Preparation and properties of organic–inorganic hybrid flexible hardcoat films

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Active research and development of hardcoat films on plastic surface has resulted in added strength on polymers which has important role in their use as advanced materials. In general, inorganic coatings produced by gas phase or vacuum deposition (e.g. chemical vapor deposition [CVD], physical vapor deposition [PVD]), show good hardness, however, such processes are very costly, and there is often a problem of poor adhesion due to the large difference between substrate (plastic) and coating thermal expansion rates. The coating of plastic surfaces by wet chemical processes (e.g. sol–gel method) is, in most cases, an interesting alternative compared to that by dry processes (e.g. CVD, PVD) due to simple processing and low cost. Hardcoating using sol–gel methods has improved the abrasion resistance of uncoated polymers by the addition of SiO_2, Al_2O_3, TiO_2 and ZrO_2 particles in the sol, however, poor adhesion has remained a problem due to inflexibility.

A large variety of organic–inorganic hybrids prepared by sol–gel method has been reported thus far [1–7]. Among these, the most common method of preparation is that of utilizing the hydrogen bonding interactions between polar functional groups of organic polymers and silanol groups of silica gels. Examples include organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) and polyethylene glycol homogeneously incorporated into silica gels at the molecular level [2–4, 6]. Such incorporation of inorganic elements at the molecular level in organic polymers has resulted in novel properties such as improved mechanical strength and thermal stability. Moreover, the incorporation of organic elements can likewise improve on the brittleness of inorganic materials.

In the present paper, we wish to report the preparation of SiO_2, $C_6H_5SiO_{3/2}$ and polyethylene glycol (PEG) hybrid flexible hardcoat layers on poly(ethylene terephthalate) (PET). Hydrogen bonding interactions between oxygen atoms of PEG and silanol groups of silica can help in dispersing organic and inorganic components at the molecular level. As a consequence, suitable levels of both flexibility and hardness are attained, and phenyl groups can also provide added adhesion to PET substrates and flexibility. Based on this concept, we have prepared novel organic–inorganic hybrid flexible hardcoat films using sol–gel methods.

Organic–inorganic hybrid flexible hardcoat films were prepared by a sol–gel method in which PET substrates were spin coated with a sol. The sol was composed of tetraethoxysilane (TEOS), phenyltriethoxysilane (PhTEOS), C_2H_5OH, H_2O and HCl in molar ratio of 0.8:0.2:10:4:0.01. PEG was added to the precursor solution in a concentration of 10 wt% the alkoxides TEOS and PhTEOS. Chemicals used were of commercially available reagent grade. The mixture was stirred for several hours at room temperature to obtain a homogeneous sol. PET films with a thickness of 125 μm were used as the plastic supports. The support was spun at a rate of 1000 rpm and 0.5 cc of the sol was dropped on the support, after which it was left to dry at room temperature for 1 hr. Following the spin-coating procedure, films were heated to 373 K and held there for 12 hr, before cooling to room temperature. The pencil hardness test was applied to determine the hardness of the hardcoat films.

The structure of the organic–inorganic hybrid was determined using a Fourier transform infrared spectrometer (FT-IR) (FT/IR-230, JASCO Co.). FT-IR spectra of the organic–inorganic hybrid and PEG are presented in Fig. 1. The hybrid shows a typical band at $\sim$960 cm^{-1} associated with the stretching mode of Si—OH, along with the characteristic bands related to the Si—O—Si bond ($\sim$1200, 1050, 800 cm^{-1}) [8, 9], which confirm the presence of Si—O—Si network in the hybrid. An adsorption band near 2900 cm^{-1} is assigned to C—H stretching vibration of PEG. A strong and broad band at $\sim$3700–3000 cm^{-1} is assigned to hydroxyl groups of Si—OH and PEG [9]. Other characteristic bands originating from PEG and phenyl groups were also observed. N_2 adsorption at 77 K of this hybrid was measured, however no adsorption was observed. This result

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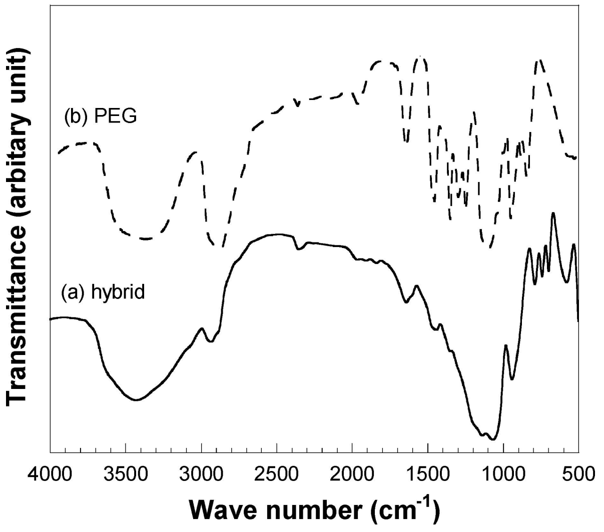

Figure 1 FT-IR spectra of the organic–inorganic hybrid and PEG.

was the same as that previously reported and indicated SiO_2-PVP hybrids and evidence of an extremely dense structure of the hybrid [4].

Table I shows the properties of the prepared organic–inorganic hybrid hardcoating film and PET film. Pencil hardness of the PET with hardcoat film was 3*H*. This value is high enough for use in hardcoating on plastics, and is due to the inorganic matrix being a main component of the hardcoat. Adhesion of hardcoat film on PET film was also good because of the existence of π–π stacking interactions between phenyl groups of PhTEOS and PET films. For flexibility test, hardcoating film was attached to a stainless rod with diameter of 5 mm and bent along with rod circle 10 times and then observed the film surface by optical microscope. No crack was observed on the film surface. This result indicated that the prepared hardcoat film was flexible. This flexibility with hardness is a novel property of the organic–inorganic hybrid hardcoat film due to dispersion of inorganic segments and organic segments at the molecular level and the effect of PhTEOS. The gelation process of acid-catalyzed silica gels started the hydrolysis and followed the condensation reaction [10]. As these reactions make progress, new siloxane bonds (Si—O—Si) are formed, creating additional cross-linking and surface area in the gel network. But, when PEG is added in this type of silica gel, these molecules can form hydrogen bond Si—OH. Without the available Si—OH groups, condensation reactions cannot form the bridging bonds and syneresis is halted. This makes the gel flexible. PhTEOS, with acid catalysts, was hydrolyzed and condensed and simultaneously hydrolyzed as in the case of TEOS. The influence of PhTEOS, however, resulted in membranes with small void spaces due to the steric hindrances of phenyl groups, thus enabling membranes flexibility with hardness. Fig. 2 indicates a possible schematic structure of the hardcoat. Transmission spectra of PET and PET with hardcoat film are shown in Fig. 3. Light transmittance of the PET with hardcoat film was higher than that of PET itself. This is due to depression of light reflectance. The hardcoat film possessed a lower refractive index than PET because main component of the hardcoat film was silica. Thus it functioned like an antireflection film. This transparency is important for the application, such as touch panel and packaging materials.

TABLE I Properties of the organic–inorganic hybrid hardcoat film

Sample	Pencil hardness	Tape test	Flexibilty test	Light transmittance (%) (wave length = 550 nm)
PET	*H*	NA	NA	87.6
PET with hardcoat film	3*H*	100/100	No cracks	89.5

NA: not available.

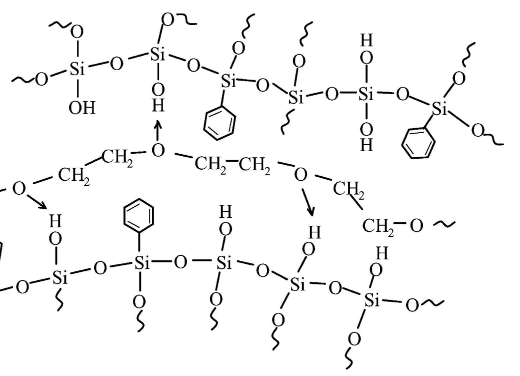

Figure 2 Schematic representation of the structure of the organic–inorganic hybrid hardcoat.

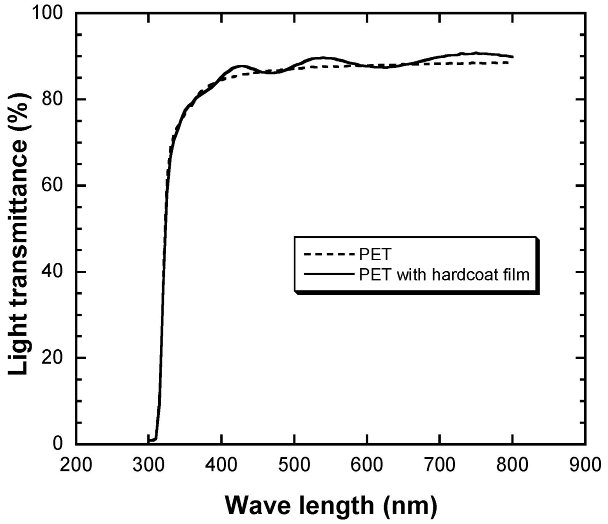

Figure 3 Photograph of the organic–inorganic hybrid hardcoat film.

In conclusion, SiO_2, $C_6H_5SiO_{3/2}$ and polyethylene glycol (PEG) hybrid flexible hardcoat layers on poly(ethylene terephthalate) (PET) were prepared by sol–gel method. Results indicated that the structure of the proposed membrane was well dispersed with inorganic (SiO_2, $C_6H_5SiO_{3/2}$) and organic (PEG) segments at the molecular level. The hybrid hardcoat films displayed both flexibility and hardness as a result of phenyl groups providing added flexibility and adhesion to PET substrates.

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Received 10 November
and accepted 16 November 2004