Oxygen Barrier Coatings Based on Supramolecular Assembly of Melamine†

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ABSTRACT: Gas permeability is one of the key performance characteristics of polymeric films. Here we explore a novel approach for modifying the oxygen transmission rate of polymers by vapor deposition of melamine. We will show that melamine, upon physical vapor deposition, forms a transparent uniform layer on polymeric films such as biaxially oriented polypropylene. X-ray diffraction, in combination with molecular modeling, has indicated that the melamine coating is crystalline and macroscopically oriented with the preferred direction of the melamine molecules parallel to the (polymeric) substrate. The vapor-deposited melamine molecules undergo a large number of cooperative hydrogen bond interactions leading to a coherent layer of an infinite supramolecular network. The melamine coating acts as a surprisingly effective barrier against gases, decreasing drastically, for example, the oxygen transmission rate through coated polymer films by 2 orders of magnitude. The effect is attributed to the crystalline nature of the deposited melamine layer, strengthened by the high level of hydrogen bonding. This is the first example of application of supramolecular chemistry for the production of health and environment friendly transparent barrier coatings against oxygen. The vacuum-coating process with melamine and related compounds is expected to bring a major breakthrough in the field of transparent polymeric barrier films for applications, for example, in food and pharmaceutical packaging.

1. Introduction

Melamine and related triazine compounds are one of the most widely applied building blocks in the field of supramolecular chemistry[1] (see Figure 1). This can be mainly attributed to the fact that melamine can act both as donor and acceptor in hydrogen bonding, which interactions are fundamental in supramolecular chemistry.[2] Owing to the perfectly symmetrical structure and crystalline nature, the solubility of melamine is very limited in most common organic solvents. This hampers the use of melamine as pure compound in supramolecular chemistry, especially when reactions are carried out in solution. Melaminecyanurate, a well-known fire retarding agent for polymers,[3] is one of the examples of the formation of a supramolecular complex of pure melamine and cyanuric acid. The action of melaminecyanurate as a flame retardant is, however, in no respect believed to be related to the supramolecular structure, consisting of a two-dimensional hydrogen-bonded network between cyanuric acid and melamine.[4]

Here we explore an alternative route for the application of melamine in supramolecular chemistry, which is based on physical vapor deposition (PVD) of this compound on substrates such as polymeric films. Although melamine starts to simultaneously melt and degrade upon heating above 350 °C, it does sublimate at temperatures typically exceeding 200 °C. We will show that physical vapor deposition of melamine on polymeric films under reduced pressure can lead to very well-defined transparent organic layers with a high barrier to gases, including oxygen. Using X-ray diffraction it is demonstrated that the hydrogen-bonded layers are oriented with a preferred direction parallel to the surface of the polymer film. The results of X-ray diffraction are compared with the results of the molecular modeling calculations. The postulated molecular structure is a hydrogen-bonded network of melamine molecules and is believed to be the first example of application of supramolecular chemistry resulting in functional polymers with a high barrier to oxygen and possibly other gases.

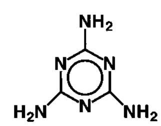

Figure 1. Chemical structure of melamine.

II. Experimental Section

Melamine (DSM standard grade of 99.8%) was evaporated by a photon-heated copper crucible situated in a vacuum chamber (Lybold Germany). The deposition experiments were carried out usually at a pressure of 1×10^{-2} to 5×10^{-3} Pa and temperatures between 220 and 270 °C.

Oxygen transmission rate measurements were conducted according to DIN 53 380, part 3.

Raman spectra were measured using the Labram confocal Raman system (Dilor). The laser excitation wavelength was 632.8 nm, the microscope objective had a magnification of 100× and the confocal pinhole was set to 100 μm. In this mode the spatial resolution is 1 μm laterally and 2 μm vertically. The spectral resolution was 1 μm. Four spectra of 60 s acquisition time each were accumulated.

Scanning electron microscope (SEM) experiments were carried out using a Philips CP SEM XL 30 in combination with an Everhart Thornley secondary electron detector at 20 kV.

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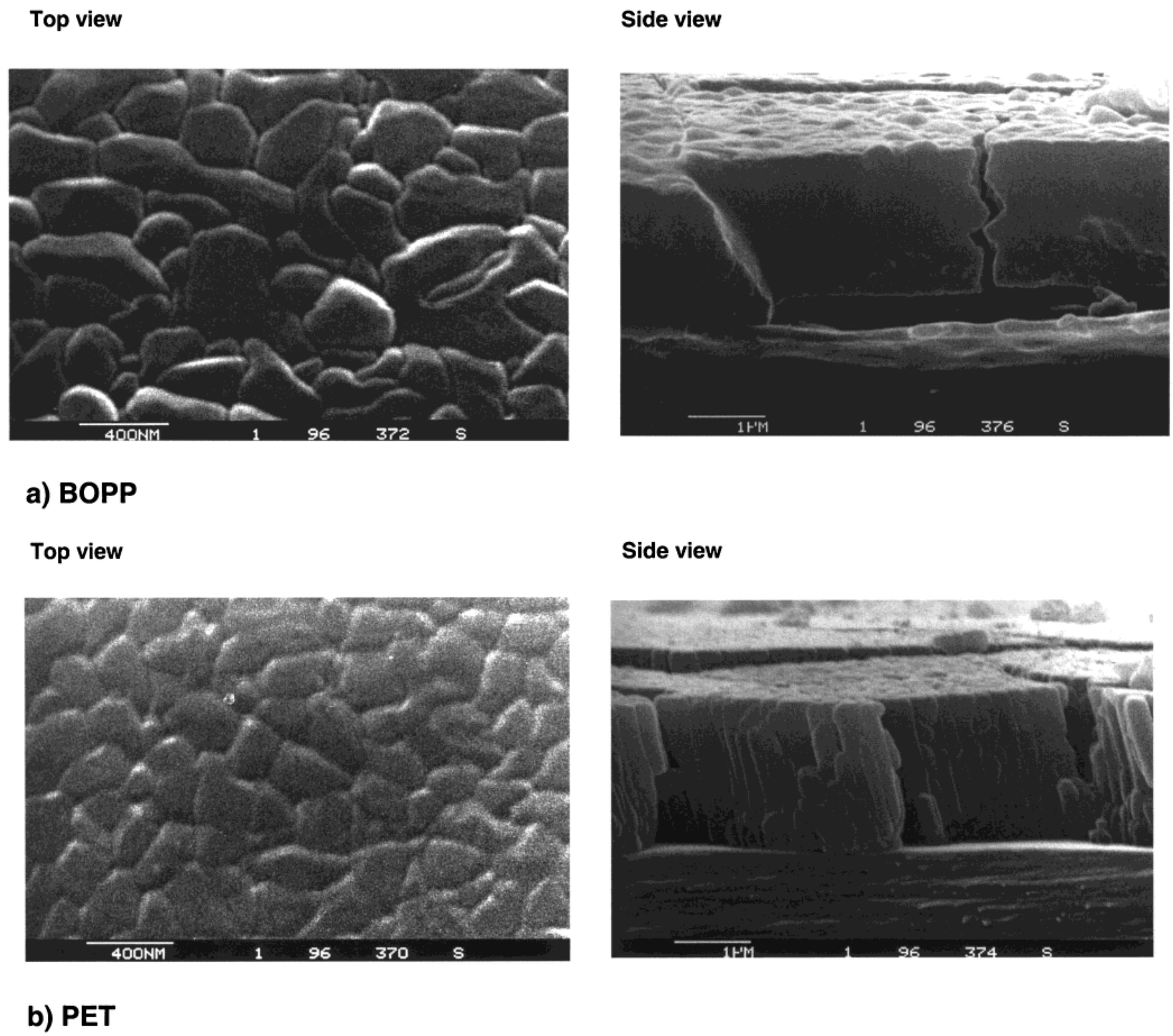

Figure 2. Scanning electron microscopy (SEM) images of melamine vapor deposited on polymeric films; (a) biaxially oriented polypropylene (BOPP) and (b) poly(ethylene terephthalate) (PET). The images show that the deposited melamine layers are quite uniform. The cracks are not formed in the vapor deposition process but result from sample preparation for SEM measurements. The transparency of BOPP and PET films did not change as result of the melamine coating.

X-ray diffraction measurements were performed with powder diffractometers PW1050 and PW1820 in Bragg Brentano geometry using fixed slits (1 divergency slit; 0.2 mm entrance slit). Cu Kα radiation was used (40 kV, 50 mA) with a monochromator in the diffracted beam.

The diffraction pattern of melamine has been modelled by means of the diffraction module of the Cerius2 molecular modeling package of Molecular Simulations. Default diffraction parameters were used and the experimental crystal structure was taken from literature. Preferred orientation has been taken into account by means of the March−Dollase function with the preferred orientation parameter R_0 set to 0.6.

III. Results and Discussion

Figure 2 shows the scanning electron microscopy (SEM) images of melamine vapor deposited on biaxially oriented polypropylene (BOPP) films and poly(ethylene terephthalate) (PET) films. As can be seen, the deposited melamine layers have a fairly uniform thickness. The coated polymer films were perfectly transparent up to a melamine layer thickness of 2 μm. In addition to SEM experiments, topographic scanning force microscopy measurements (not shown here) indicated that melamine forms a continuous layer upon vapor deposition. To determine the chemical structure of the deposited layers, Raman measurements were conducted at various depths into the surface of melamine-coated BOPP film (see Figure 3). Subtraction of spectrum 3a of the surface from 3b (10 μm under the surface) results in spectrum 3c. Comparison of spectrum 3c with the reference spectrum of melamine reveals that no noticeable chemical changes have occurred during vapor deposition of melamine.

The top view of SEM images in Figure 2 suggests the formation of some type of columnar structure during vapor deposition. We may interpret these results as follows: upon deposition of melamine from the vapor phase, nucleation occurs at different locations on the polymer surface. The growth of the crystalline regions, parallel to the polymer film, is halted when the borderlines of the crystallites meet. At this point, a continuous melamine layer is formed and the coating starts to grow

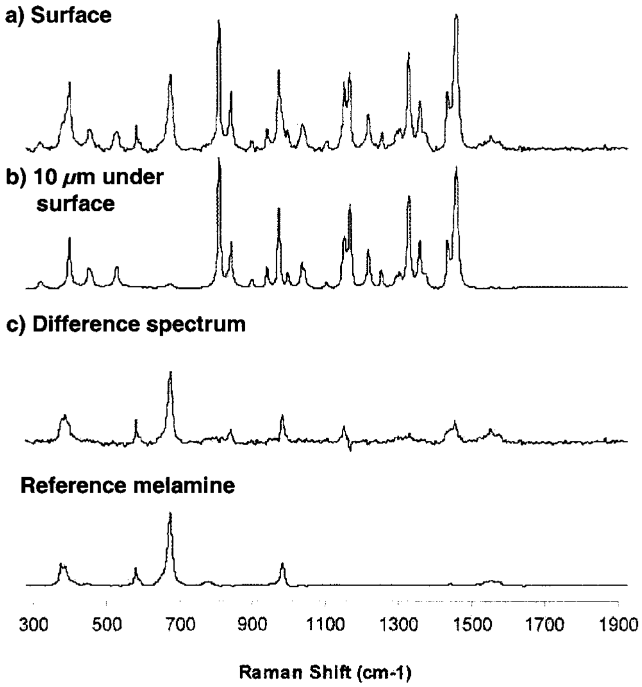

Figure 3. Raman spectra of a melamine-coated BOPP film. The subtraction of the Raman spectrum of the surface (a) from the spectrum measured 10 μm under the surface (b) results in the difference spectrum (c). From the comparison of the difference spectrum (c) with the spectrum of standard melamine, it can be concluded that the deposited layer consists of melamine.

mainly in the direction perpendicular to the polymer film. This model is schematically shown in Figure 4.

The above model suggests that the triazine rings of melamine have preferred direction of orientation parallel to the surface of the polymer film. To investigate the molecular orientation of the deposited melamine layer, we have conducted X-ray diffraction experiments. The interpretation of the measurements carried out directly on the coated polymeric substrates is hampered by the crystalline nature of BOPP and PET films. Alternatively, X-ray diffractograms were recorded of melamine layer deposited under similar conditions on a silicon plate, which is transparent to X-ray radiation (see Figure 5). The X-ray diffraction patterns of the deposited melamine on a silicon plate are shown in Figure 5. Comparing this diffractogram with the diffractogram of standard powder melamine, we can conclude that the crystalline structure of melamine does not change upon vapor deposition. The difference in the peak intensities indicates, however, a preferred direction of orientation of melamine molecules induced during vapor deposition.

To elucidate the nature of the orientation in the vapor-deposited melamine layers, we have calculated X-ray diffraction patterns with Cerius2. Using the crystal structure of melamine,[5] the diffraction pattern is calculated with the 2 0 1 direction normal to the

Table 1. Oxygen Transmission Rate of Melamine-Coated Polymeric Films

polymeric film[b]	OTR[a] [cm^3]/m^2 d bar noncoated	OTR[a] [cm^3]/m^2 d bar coated with melamine
BOPP (20 μm)	1600	30
PET (12 μm)	110	1

[a] Oxygen transmission rate (OTR) at 23 °C and 0% humidity. [b] The number in parentheses is the thickness of the polymer film before coating.

surface. Figure 6 shows the experimental and calculated diffractograms. As can be seen in this figure, there is an almost perfect match between the simulated and the experimental results. In Figure 7 the corresponding supramolecular structure of melamine is displayed. Here the data are shown for the first molecular layer of melamine coating at the interface with an imaginary substrate. During the deposition of melamine, the triazine rings apparently lie on the surface and undergo extensive hydrogen bonding; according to the simulated results almost all hydrogen bonding sites are occupied. The major cooperative hydrogen bonding interactions result in a high dimensional stability of the deposited melamine layer, which exceeds the grain boundaries of the crystal. In addition, provided the underlying substrate is susceptible to hydrogen bonding, such interactions with the deposited melamine layer will undoubtedly improve adhesion.[6]

As mentioned earlier, the interpretation of the X-ray results of deposited melamine layers on BOPP and PET was frustrated by the diffraction peaks originating from these crystalline polymers. The major diffraction peak of the 201 reflection at 3.4 Å was, however, present in all difractograms, regardless of the nature of the underlying substrate. This indicates that the orientation of deposited melamine layers, shown in Figure 7, is independent of all the substrates studied here, i.e., Si, BOPP, and PET. Notably, there is no line-broadening effect detectable besides the usual instrumental effects. This implies that the apparent crystallite sizes are larger than 100 nm. This is, in turn, in agreement with the SEM images showing dimensions larger than 100 nm (see Figure 2).

Finally, we should discuss the performance of polymer films coated with deposited melamine in terms of gas permeability. As can be seen in Table 1, the oxygen transmission rate (OTR) of BOPP and PET is drastically reduced upon coating with melamine.

The dependence of the OTR on the thickness of the melamine layer is seen in Figure 8. The OTR value of BOPP has decreased by a factor of approximately 50 already upon deposition of a melamine layer with a thickness of 36 nm. Further increase of the coating thickness does not seem to influence the OTR values significantly. Similar behavior was observed in the case of melamine-coated PET films. The enormous effect of melamine on the oxygen transmission rate of BOPP and PET can be attributed to the high degree of crystallinity

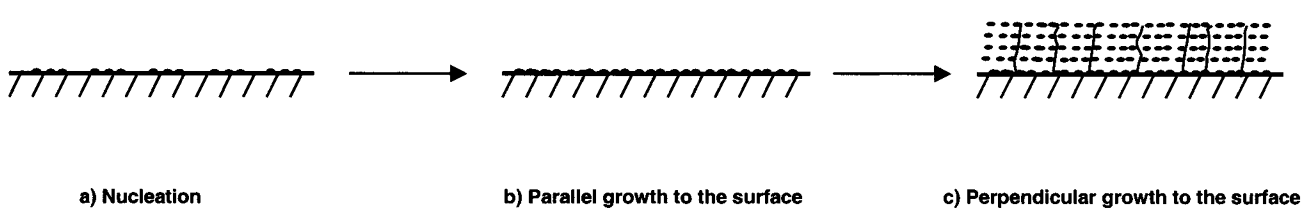

Figure 4. Schematic representation of the melamine coating process: (a) nucleation at various locations on the polymer surface; (b) growth parallel to the polymer surface until the crystallites meet, resulting in the formation of a coherent melamine coating; (c) growth perpendicular to the polymer surface, resulting finally in the columnar texture as shown in Figure 2.

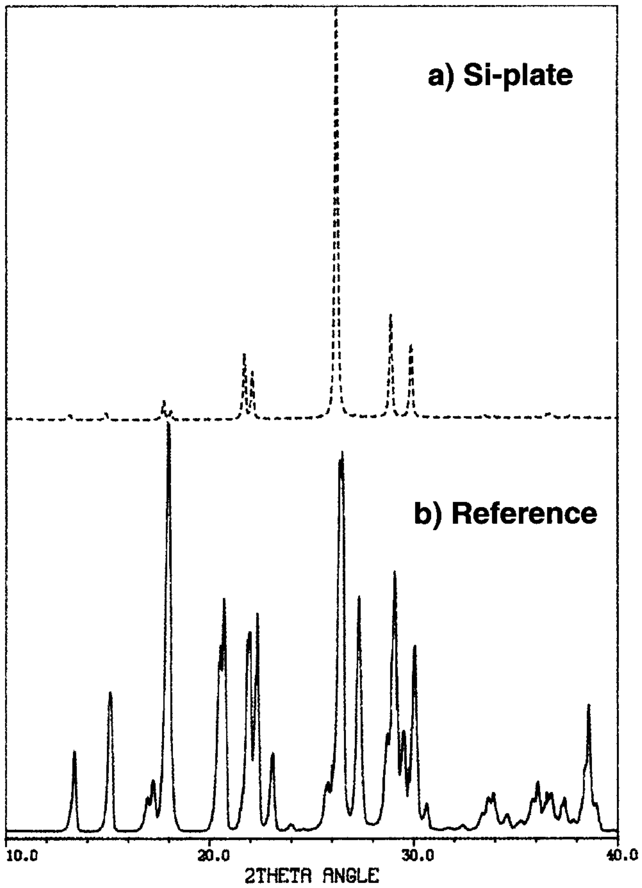

Figure 5. X-ray diffractograms of melamine vapor deposited on Si-plates (a). From the comparison of diffractogram a with the diffractogram of the standard melamine powder (b) the following conclusions can be drawn: (1) the crystalline structure of the deposited melamine coating is similar to the structure of standard melamine; (2) the deposited melamine coating is highly oriented because of the major differences in peak intensities compared with the reference diffractogram.

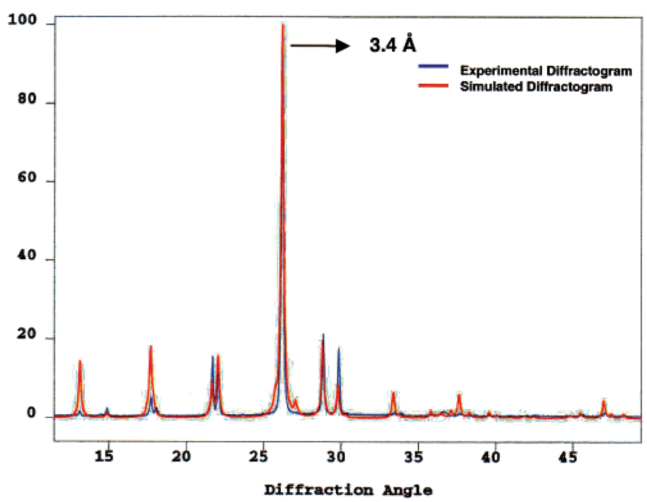

Figure 6. Overlay plot of the experimental X-ray diffractogram of melamine vapor deposited on a silicon plate and the simulated diffractogram based on the preferential orientation of the crystals in the direction 201. This diffractogram is simulated using the computer program Cerius2, with the well-known crystalline structure of melamine as the input.

of the deposited layer. The crystalline layer is dimensionally strengthened by the occurrence of cooperative hydrogen bonding interactions between the melamine molecules, leading eventually to an infinite macroscopically oriented supramolecular network. Apparently, the diffusion of oxygen through this network, strengthened by hydrogen bonds, is very low. It is well-known that the OTR of polymers decreases with the degree of crystallinity. It has even been stated that the OTR of a 100% crystalline polymer should hypothetically be close to zero.[7] By depositing melamine, we cover the surface of the polymer film with a crystalline substance, resulting in a very low permeability to oxygen.

The effects of mechanical distortion and relative humidity on OTR values are important especially from the viewpoint of practical applications. Since for food packaging purposes the barrier layer is often sandwiched between two polymeric films, we have conducted our investigations on a standard laminate with the following structure: PET/melamine layer/polyurethane adhesive/polyethylene (PE) film. The effect of mechanical stress on OTR is determined by elongating the laminates and measuring the OTR values. The OTR did not change after elongation at 1%, 2%, and 3%. This performance is more than sufficient for high-speed packaging machines, since during such processing steps the elongation of the films is not higher than 2%. In view of the slight solubility of melamine in water (0.5% at RT and 5% at 100), we observed that OTR of the laminates tended to increase as a function of relative humidity especially above humidity values of 50%. Considering the performance of melamine layer sandwiched between PET and PE, we can state that these laminates can be used for packaging of dry foods, i.e., applications at low humidity. For packaging applications at high humidity, melamine barrier layer should be sandwiched most probably between two apolar polymers with low water transmission rate such as BOPP and PE.

The OTR of polymeric films, in particular BOPP and PET, is of major importance in the food and pharmaceutical packaging industry.[8] Co-extrusion lamination to an aluminum foil or a metallization process using aluminum is among the most widely used methods to improve the barrier properties of polymeric films. In general, these processes have two major disadvantages. First of all, application of aluminum in packaging becomes less attractive mainly because of environmental concerns. From a technical point of view, metallized films may be disadvantageous owing to the lack of transparency. Transparent barrier materials are highly desirable for a number of packaging applications.[9] At the moment, intensive research is taking place at a global level to develop environmentally friendly clear barrier materials. These activities are further accelerated by Japan's recent ban of polyvinylidene chloride-(PVDC-) coated films, which are yet another type of clear barrier material, suspected of negative health and environment effects.

Physical vapor deposition of metal oxides such as SiO_x and AlO_x to form barrier layers against oxygen is at the moment state of the art.[10] However, a major breakthrough for these barrier materials has been hampered by a number of factors. First of all, the technology is quite complicated because of the high evaporation temperatures (>1000 °C) and very low pressures, which requires the use of expensive electron beam guns as a heat source and diffusion pumps, respectively. The cost of vapor-deposited coatings is further increased by the high price of the SiO_x raw materials. In addition, a coating process at such elevated operation temperatures limits the use of heat sensitive polymers, like polyethylene, with a low glass transition temperature. The

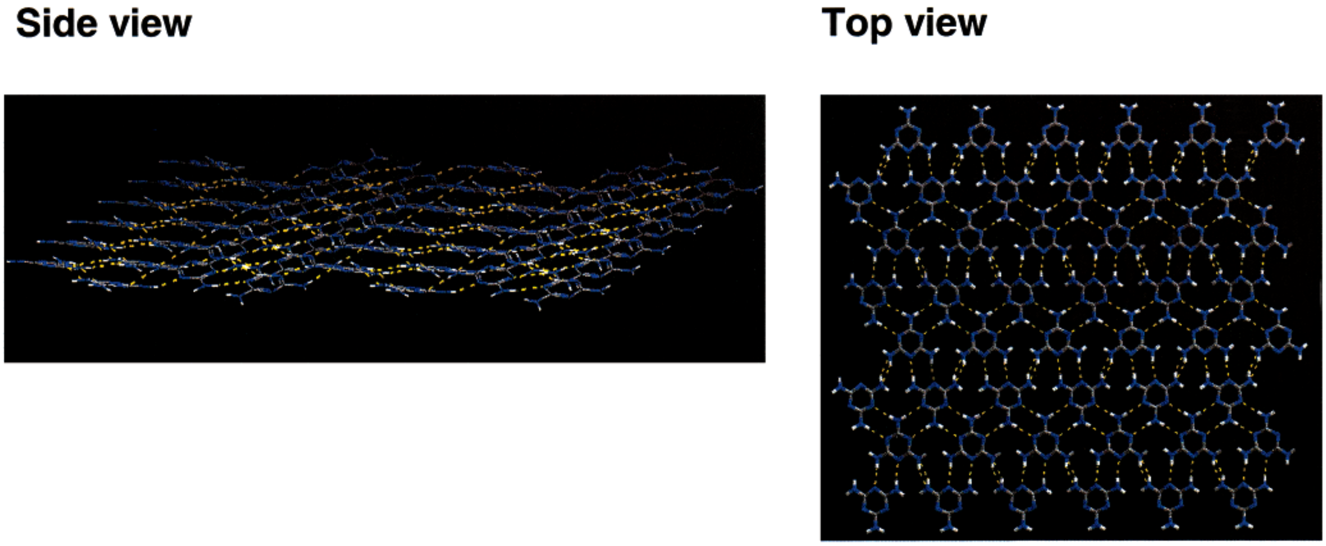

Figure 7. Simulated supramolecular structure of the first layer of melamine vapor deposited on an imaginary surface. The hydrogen bonds are shown in yellow.

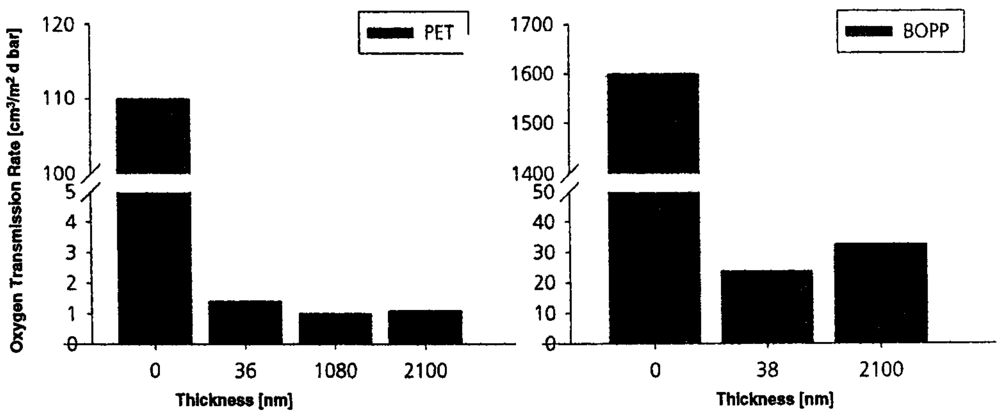

Figure 8. Dependence of the oxygen transmission rate (OTR) of BOPP and PET films on the thickness of the melamine coat. As can be seen, the OTR values are almost independent of the melamine layer thickness.

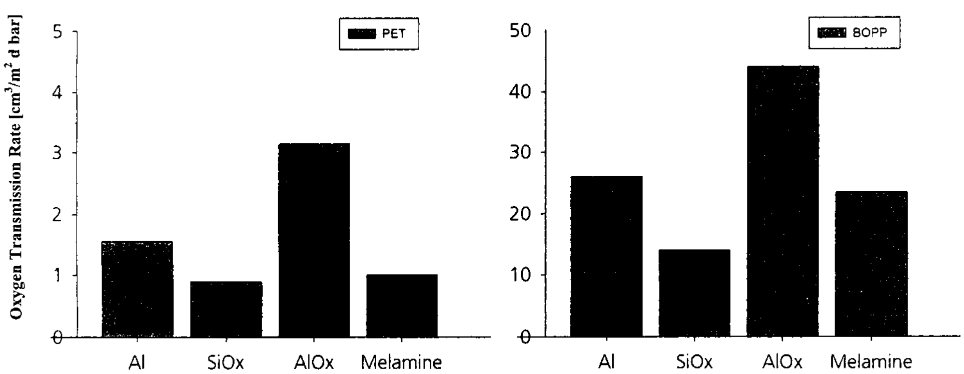

Figure 9. Oxygen transmission rate (OTR) of BOPP and PET coated with various conventional barrier materials. For comparison the OTR values of melamine coating are also given.

vapor deposition of a bulk chemical like melamine does not suffer from these drawbacks; i.e., the evaporation takes place at moderate temperatures and results in a completely transparent barrier layer. In Figure 9, we compare the OTR values, typically achieved with metal oxides and the metallization process, with the OTR value of melamine. For both BOPP and PET, the performance of the melamine coating is in most cases comparable and in some instances better than the performance of conventional barrier materials. On the basis of these results, we expect that vapor deposition of melamine will bring a breakthrough in the field of transparent barrier materials for food and pharmaceutical packaging.[11] Vapor deposition of melamine may also find application in other areas such as insulating layers in electronic devices.

IV. Conclusions

Melamine is presented as a first example of a physically vapor-depositable organic material giving a transparent coating with a high barrier to oxygen. The barrier properties can be attributed to the crystalline nature of vapor-deposited melamine layer. The supramolecular interaction, i.e., hydrogen bonding, between melamine molecules provides dimensional stability of the layer and good adhesion to the underlying polymer substrate. Because melamine is a widely available commodity chemical and vapor deposition can be accomplished using relatively simple technology, we expect that the present concept may bring a breakthrough in the field of transparent barrier materials for food and pharmaceutical packaging.

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