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Practical applications of the direct fluorination of polymers

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Abstract

Applications are reviewed of direct fluorination to enhance the following commercial properties of polymeric goods: separation factor of polymeric membranes for gas separation and purification, barrier properties, adhesion, wettability, friction, transparency, etc. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Direct fluorination; Barrier properties; Adhesion

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1. Introduction

Direct fluorination is a well known method for the surface modification of polymers [1–3]. The thickness of the modified layer of polymer is controlled over a ~0.0l–10 μm range. This technology is the so-called ‘dry’ one (only gases are used) and polymer articles of any shape can be modified. The process proceeds at room temperature or below and does not need initiation or catalyst. One of the main advantages of direct fluorination is that only a thin surface layer of polymer is modified and hence the bulk properties of the polymer are practically not changed. There are different ways to apply direct fluorination to modify polymeric materials.

1. Ordinary direct fluorination, i.e. treatment of polymeric materials with fluorine or fluorine-inert gas (nitrogen, helium etc.) mixtures. In this case hydrogen atoms are substituted by fluorine, double and conjugated bonds are saturated with fluorine. Crosslinking (formation of C–C bonds) and destruction of C–C and C–Si bonds can take place. The degree of chemical transformations in a very thin (10^{-3}–$l0^{-2}$ μm) upper layer depends on the fluorine partial pressure and treatment duration.
2. Oxyfluorination, i.e. treatment of polymeric materials with fluorine-oxygen mixtures. In this case $>\mathrm{C{=}O}$, $\mathrm{-C{<}^{O}_{F}}$ and $\mathrm{-C{<}^{O}_{OH}}$ groups can be inserted into the polymer structure.
3. Oxyfluorination accompanied with graft polymerization. It is well known that in polymers treated with fluorine–oxygen mixtures a controlled amount of long-life peroxy $RO_2^{\bullet}$ radicals is generated. Additional modification of a polymer may be carried out by graft polymerization of monomers having double bonds, e.g. tetrafluoroethylene, acrylonitrile, acrylic acid, methyl methacrylate. This method of modification of polymeric goods is of great interest and to our mind has the best prospects because the surface properties of the modified polymer will be determined by the grafted polymer and there is much greater possibility to vary the surface properties — e.g. from hydrophobic to hydrophilic. Moreover the grafted polymer on the surface of the starting polymer can again be fluorinated.

There are some modifications of the procedure of direct fluorination:

1. Fluorination under static conditions. Polymeric goods can be put into the vacuum chamber. After the evacuation (high vacuum is not necessary: residual air pressure can be ~1–10^{-1} Torr) the chamber is filled with fluorine or fluorine mixtures followed by evacuation of fluorine after the treatment.
2. Fluorination in stream. Polymeric goods can be put into the chamber (isolated from the environment) and the stream of fluorine or fluorine mixtures at atmospheric pressure or below it is allowed to flow through the chamber.
3. Fluorination during the fabrication. The treatment of polymeric goods takes place during the blow molding when the temperature of polymer is above room temperature so fluorination occurs at an increased rate.

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The apparatus for fluorination under static conditions and in stream is described in [3–8], for fluorination during fabrication in [3,9–17].

Direct fluorination can be used to enhance various application properties of polymeric articles. Below the possible application areas of the direct fluorination of polymers are described.

2. Barrier properties

At present time one of the most commercially significant applications of direct fluorination of polymeric goods is the enhancement of their barrier properties [3]. Direct fluorination creates a barrier to permeation of hydrocarbons. This is due to several reasons. At first fluorination results in a significant increase of the specific gravity [1,18–21] and the free volume is decreased and hence the permeability of fluorinated polymers should be decreased. Also direct fluorination results in the crosslinking of polymers [1,18–24] so the swelling and plasticization effects under the action of hydrocarbons are suppressed and permeability values decrease. Finally the surface energy of fluorine treated polymer surfaces in many cases is increased and hence the solubility (permeability also) of low polarity organic liquids in fluorinated polymers is decreased.

There are some possible application areas where the enhancement of the barrier properties can be of commercial importance.

The fluorination of the interior of polymeric automotive fuel tanks prevents non-polar or low-polar substance (e.g. hydrocarbons) emission and reduces air pollution. According to estimates of Hobbs and Anand [25] the permeability value of fluorine treated HDPE (high density polyethylene) is around 10^{-13}–10^{-14} (cc(STP) cm cm^{-2} s^{-1}). This value is 6–7 orders of magnitude lower than one of an untreated HDPE. The main attention of investigators was paid to polyethylene (especially HDPE) [4–6,9–15,25–38]. The loss of liquids such as gasoline from polymeric fuel tanks can be reduced upon the direct fluorination by a factor of 100 [25], 10–20 [4], 100 (for Pb-free fuel, [27]), 70 [32]. Spread in the above data may be due to several reasons: different treatment conditions (composition of fluorinating mixture, duration of treatment), variations in chemical structure of polyethylene, etc. The leakage of petrol/alcohol mixture can be reduced by fluorination by a factor of 18 [25]. The loss of petrol (petrol grade = 93 octane high altitude) from HDPE pipes used between reservoirs and pumps at filling stations can be decreased upon fluorine treatment by a factor of 80 [33,34].

Direct fluorination of polymer containers for packaging of industrial and consumer chemicals decreases the loss of liquids which are stored inside the containers. Carstens [33,34] has shown that the loss of chemicals such as creosote, paints, polishes, hand cleaners etc. from HDPE containers can be reduced upon direct fluorination by a factor of one or two orders of magnitude. Leakage of toluene from HDPE containers can be also reduced by a factor of 100 [14], 50–60 [15], 15 [37] and leakage of pentane by a factor of 100 [7]. Direct fluorination of HDPE reduces the permeability of non-polar liquids (C_7H_{16}, C_6H_6, $C_{12}H_{26}$, CCl_4 [29,35] and pentane, CCl_4, toluene, chlorobenzene [12]) through the treated polymer but do not influence the permeability of highly-polar CH_3OH [29]. The barrier properties of LDPE can be also improved under the direct fluorination: the loss of *n*-heptane and pentane can be reduced by a factor of 200 [30] and 100 [7], respectively. Direct fluorination was shown to decrease permeability of PVC, thermosetting resins, natural and synthetic fibers [8], polyurethane [6], low density polyethylene, polypropylene, PET [33,34]. Utilization of fluorine-oxygen mixtures can increase the barrier effect in some cases [3,7,25].

Direct fluorination inhibits the migration of plasticizers from polymers and improves thermal aging resistance [39]. Rubber sheets used in sealing electrolytic capacitors become impermeable to paste and gas upon fluorination [40,41].

3. Membrane technologies

Polymeric membranes can be used for the separation of gas mixtures such as He–CH_4, H_2–CH_4, H_2–CO_2, CO_2–CH_4, CO_2–N_2, CH_4–N_2, H_2–N_2, O_2–N_2, CO_2–H_2S, CH_4–CO_2–H_2–He etc. There is, however, a common problem in a gas separation if a polymeric membrane is used: membranes with high gas permeability often have low as separation factor and on the contrary membranes with high separation factor have low permeability factors. Direct fluorination results in a significant decrease of permeability of multiatomic gases (CH_4, C_2H_4 etc.) as compared to diatomic and monoatomic ones (H_2, He, etc.). So direct fluorination can be used to enhance the separation factor value α of a polymeric membrane without significant reduction of the permeability value. For example, the gas separation value α of poly(4-methyl-pentene-1) (PMP) membrane for a CO_2–H_2S mixture can be increased from $\alpha \sim 1$ (starting membrane) to $\alpha \sim 4$ and moreover the permeability of CO_2 through the membrane is reduced only by a factor of 1.6 [42]. The value of α depends on the thickness δ_F of the fluorinated layer and for a set of membranes has a maximum at any δ_F value [42,43]. For 'Seragel'® (polysulfone/polybutadiene block-copolymer) homogeneous membrane (modification S-3760) the α value for separation of a CO_2–CH_4 mixture continuously increases from $\alpha \sim 7$ (starting membrane) to $\sim$54 when the δ_F value increases from 0 to $\sim$1.6 μm and goes down with δ_F when the latter is increased whereas the permeability value of CO_2 is decreased by a factor 2.5–3 only when the α value reaches the maximum value [43].

A large contribution to the modification of gas separation properties has been made by Paul and Le Roux [44–48].

They have investigated the influence of treatment conditions (fluorinating mixture composition, fluorination duration) on the transport properties of polysulfone (PSF) asymmetric membranes and films, PMP composite membranes, PVTMS composite membranes and films and PPO composite membranes. The fluorination conditions were optimized to yield an improvement in the selectivity of the PSF membranes for the gas pairs O_2–N_2, H_2–N_2, He–CH_4, H_2–CH_4 and CO_2–CH_4 with varying decrease in the permeability of all the above gases [45–48]. The selectivities for He, CO_2, Kr and Xe relative to N_2 and CH_4 were increased upon fluorination when PVTMS membrane was used, but the selectivity for the O_2–N_2 pair remained unchanged [47]. For PPO membranes fluorination slightly increased the selectivity of He and H_2 relative to N_2 and CH_4 [46]. Langsam and Anand have investigated the influence of the treatment conditions on the gas separation properties of poly(1-(trimethylsilyl)-propyne) (PTMSP) which has one of the highest gas permeability coefficients among known polymers [49,50]. But a high permeability value is associated with a very low selectivity α value. Upon fluorination, the α values for O_2–N_2 and He–CH_4 pairs were increased to 5.1 and 248, respectively, as compared to 1.5 and 0.41 values for the starting polymer. Similar investigations were carried out for poly(trialkylgermylpropyne) [51]. The influence of direct fluorination on the selectivity of the gas separation of He–CH_4, CO_2–CH_4, He–N_2 and O_2–N_2 was investigated for PVTMS membranes which have very large productivity and are the basis of membrane production in Russia [52]. The selectivity α value can be increased by a factor of 3, 2 and 1.5 for the first three pairs, respectively, but the selectivity of the O_2–N_2 pair remains unchanged. Fluorination of PSF membrane provides hydrophilic surface properties and increases the water permeability (at 690 kPa) by a factor of 54 [53]. The α value for H_2–CH_4 and CO_2–CH_4 pairs for aromatic polyimide membranes can be increased by factors of 23 and 3.3, respectively, under fluorine treatment whereas permeability values of H_2 and CO_2 are decreased by factors of 3 and 21, respectively [54]. The α value for O_2–N_2, CO_2–CH_4 and N_2–CH_4 pairs can be increased by a factor of 2 to 3 upon direct fluorination of PSF, PS, polyarylate, PE, polycarbonate, ethylcellulose, styrene-acrylonitrile copolymer, poly(4-vinylanisol-4-vinylpyridine) and acrylonitrile-butadiene-styrene copolymer [55].

Direct fluorination can be used to modify polymer films used for food storage and preservation. At first the permeability of oxygen can be greatly decreased by fluorination of polymers, e.g., by a factor of 16 for HDPE films [56]. Kharitonov et al. have shown that the effect of the permeability reduction can be enhanced by incorporation of oxygen into the fluorinating mixture [18–21,57,58]. The following polymers were studied: PET, PS, PVTMS, PPO and polysulfone/polybutadiene block-copolymer. Oxygen incorporation into the fluorinating mixture can reduce the gas permeability by a factor of 10–200 for the above polymer as compared to the case where oxygen is absent. Carstens has also shown that direct fluorination of LDPE, HDPE, PP. PS and PET results in an oxygen permeability reduction by factors of 47, 8, 18, 10 and 19, respectively [33,34]. As direct fluorination varies the selectivity of separation of gas mixtures, fluorination can be used to modify polymer packagings for food storage such as modified atmosphere packaging (air in a pack is replaced by a mixture of different gases, where the proportion of each component is fixed when introduced but is not controlled during storage), controlled-atmosphere packaging (composition of the gas mixture is continuously controlled during storage) and equilibrium-modified atmosphere (the pack is flushed with the required gas mixture) [33,34]. However –COF groups (formed due to an oxygen admixture in a commercial fluorine) will be hydrolyzed by moisture: $-COF + H_2O = -COOH + HF$ [19–21].

4. Adhesion and printability properties

One of the main disadvantages of polyolefins and some other polymers is a low adhesion which is due to a very low total surface energy γ_S and low polarity of the polymer surface (i.e. the polar component of the total surface energy $\gamma_S^P \sim 0$). Upon direct fluorination the polar component of the surface energy can be greatly increased [59,60]. For example, the γ_S^P value for treated PE can be increased from ~0 up to ~12 mJ m^{-2} for the case when F_2–N_2 mixtures are used and up to 40–43 mJ m^{-2} when oxygen is introduced into the fluorinating mixture [60]. As we have shown [61], the γ_S^P value for PVTMS can be increased from 1.9 (starting PVTMS) up to 12.9 mJ m^{-2} upon fluorine treatment (undiluted fluorine was used).

Direct fluorination was shown to improve adhesion of polyolefins (HDPE) [33,34,62–64], LDPE [63], ethylene-vinyl acetate copolymers [65], rubber [66], PP [33,34,67], polymers of aliphatic mono-1-olefins and elastomeric, resinous polymers of conjugated dienes and vinyl-substituted aromatic compounds [68], poly(arylene sulfide) [69], polyamides and polyethers [70], butadiene-styrene copolymer, PE-vinylacetate copolymer [64] and other polymers [71]. Wettability (printability), hydrophility and hydrophobicity of polymers can also be modified [70,72,73]. A review of the influence of fluorination on the adhesion and surface energy can be found in [3]. The possible commercial applications of the adhesion improvement are as follows: enhancement of adhesion of PET cord (fabric) to rubber, improvement of the paint receptivity of polymer goods, reinforcement of polymer composites, increased resistance to delamination in coated flexible films [3,33,34]. Equipment to improve adhesion of polymers by direct fluorination is described in [3,74].

5. Friction coefficient

Direct fluorination was found to decrease the friction coefficient of polymers [75–78]. The main attention was paid to elastomers [75–77]. It was found that direct fluorination can be applied to reduce the static and dynamic friction coefficient and to improve the wear life of elastomeric articles made of copolymers of ethylene-propylene, acrylonitrile-butadiene, vinylidene fluoride-hexafluoropropylene, tetrafluoroethylene-propylene, isopropylene-isobutylene, ethylene-methyl acrylate and of poly-(chlorobutadiene) and chlorosulfonated PE [76,77]. The modification proceeds without promoting degradation of the tensile properties of the article. According to the results of preliminary investigations [78] the direct fluorination of extra high molecular weight PE used as ski coating resulted in a decrease of the friction coefficient.

6. Antireflecting coating and reduction of UV radiation

Fluorinated polymers have reduced refractive indexes n_F over the $n_F \cong 1.36$–1.4 range. Also fluorinated and untreated polymer layers are separated by a very thin boundary layer and the thickness of this layer is much less than one quarter of the wavelength of the visible light [18–21,57,79]. So an antireflecting layer (in the visible and IR regions of spectra) can be formed on the polymer surface during the direct fluorination. For this reason fluorine partial pressure and treatment duration are chosen to form the fluorinated layer having thickness $\delta_F = \lambda/(4\,n_F)$, where λ is the wavelength for which the transparency should be enhanced. Enhancement of sunlight transmission by fluorine treatment has been obtained for PP, poly(acrylonitrile), PE, polyesters, polycarbonate, poly(4-methyl-pentene-l) [80]. The influence of direct fluorination on optical properties in the visible region was studied for PS, PMMA and polycarbonate [79].

Direct fluorination can be used to produce a protecting coating which decreases the transparency of UV light through polymer articles [81].

7. Protecting coating, improvement of chemical resistance

As it was mentioned earlier (see Sections 1 and 2), fluorine treated polymers have reduced permeability for gases and liquids. Also the direct fluorination improves the chemical resistance of polymers. In part this is due to crosslinking of polymers under fluorine treatment. For example, fluorinated PS and PET cannot be dissolved by ordinary solvents and by Freons-62, -63, -112, -113 [18–20,57]. More detailed information on the utilization of fluorine in protecting coating can be found in papers of the series of Conferences 'Fluorine in Coatings' (Munchen, Germany, 24–26 February 1997; Manchester, 28–30 September 1994, etc.).

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