,14,56,59–61,69–108] and the various forms of polyethylene (PE) [5,13,22–61]. These are followed by polyimide (PI) [14,104–106,109–120], polystyrene (PS) and its copolymers [13,104,106,107,124–136], poly(tetrafluoro ethylene) (PTFE) and poly(vinylidene difluoride) (PVDF) [5,57,137–143], polycarbonate (PC), including poly(bisphenol A carbonate) and CR-39 [8–15], poly(ether ether ketone) (PEEK) [14,62–68], poly(dimethyl siloxane) (PDMS) and silicones [13,16–21], poly(methyl methacrylate) (PMMA) and other polyacrylates [12,15,121–123], polyurethane (PU) and its copolymers [108,151–154], polyamide (PA) and its copolymers [4–7], and poly(vinyl chloride) (PVC) [13,155–157]. Furthermore, a few other PBII-treated polymers can be also mentioned like amorphous polyolefins (APO) [144,145], cellulose nitrate [146], ethylene–propylene–diene monomer (EPDM) rubber [19,21], ethylene–vinylalcohol copolymer (EVOH) [147,148], poly(butylene succinate) (PBSu) [149], poly(ethylene naphtalene) [13], polypropylene (PP) [61,105,150] and poly(phenylene oxide) (PPO) and its modified version [7,104,106].

Fig. 3 demonstrates the distribution of publications according to the modified properties studied. The overwhelming majority of the papers report results of surface chemical investigations. Further characteristics studied are (in decreasing order): topological and morphological ones [5–9,14,16–19,24–27,29,30,32,38,41,45,51,55–57,61,63,66,75,78–83,91,93,102–104,106,108,112,113,115,117,120,127–130,132,133,138,140,142–145,147–149,151,152,157], wettability and hydrophobic recovery [4,11–13,15,17,21,22,25,38,41,48,51,54,55,59,64,65,67,76,79–82,84,92,100,101,107,111,119,121,125,127,129,130,132,134,135,137,138,141–143,147–149,151,155,159], biomedical properties (like attachment of proteins, platelets or cells, cell growth, antibacterial properties, controlled drug release, patterning, etc.) [17,18,36–38,40,41,44–46,48,51–53,55,57,64,70,73,76,79,80,82,84,91,92,108,128,131,133,141,143,149,151,153,154,157], mechanical and tribological properties (like hardness, elastic modulus, friction, wear, stress, etc.) [5,6,8,9,15,21–24,26,27,29,31–34,39,43,56,58,63,66,68,81,90,94,95,98,100,110,121,139,140,144,145], optical properties [15,25,65,68,95,99,103,120,126–128,130,133,139,150], gas barrier properties (to O_2, CO_2, H_2O, etc.) [58,69,71,72,74,75,77,87,88,90,95,99,105,147,148], electrical properties [93,97,104,106,109,111,112], and adhesion to various materials [5,56,58,113–115,117,154].

Finally, several theoretical and experimental studies deal with the processing conditions of polymers and insulating materials in general [10,86,89,96,125,152,158–167]. These include studies on the effect of applied voltage, plasma density and pulse duration [10,125,158,164], on application of conducting mesh-assisted processes [159–163] and of various deposited and embedded conducting layers [165–167].

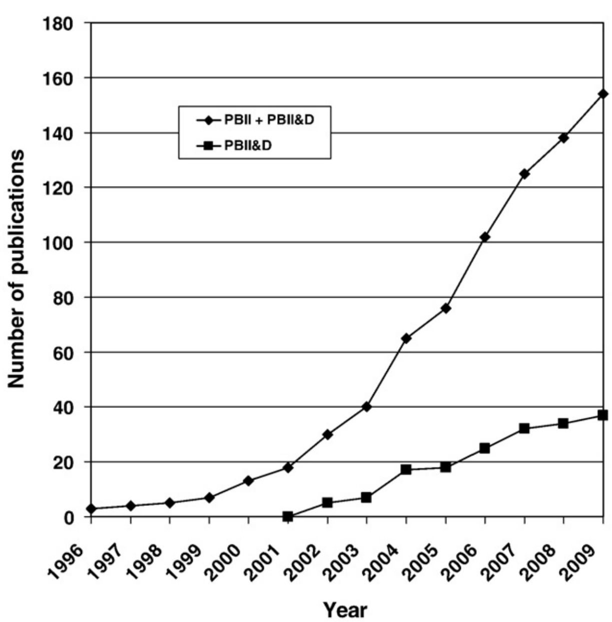

Fig. 1. Publications on PBII and PBII&D of polymers vs. time.

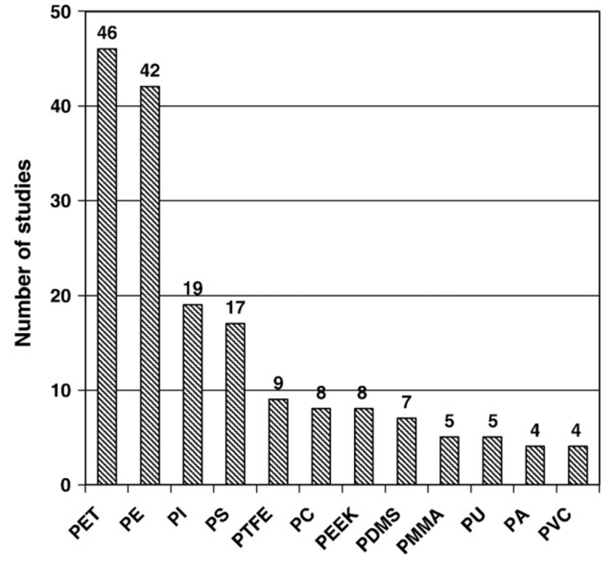

Fig. 2. Distribution of related publications by polymers modified.

3. Experimental

Commercial polyamide 6, (PA), type Ertalon, manufactured by Erta N.V., DSM and poly(bisphenol A carbonate), (PC), type Axxis PC,

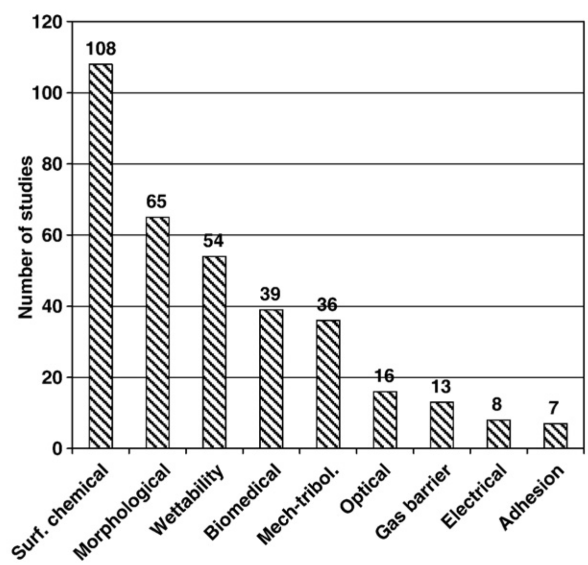

Fig. 3. Distribution of related publications by properties studied.