

# Investigations on the Reactive Surface Modification of Polycarbonate by Surface-Reactive Injection Molding

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**ABSTRACT:** A new procedure of surface modification was investigated in which the modification was coupled with the injection molding process. This procedure could save other commonly used surface modification procedures such as flame or plasma treatment. According to the procedure, a reactive modifier was applied to the surface of the mold cavity. On injection of the plastic melt, a chemical reaction took place, which attaches the modifier covalently to the resultant plastic part. In this contribution, conditions are considered for the modification of polycarbonate with poly(vinyl alcohol) and polyethylenimine as modifiers. The reaction in the melt was investigated and the modified sur-

faces of injection-molded plates were characterized. The surface modification, realized with the new approach, was permanent. It allows for the introduction of special functional groups, which may be useful for further reactive processing stages such as reactive adhesive joining, reactive coating, metallization, or functionalization for special applications. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1186–1191, 2004

**Key words:** polycarbonates; injection molding; reactive processing; surface modification; fluorescence

## INTRODUCTION

Plastics, as well as related processing technologies, have experienced extended development in the last decades with the result that plastic materials now cover a broadened application area. Demands on the surface properties of plastic parts are getting more and more important (e.g., to ensure rational and environmentally friendly paintability, adhesive properties, and printability). The extended use of water-based paints and adhesives, and the hydrophobic properties of most plastics, lead to increased demands on the surface properties.

The problem of modification of plastic surfaces has been worked on intensively for a long time. A common way of activating plastic surfaces is by flame or plasma treatment. With these methods, some atom groups on the outer surface layer are chemically converted into more reactive species such as carboxylic acids, amines, and radicals, which lower the surface energy.<sup>1</sup> The conversions are seldom selective, so that a broad range of functional groups is formed. Many approaches to modification of plastic surfaces (e.g., of polycarbonate) have been investigated.<sup>1–6</sup> It was frequently observed that the effects were not permanent

but disappeared after a short period of time.<sup>7</sup> All the procedures of surface pretreatment have to be done shortly before any further processing. Moreover, the surface pretreatment always forms an additional step in the processing chain.

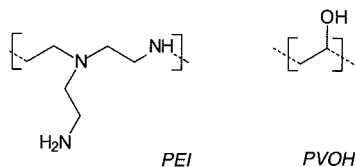
In this contribution, we describe a new approach of surface-reactive injection molding that will allow the surface of injection-molded plastic parts to be modified while the part is molded. Thus, molding and surface modification occur in one step. The method is based on the reaction of the flowing melt injected into the mold cavity with a reactive modifier that has been applied to the mold surface before. The functional groups on the surface created by this approach are well defined and can be tailored for any further processing. The idea of the method is explained. In this article a polycarbonate (PC) is used as the plastic material for the experiments. Some investigations of melt reactions lead to a selection of modifiers that are used in injection-molding experiments. Finally, the modified surfaces are characterized by different approaches.

## EXPERIMENTAL

PC Lexan 121 (General Electric) was used as the plastic material for the surface modification experiments as well as for investigations in the melt. As reactive modifiers, poly(vinyl alcohol) (PVOH; Moviol 28–99, hydrolysis > 99%, Clariant GmbH, Germany), polyethylenimine (PEI; Aldrich,  $M_w$  750,000 by light scatter-

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**Scheme 1** Chemical structure of the polymeric modifiers.

ing, branched, aqueous solution, 50% by mass), dextran (Dextran T 10, Biotech, Sweden), and triethylene glycol (TEG; Aldrich) were used. The chemical structures of PEI and PVOH are shown in Scheme 1.

For injection-molding experiments, the modifiers were dissolved in a water/ethanol mixture with concentrations of 1 mass % for PVOH and dextran and 5 mass % for PEI. Fluorescamine (Aldrich) was used as a  $10^{-4}M$  solution in ethanol as a spectroscopic marker.

The experiments were carried out with a DEMAG injection-molding machine (Germany) of up to 1000 kN clamping force. The mass temperature of PC was  $320^{\circ}C$ , and the mold temperature was  $80^{\circ}C$ .

The mold produced quadratic plates with a length of 80 mm and a thickness of 1 mm. The modifier solution was applied with a thin-layer chromatography spray head.

The plastic plate surfaces were cleaned by rinsing with ethanol before they were characterized. The contact angle against water was measured dynamically with an Axisymmetric Drop Shape Analysis (ADSA)<sup>8</sup> device approximately 4 weeks after the samples were prepared. The advancing and receding angles were averaged from at least 10 single data measurements.

ATR-FTIR measurements were carried out with a Bruker IFS-66 spectrometer with a Golden Gate ATR stage (Specac). UV spectra were performed with a Perkin-Elmer Lambda 800 spectrometer in transmission. Fluorescence spectra were measured with a Perkin-Elmer Lambda 50 spectrometer. For these measurements, a special sample holder was used in which the excitation beam hit the sample surface at an angle of  $45^{\circ}$  and was reflected into a light trap. With this setup, stray light from the excitation beam could be suppressed from hitting the detector. For the DSC measurements, a DSC 7 device (Perkin-Elmer) was used. The PC granules were ground to yield a powder, using liquid nitrogen to prevent thermal decomposition. In the case of mixtures, the powders were mixed beforehand.

Electrokinetic measurements of the surfaces were carried out with an Electrokinetic Analyzer device (Anton Paar GmbH, Austria). The values of zeta potential ( $\zeta$ ) were calculated according to the Smoluchowski equation:  $\zeta = -\eta\Delta U\kappa/(\varepsilon_0\varepsilon_r\Delta p)$ . Here  $\Delta U$  is streaming potential, measured between two Ag/AgCl electrodes located at the opposite ends of the substrate;  $\eta$ ,  $\varepsilon_r$ , and  $\kappa$  are the dynamic viscosity, relative

permittivity, and conductivity of the flowing electrolyte solution ( $10^{-3} \text{ mol L}^{-1}$  KCl), respectively;  $\varepsilon_0$  is the permittivity of vacuum; and  $\Delta p$  is the applied pressure (150 mbar). Solutions of KOH and HCl ( $0.1 \text{ mol L}^{-1}$ ) were used to change the pH value of the streaming electrolyte solution in the range between 9 and 2.

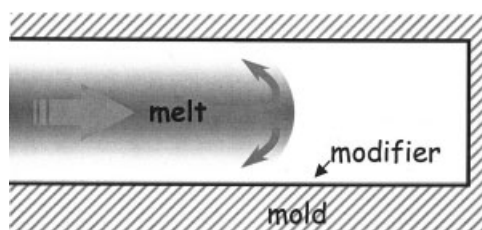
## RESULTS AND DISCUSSION

### The procedure of surface-reactive injection molding

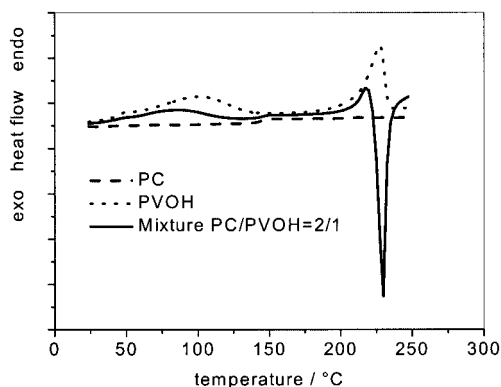
A solution of a macromolecular modifier with reactive groups was applied to the surface of the mold cavity, usually by spray coating. Due to the elevated mold temperature, the solvent evaporated quickly. A thin film of the modifier was retained at the mold surface. On injection of the polymer melt, the melt front hit the modifier at the mold surface (Figure A) and, due to the high temperature, a reaction was initiated that attached the polymeric modifier covalently to the formed plastic part. Thus, the modification of the plastic part of the surfaces was done in the molding step. One condition for effective modification was that the modifier contained functional groups, acting as bond sites, had to be reactive to the plastic material at the temperature of the melt-mold interface. Due to rapid cooling, a high peak temperature was available only for a very short time,  $\sim 1$  s.

### Investigations of reactions in the melt

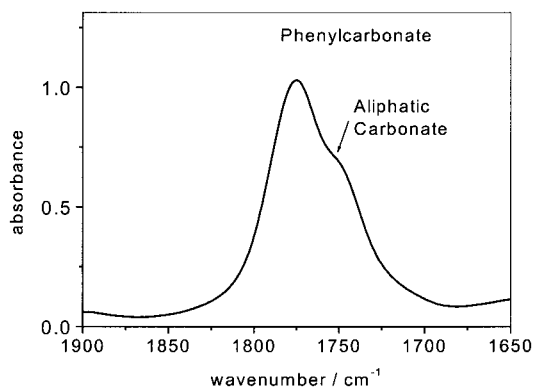
As the reactivity of the modifier is an important aspect for injection-molding experiments, a suitable modifier had to be identified. For this reason, investigations of the reaction in the melt state were carried out. A suitable modifier should react under the conditions in the following experiments, although the conditions for a reaction to take place at the mold surface were more restricting because of the rapid cooling. The experiments were done with PVOH as modifier. In Figure 1, DSC curves of PC, PVOH, and of a mixture of both are shown. In the heating curve of PC, the usual glass transition at  $147^{\circ}C$  could be seen. The heating curve of PVOH showed a glass transition at  $40^{\circ}C$  as a shoulder of a broad band. This broad band did not appear in the



**Figure A**



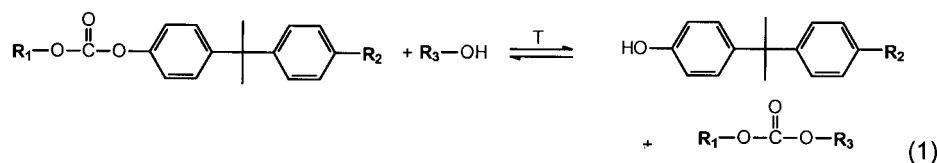
**Figure 1** DSC curves of PC, PVOH, and of a mixture of two parts PC and one part PVOH. First heating shown, 10 K  $\text{min}^{-1}$ . Netzsch 204 under  $\text{N}_2$ .



**Figure 2** Spectrum of the melt reaction product of PC and PVOH. 10 mass% PVOH, processing in a microcompounder (DACA) at 200°C, 5 min, KBr tablet.

second heating (not shown) and may originate by evaporation of adsorbed water. Finally, a melting peak at  $\sim 230^\circ\text{C}$  was measured. The mixture exhibited the same characteristics as the single compounds up to a temperature of  $\sim 225^\circ\text{C}$ . After a certain amount of PVOH melted, a steep and large exothermic peak appeared, which pointed to a reaction between PC and PVOH. The minimum of the reaction peak was at  $230^\circ\text{C}$ . Because PC is commonly processed at around

$300^\circ\text{C}$ , PVOH may be indicated as a suitable modifier. To analyze the product of the melt reaction, PC and PVOH were processed in a microcompounder. The product was analyzed by infrared measurements. The spectrum (see Fig. 2) exhibited the typical absorption of the aromatic carbonate bond at  $1775\text{ cm}^{-1}$ .<sup>9</sup> At  $1750\text{ cm}^{-1}$ , a shoulder emerged. This absorption pointed to the formation of an aliphatic carbonate.<sup>10</sup> Consequently, alcoholysis, as shown in eq. (1).



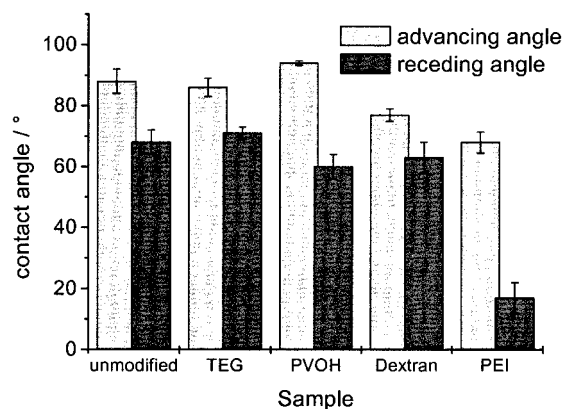
may have taken place, in which the PC chain was split into one fragment bound to a PVOH site and one fragment with a phenolic end group. In the case in which amine groups are present such as in PEI, the amine-bearing component would be bound to PC via a urea bond. Because PVOH had a high number of hydroxyl groups, branching was likely to occur. Experiments in a Haake kneader showed that the torque decreased, on addition of 2 g PVOH to 50 g PC, from 3 Nm to less than 0.1 Nm after 3 min. Probably chain degradation or branching took place, which supports the DSC and IR investigations.

### Surface properties of modified plastic parts

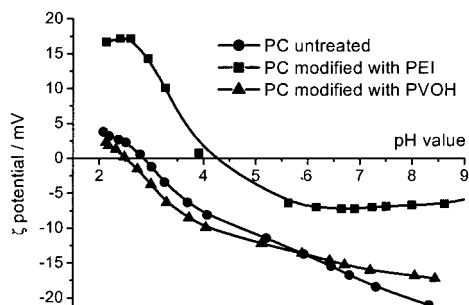
As PVOH was shown to react with PC in the melt state, it was used as a modifier in the new method of surface modification. The reaction was found to be based on the hydroxyl groups. Therefore, in some injection-molding experiments, dextran and TEG were used in comparison. PEI, having even more reactive amine groups, was also used as modifier, although

investigations in the melt could not be carried out, because PEI is available only as an aqueous solution.

The contact angles of the unmodified PC surface were  $84^\circ$  and  $63^\circ$  for the advancing and receding



**Figure 3** Contact angle against water of PC samples, treated with different modifiers at the injection molding. Standard deviation of measurements is included.



**Figure 4**  $\zeta$  potential as a function of the pH value for unmodified and modified PC surfaces.

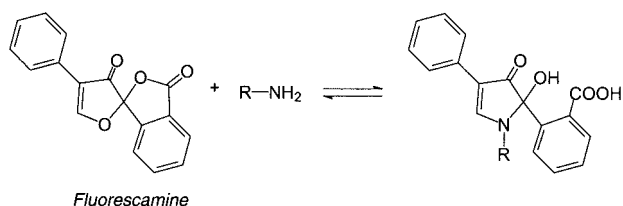
angles, respectively, see Figure 3. These values are usual for PC.<sup>11</sup> The values, for PC treated with TEG as modifier according to the procedure explained before, did not show a significant deviation from those of the unmodified PC. Thus, the products of a surface reaction may be unstable, or TEG may be removed from the mold surface by injection of PC, so that a reaction could not take place at the surface of the melt. A significant change of the wettability could not be observed with either Dextran or PVOH as modifier for which both polymers have a high number of hydroxyl groups. As shown in the DSC experiments, reaction with PVOH should have taken place under the conditions used. The sample, which was modified with PEI, showed a small decrease of the advancing angle. The receding angle (20°), however, was drastically affected by the modification with PEI. This led finally to total wetting of the PC surface. The PC surface was, consequently, covered by a thin layer of PEI, which made the surface hydrophilic. Because the advancing angle was rather high, it may be assumed that this layer had to swell before total wetting was achieved. The wetting properties were measured some weeks after the samples were prepared.

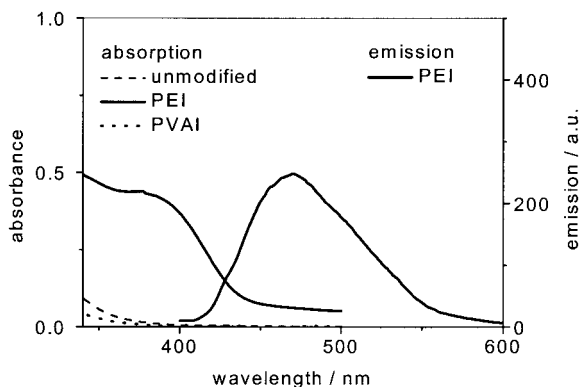
In the ATR-FTIR spectra of the surfaces modified with PEI,  $\nu_{(N-H)}$  as well as  $\nu_{(C-H)}$  vibrations were evident (not shown), which pointed to a PEI layer at the PC surface. This confirmed the conclusions from the wetting measurements. However, an indication of a PVOH layer could not be found in the spectra.

The zeta potential-pH curve of the unmodified PC surface (see Fig. 4) decreased continuously with increasing pH and, thus, was characteristic of that of a surface without functional groups. The surface, which was modified with PEI, exhibited a shift of the isoelectric point by approximately +1.5 pH units. At pH higher than 5.5, the potential stayed constant. This pointed to a thin layer of macromolecules with basic groups at the PC surface, a conclusion consistent with those of the wetting experiments. The rise of the potential curve of the surface modified with PVOH was slightly lower than that of the unmodified PC surface, which revealed that some functional groups were in-

troduced at the surface. Further, the isoelectric point was shifted to lower pH by  $\sim 0.4$  units: this was an indication of acid groups. The reason for that was not clear because PVOH did not bear acid groups. Probably, PVOH was partly oxidized during contact with the melt surface that had a high temperature. On the other hand, phenolic end groups resulting from the splitting reaction, according to eq. (1), may be responsible for the acidic behavior. Although those groups must have been formed on modification with PEI, too, the effect was more than compensated by its residual basic groups. The results showed that a PEI layer with active amine groups is fixed at the PC surface, and the bonding is stable within the frame of the experimental procedure. Electrokinetic measurements gave an indication of successful surface modification with PVOH, which was expected from the melt investigations, whereas the wettability and infrared measurements did not give any evidence. This may be caused by the different sensitivities of the methods with regard to the penetration depth. A relatively small number of acidic groups at a nonpolar surface may be detectable by electrokinetic methods, whereas the wettability is rather an integral method, which needs higher concentrations on the top-most surface. The ATR-FTIR signal has a penetration depth of several micrometers and, thus, needs a higher amount of material at the surface to be detectable, too. Therefore, the detection of PVOH is restricted by its lower reactivity as well as by the lower sensitivity of the methods used to analyze the surfaces.

According to the concept of reactive modification, functional groups introduced by the new approach should be available for further reactive processing as for example, for reactive bonding or paint adhesion, provided that the functional groups at the surface are stable during the injection processing. The decrease of the isoelectric point in the case of PVOH gave an indication that some of the reactive groups may be converted. Amine groups, particularly primary amines, are usually even more susceptible to oxidation. For this reason, experiments were carried out to probe the primary amines at the modified PC surface. In these experiments, fluorescamine was used as a label. Fluorescamine is a colorless compound that converts by reaction with primary amines to a compound with distinct UV absorption and fluorescence spectra,<sup>12,13</sup> according to





**Figure 5** Absorption and fluorescence spectra of an unmodified sample and samples modified with PVOH or PEI, treated with fluorescamine.

This compound has an absorption maximum at 380 nm and emits light with a maximum of 470 nm. In a first experiment, a solution of fluorescamine was added to PEI solutions at different molar ratios to determine the content of primary amine groups in the macromolecule according to ref. <sup>14</sup> with PEI concentrations being between  $10^{-4}$  and  $10^{-5}$  M. With that method, a  $\text{NH}_2$  molar content in PEI of 25% was obtained, which is a typical value for that highly branched macromolecule.

The unmodified and modified PC surfaces were cleaned in a Soxhlet and then treated with a diluted ethanolic fluorescamine solution at room temperature, followed by rinsing with ethanol. The spectra in Figure 5 show the characteristics of the reaction product with adsorption and emission bands at 380 and 470 nm, respectively, which established that primary amines could be detected at the PC surface modified with PEI by conversion with fluorescamine. In contrast, the unmodified surface, and the surface that was modified with PVOH, did not show the characteristic spectra. The advantage of the labeling is that, unreacted, dye adsorption did not interfere, but only the chemically specific conversion contributed to the signal. It should be remarked that the detected primary amines of PEI at the PC surface were not converted by the injection processing and are stable against extraction with ethanol at elevated temperature. The amine groups stay reactive and are accessible and permanently bound to the surface. This would enable reactive processing of the surfaces.

A quantitative determination of the amine groups was carried out by means of the known extinction coefficient.<sup>15</sup> The surface concentration was found to be  $\geq 6 \times 10^{-4}$  mol  $\text{m}^{-2}$ . Such a high density may only be realized with macromolecules in which several functional groups are bound over a low number of coupling sites. Indeed, geometric considerations lead to the assumption that the conversion was rather limited by the

size of the fluorescamine molecule, which had to diffuse through the modifier layer, and that the surface concentration of primary amines was even higher. It may be further assumed that the total amine concentration was several times higher, according to the molecular structure of PEI (see Scheme 1). The investigations on the PC surface modified with PEI may be summarized as follows: The branched macromolecule was bound by several sites to the PC macromolecules. The PC molecule was split into two chain fragments due to the reaction. A high number of reactive residual primary amine groups stayed on the PEI macromolecule and are, thus, bound chemically to the PC surface.

## CONCLUSION

Fundamentals of a new process of surface modification of plastics were acquired. The process is based on the reactive coupling of a modifier onto the plastic surface at the injection-molding step. First investigations on this surface-reactive injection molding process were carried out with PC in this work. Application of the new method for surface modification of other plastic materials may be possible. A suitable modifier has to provide reactive groups specific to the plastic material. Work is in progress for a number of plastics.

The reaction with PC was first studied in the melt state and then transferred to the injection-molding process. Investigations revealed that the modifier was bound covalently to the plastic surface. On the other hand, there were residual functional groups, which were accessible and reactive, that could be used for further reactive processing of the surface. The surface density of the residual functional groups was high.

The new method has several advantages. The thermal energy applied once for the melting of the plastic could be used to initiate the reaction. A pretreatment (flame, plasma), commonly used to activate the plastic surface for further processing, can be avoided. The modification effect remained some weeks after preparation. The functional groups at the plastic surface can be tailored for the effect required.

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