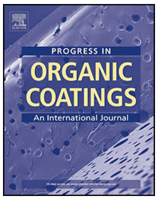
Progress in Organic Coatings 88 (2015) 127–136

Contents lists available at ScienceDirect

Progress in Organic Coatings

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



Enhanced anti-graffiti or adhesion properties of polymers using versatile combination of fluorination and polymer grafting

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ARTICLE INFO

Article history:
Received 25 August 2014
Received in revised form 29 May 2015
Accepted 22 June 2015
Available online 21 July 2015

Keywords:
Direct fluorination
Polymers
Grafting
Hydrophobicity/hydrophilicity
Adhesion
Printability

ABSTRACT

Commonly used polymers and polymer articles have some advantages, e.g. low. But very often they have not very good adhesion, barrier properties, low conductivity, etc. Specialty polymers possessing necessary properties, e.g. fluoropolymers, can be used to fabricate polymer articles. However, practical use of specially synthesized polymers is restricted due to their high cost and complexity of synthesis. It is possible to coat a polymer with another polymer layer with necessary properties but this co-extrusion method is difficult to apply due to a complexity of applied equipment. Also the problems of adhesion between two polymers and polymers compatibility are to be solved. Very often application properties of polymer goods (adhesion, barrier properties, conductivity, etc.) are defined mainly by their surface properties. Hence, it is not necessary to fabricate articles from specialty polymers but simpler, cheaper, and more convenient to apply a surface treatment of articles made from commonly used relatively cheap polymers. In this case, only thin surface layer several nm to several μm in thickness is to be modified and direct fluorination (treatment with mixture of F_2 and other gases) can be effectively used. For our research we have chosen common widely used polymers. We targeted to improve hydrophobicity/hydrophylicity, adhesion properties and surface conductivity of polymers. For the first time modification of the surface of high density (HDPE), low density (LDPE) and ultrahigh molecular weight polyethylene (UHMWPE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinylchloride (PVC) was performed by direct fluorination followed by a grafting of acrylic acid, styrene, acrylonitrile, vinylidene chloride, aniline and thiophene from the gas phase. Aniline grafting was studied to improve surface conductivity of polymers. Grafting of polymers was confirmed by ATR and MATR FTIR spectroscopy and energy-dispersive X-ray microprobe spectroscopy (cartography). AFM was used to study polymers surface. Influence of the nature of grafted monomers on the surface energy was studied. It was shown that depending on the nature of a grafted monomer hydrophobicity or hydrophilicity can be markedly improved. The hydrophobicity of modified polymers is not changed and is even improved with time contrary to virgin polymers. For the case of PP and UHMWPE grafting of styrene and acrylonitrile improved anti-graffiti properties (graffiti and pollutions from the polymer surface can be easier removed). For the case of HDPE and LDPE grafting of styrene and acrylonitrile improved printability. Grafting of aniline did not improved electrical conductivity. The uniformity of grafted polymers distribution was investigated by energy-dispersive X-ray microprobe spectroscopy (cartography) for the first time.

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1. Introduction

Polymers are widely used in industry although they have a lot of disadvantages: low adhesion, printability, barrier properties, etc. Specialty polymers possessing necessary properties, e.g. fluoropolymers, can be used to fabricate polymer articles. Fluorinated polymers have a set of unique properties such as enhanced

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http://dx.doi.org/10.1016/j.porgcoat.2015.06.021
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chemical stability, thermal stability, good barrier properties. However, practical use of specially synthesized polymers, such as fluoropolymers, is restricted due to their high cost and complexity of synthesis. It is possible to coat a polymer with another polymer layer with necessary properties but this co-extrusion method is difficult to apply due to a complexity of applied equipment. Also the problems of adhesion between two polymers and polymers compatibility are to be solved. Very often application properties of polymer goods (adhesion, barrier properties, conductivity, etc.) are defined mainly by their surface properties. Hence, it is not necessary to fabricate articles from specialty polymers but simpler, cheaper, and more convenient to apply a surface treatment of articles made from commonly used relatively cheap polymers. In this case, only thin surface layer several nm to several μm in thickness is to be modified and direct fluorination (treatment with mixture of F_2 and other gases) can be effectively used [1–8]. For our research we have chosen common widely used polymers. We targeted to improve hydrophobicity/hydrophylicity, adhesion properties and surface conductivity of polymers. Direct fluorination of polymers is a heterogeneous reaction of mixtures of F_2 and other gases (N_2, O_2, He, etc.) with a polymer surface. This is a method of a surface modification: for the majority of glassy polymers, only the upper surface layer is modified (several nm to several μm in thickness), but the bulk properties remain unchanged. Since fluorination is one of the most effective chemical methods to modify and control physicochemical properties of polymer surfaces over a wide range, this process has become an important tool of great interest. Direct fluorination has many advantages when applied in industry. Owing to a high exothermicity of the main elementary stages, fluorination proceeds spontaneously at room temperature with a sufficient rate for industrial applications. Direct fluorination is a dry technology. Polymer articles of any shape can be treated. There are safe and reliable methods to neutralize (by converting into the solid phase) unused F_2 and the end-product HF. These features of direct fluorination initiated wide industrial utilization for enhancement of the barrier properties of automotive polymer fuel tanks and vessels for toxic and volatile liquids storage. Gas separation properties of polymer membranes can also be highly enhanced by direct fluorination. Adhesion properties of polymer articles of any shape can be substantially improved. Also friction coefficient can be reduced, antibacterial properties and chemical resistance can be improved. In the current paper, we propose to use the following modification of the direct fluorination called "fluorine initiated grafting of monomers". It was shown previously [2,3,9] that rather large concentration of long-lived radicals (fluororadicals and peroxy $RO_2^{\bullet}$ ones) having half-termination time over 0.5–15 h range depending on the polymer nature is formed inside fluorinated layer. So it is possible to provide grafting of monomer with double bonds to the surface and inside fluorinated layer. If the thickness of a grafted monomer layer is sufficiently large, the surface properties of a modified polymer will be defined mainly by the properties of a grafted monomer layer. So the polymer surface may acquire hydrophilic or hydrophobic properties depending on the grafted monomer nature and the texture of the grafted layer. We have applied grafting from the gas phase because in this case (as compared with grafting from a liquid phase) no homopolymer is formed. No solvents are used that must be removed and stored.

Previously it was shown that direct fluorination of polymers results in a formation of long-lived radicals (half-termination time is around several hours) inside fluorinated layer [9]. Possibility of acrylonitrile grafting to fluorinated polyethylene was primarily demonstrated by Florin [10,11]. Kharitonov et al. investigated the kinetics of grafting of acrylonitrile to fluorinated polyimide and polyvinyltrimethylsilane [2,3] to improve gas separation properties of polymer membranes. In our previous paper [12] we have shown that the total surface energy and its polar component can be highly increased and hydrophilicity can be also highly improved. Treatment with F_2–O_2 mixtures provides more pronounced effect as compared with fluorinating mixture without oxygen. Radicals were observed in polystyrene and lignin treated with fluorine at room temperatures and below it (even at 77 K) [13] and in fluorinated polyparaphenylene [14] but the lifetime of radicals was not measured. Authors of [15,16] investigated the influence of acrylic acid grafting to fluorinated low density polyethylene on hydrophilicity and hydrophobicity but the grafting was carried out from the liquid phase so formation of homopolymer cannot be excluded. It was shown that treatment of LDPE and UHMWPE with F_2–O_2–N_2 mixtures highly increased surface energy and improved hydrophilicity [2,3,12]. Grafting of acrylic acid to fluorinated LDPE resulted in a more marked improvement of hydrophilicity. Nevertheless hydrophobicity was not improved as compared with a starting polymer. The dependence of the surface properties of fluorinated and grafted polymers on storage duration was not investigated [17].

A large panel of polymers, i.e. polystyrene, polyacrylonitrile, polyacrylic acid, polyvinylidene chloride, polyaniline, was covalently grafted onto polyethylene (high density and ultrahigh molecular weight) and polypropylene films (biaxially oriented). A two steps-process was applied for the first time. Direct fluorination (i.e. treatment with mixture of fluorine and other gases) was prior applied to the polymer surface in order to both change the surface energy and generate radicals at the top polymer surface. Then fluorine was removed from the reaction vessel and gaseous monomers (styrene, acrylonitrile, acrylic acid, vinylidene chloride or aniline) were inserted into the reaction vessel to provide graft polymerization. According to the grafted polymer/polymer film system, changes of the surface energy and chemistry might result either in an enhanced hydrophobicity, in a good anti-graffiti properties or in a conductive layer (for the case of polyaniline).

2. Materials and methods

High density polyethylene (HDPE), colourless, UV stabilized, was obtained from "Borealis". Its density was equal to $0.948 \pm 0.001\,\mathrm{g\,cm^{-3}}$. Ultrahigh molecular weight polyethylene (UHMWPE, molecular weight 2×10^6) was supplied by Institute of Catalysis of the Russian Academy of Sciences (Novosibirsk, Russia). Density of pressed UHMWPE films was measured by a conventional method and was equal to $0.933 \pm 0.001\,\mathrm{g\,cm^{-3}}$. The total relative concentration of residual double bonds with respect to amount of moles of elemental units of a polymer chain was equal to 7.2×10^{-5}. Amount of $-CH_3$ groups was less than 0.01 per 1000 carbon atoms. Concentration of residual groups was determined by IR spectroscopy [18,19]. HDPE and UHMWPE films were fabricated by hot pressing at 130–150 and 160–180 °C, respectively. Films of low density polyethylene (LDPE, density $0.911\,\mathrm{g\,cm^{-3}}$, film thickness 60 μm) were purchased from "Agrotema Ltd." (Moscow, Russia). Films of biaxially oriented polypropylene (BOPP), 20 μm in thickness, and polyvinylchloride (PVC) were obtained from "Tom Ltd.", Tomsk, Russia.

Fluorine contained less than 0.1 vol.% of admixtures (mainly oxygen). Nitrogen was 99.999% purity. Mixtures of 10% F_2 + 90% N_2 (vol.%) were prepared in advance in special cylinders. Acrylonitrile $CH_2{=}CHCN$, styrene $C_6H_5CH{=}CH_2$, acrylic acid $CH_2{=}CHCOOH$, vinylidene chloride $CH_2{=}CCl_2$, aniline, thiophene, diiodomethane and ethylene glycol were purchased from Aldrich and used without further purification. Double distilled water was used.

ATR and MATR FTIR spectra were measured with FTIR spectrometer FT-02 (Lumex, Russia) equipped with MATR accessory (ZnSe

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