Mechanical Properties Study of Photocured Paperboard Surface Treated with Aliphatic Epoxy Diacrylate

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ABSTRACT: In order to improve the quality of paperboard (a well-known packing material) surface by photocuring method, different formulations were developed with aliphatic epoxy diacrylate (EA-1020) oligomer along with reactive monomers of various functionalities. The reactive monomers are tripropylene glycol diacrylate (TPGDA), a difunctional monomer, and trimethylol propane triacrylate (TMPTA), a trifunctional monomer. 2-Benzyl-2-dimethylamino-1(4morpholinophenyl) butanone-1 (Irgacure 369), a photoinitiator (2%), was incorporated into the formulations to initiate photocuring reaction. The formulated solutions were coated on clean glass plate and irradiated under UV radiation of different intensities. Different physical properties like pendulum hardness and gel content of the cured films were studied. The formulation containing TMPTA showed better properties. After characterization of the films, these formulations were applied on paperboard surfaces and cured under the same UV radiation. Various physico-mechanical properties such as pendulum hardness, tensile properties, surface gloss, adhesion, abrasion, and water uptake were studied. The best performance was obtained at 12 passes of radiation with 18% TMPTA-containing formulation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1774–1780, 2003

Key words: photocuring; paperboards; epoxy diacrylate; mechanical properties; UV radiation

INTRODUCTION

The protective coatings on surfaces of various materials used today in outdoor and indoor applications are fabricated of solvent-based formulations, mainly thermosetting acrylates and unsaturated alkyd esters. UV-curable resins appear as an alternative, as solvent-free formulations can be cured rapidly at ambient temperature to produce highly crosslinked polymers. These formulations offer several advantages as well—for instance, curing occurs at ambient temperatures, which reduces reaction time; continuous operation; improved monomer stability; less atmospheric pollution; increased design flexibility through process control; and production of very high quality products. The light stabilization of UV-curable coatings has been reported in several studies,[1–6] but no major industrial openings have enlarged so far. One of the vital and intrinsic problems of this system is that the inner filler effect of the added UV absorber is slowing down the curing speed and is shortening the cure depth as well.[7] Board, sheets, panels, and other structural material are manufactured from wood fibers and various other vegetable fibers. Paperboards are one of the products of paper industries that are low qualities unbleached products. These boards are mainly used for packing purposes and in the manufacture of cartoon. Board making is basically similar to papermaking, and involves refining, screening, mixing of additives, sheet forming and drying operations. Paperboards are generally made from cellulose materials, and these materials are hydrophilic in nature, which absorbs water within a short period of time. Paperboard also has less hardness and less tensile property. Different formulations were developed for curing surfaces of wood,[8,9] partex,[10,11] and leather[12,13] in our laboratory. The present work was undertaken to develop some formulations to improve paperboard surfaces through enhancing tensile strength, flexibility, abrasion resistance, adhesion strength, and surface gloss, and to reduce water absorption property.

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EXPERIMENTAL

Materials

Aliphatic epoxy diacrylate (EA1020) oligomer (prepolymer) was procured from Shin-Nakamura Chemical Co. Ltd. Japan. It has specific gravity 1.2 ~ 1.22 at 25°C, epoxide equivalent weight (g/eq) = 193–205, softening point (°C), Ring and Ball method = 60 ~ 85.

TABLE I
Composition of Different Formulations (% w/w)

Formulations	Oligomer EA 1020	Monomer TMPTA	Monomer TPGDA	Photo initiator Irgacure 369
A_1	90	8	—	2
A_2	80	18	—	2
A_3	70	28	—	2
A_4	90	—	8	2
A_5	80	—	18	2
A_6	70	—	28	

The difunctional monomer, tripropylene glycol diacrylate (TPGDA), was obtained from BASF, Hungary, and the trifunctional diluent, trimethylol propane triacrylate (TMPTA), from Ajax Chemical Co., Australia. The free radical initiator or the photoinitiator, Irgacure 369 [2-benzyl-2-dimethylamino-1(4-morpholinophenyl) butanone-1], was procured from Ciba-Geigy, Switzerland. The substrate paperboard samples were collected from the local market of Bangladesh, which are mainly used for packing purposes and is commonly known as *cartoon*.

Methods

Formulated solutions as shown in Table I were prepared by different proportions of oligomer, monomer, and fixed concentration of photoinitiator (2%). The formulated solutions were coated on glass plate (8 × 10 cm) with the help of bar coater (no. 0.0018, Abbey Chemical Co., Australia), which gives 36 ± 3 μm thick film. The coating was cured under ultraviolet (UV) radiation using UV-minicure (IST-Technik, Germany, accuracy margin is ±1%) at different durations represented by the number of passes with conveyor speed 4 m/min. The lamp has 2 kW power capacity with wavelength from 254 to 313 nm. After 24 h of radiation, the cured films were subjected to various characterization tests.

Characterization of cured film

Pendulum hardness of cured films was determined by using a digital pendulum hardness tester (model 5854, BYK, Labotron, Germany).The pendulum was deflected to 6° (koing position). The gel content of the cured film were determined by wrapping a known weight of the film in a finely meshed steel net that was put into a sox-let extractor for extraction with hot benzene for 48 h. The difference of weight before and after extraction determines the amount of gel content. Thus percent of gel content = $[(W_i - W_f)\ /W_i] \times 100$, where W_i is the initial weight of the film and W_f is the weight loss by the film after 48 h of extraction.

Application on paperboard surface

Paperboard sheets were cut into small pieces of the size 10 × 10 cm. These samples were dried in an oven at 105°C. The formulated solutions were coated on the paper board surface using a suitable bar (0.0018) and finally the coating was irradiated on the same UV light of different intensities. Treated paperboard was used for different characterization tests after 24 h of radiation. Tensile property of the treated surfaces were measured using a tensile strength machine (Instron, model 1011, Instron Corporation, UK) maintaining a gauge length of 30 mm at crossed speed of 2 mm/min and the load capacity was 500 N. The enhancement of tensile strength and elongation of the treated paperboards were expressed as tensile strength factor (T_f) and elongation factor (E_f). Hence $T_f = TS_a/\ TS_b$ and $E_f = Eb_a/Eb_b$ where, TS_b, TS_a, and Eb_b, Eb_a are the tensile strength and elongation at break of the paperboards before and after coating, respectively. Pendulum hardness (PH) of the UV-cured paperboard surfaces was measured as on the cured polymer films. Surface gloss is another important property for coated surface and this property was measured at two angles of the plane (20° and 60°) with the help of a micro gloss meter (Sheen Co. England). The percentages of gloss were determined with using a reference plate supplied by the company whose gloss at 20° and 60° angle was 86.8 and 92.1 units, respectively. Abrasion resistance (wearing resistance) in terms of taber wear index of the coated paperboard was determined by using a taber abraser (model 5130, D-5870, Erichen GMBH and Co. KG, Germany).The coated paperboard was abraded between two abradent revolving wheels (cs-10) applying a force of 500 grams per cycle with setting 100 vacuum and a total 50 cycles in the abraser. The results are expressed as a wear factor or taber wear index (rate of wear is the loss of weight in milligram per thousand cycles of abrasion). Adhesion is a test, which applies to a certain force to pull out the coating from the surface of the paperboard. The test was carried out with an adhesion tester (model 525, D-58675 Hemer, Erichen Sundwig, Germany). Adhesion force was determined in N/mm^2 unit. Paperboards are mainly used as packing purposes and in this respect water uptake is a prime factor in considering its applications. Percentage of water uptake was measured before and after coated by polymeric formulations by dropping method using a dropper. Percentage (%) of water uptake = Wa/Wi, where Wa and Wi are the weight of absorbed water and the initial weight of paper board before and after coating.

RESULTS AND DISCUSSION

In the present investigation six different formulations—namely, A1, A2, A3, A4, A5, and A6—were

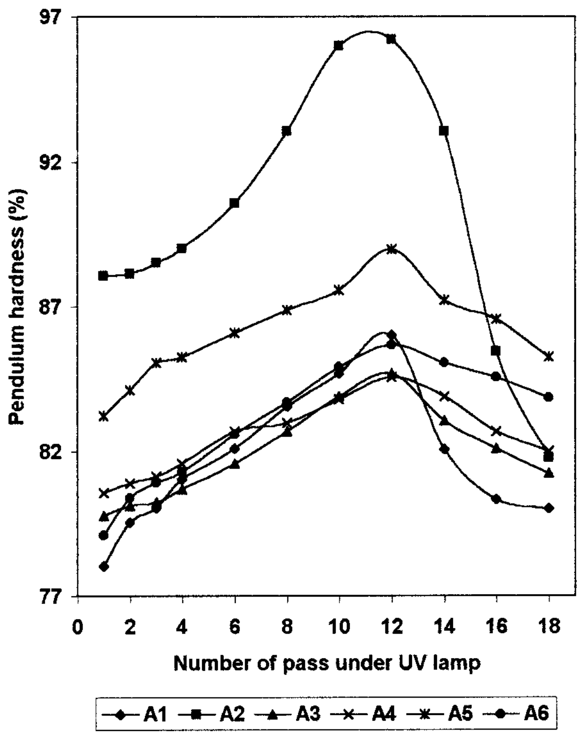

Figure 1 Pendulum hardness (PH) of UV-cured polymer film against the intensities of UV radiation.

used to improve the surfaces of paperboards. The first three formulations were prepared with monomer TMPTA, whereas the remaining three were prepared with the monomer TPGDA. Experiments with these formulations were conducted on a glass plate before using them on paperboard surfaces.

Characterization of cured polymer film

Pendulum hardness (PH)

Surface hardness of UV-cured thin polymeric films prepared on a clean glass plate was determined by the pendulum method, and the results are graphically presented in Figure 1 against the number of passes of UV radiation. The increase in PH with the increase of UV doses up to 12 passes manifests the crosslinking. In the early stage at a low dose of UV radiation, the crosslinking was less effective and was increased up to 12 passes. However, after an optimum dose (12 passes), a higher dose causes degradation of the film, resulting in a decrease of PH. The decrease could be caused by the degradation of the films with higher radiation doses.[14] The mechanism of this degradation is not clearly known; however, it could be the cleavage of the polymer chain due to overdose of UV radiation. It is evident from the figure that with formulation A_2 the hardness increases sharply with UV radiation and reaches maximum after 12 passes of UV radiation. The hardness then decreases with an increase of the number of passes of UV radiation. For other formulations PH does no not increase so sharply with the increase of UV doses as on formulation A_2. The highest PH value (96%) is observed for formulation A_2 followed by formulation A_5, and the value is 89%. TMPTA is a trifunctional reactive monomer with the ability to make crosslinking in three-dimensional manners. TMPTA has a branch-like effect to create crosslinking.[15] The physical properties of UV-cured film generally increase with the increase of glass transition temperature. The glass transition temperature of TMPTA (250°C) is higher than that of TPGDA (90°C).[16] At low concentration of TMPTA PH is lower because vinyl monomer promotes rapid free radical reaction with the help of photoinitiator leading to network structures through copolymerization reaction via their double bonds.[16] The increase of TMPTA increases the amount of residual unsaturation and subsequently results in further rate of formation of the three-dimensional crosslinking, causing higher hardness of the films.[17]

Gel content of the cured film

The gel content is a representation of crosslinking density in the cured film as a whole. The gel content of the cured film prepared from these formulations was determined by hot benzene extraction and is presented graphically in Figure 2 against UV doses. It is

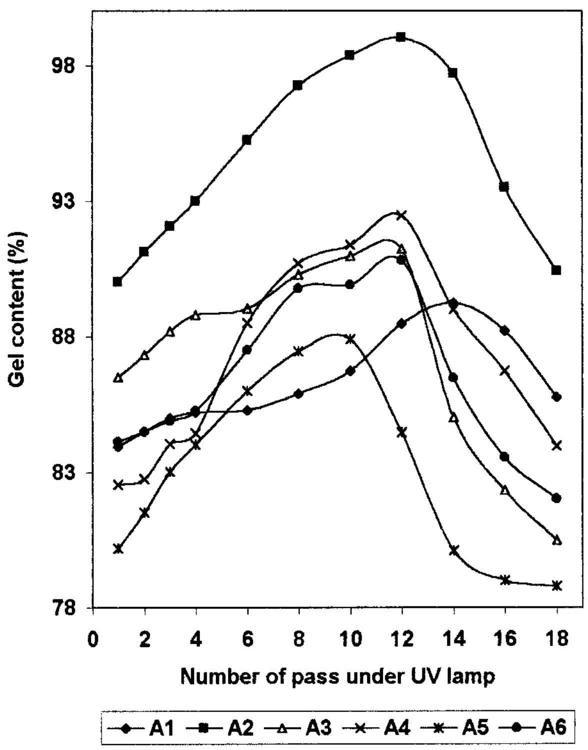

Figure 2 Gel content of UV-cured polymer film against the intensities of UV radiation.

observed from the figure that gel content values of all these films vary from 76 to 99%. For all formulations, gel content increases with UV doses and attains a maxima, and then decreases with increasing radiation doses. This is also a manifestation of the crosslinking during UV radiation and in agreement with PH. Most of the formulation yields maximum gel content values after 12 passes of radiation, except formulations A_1 and A_5, and these two shows maximum gel values at the 14th and the 10th pass of radiation. The highest gel value (99%) is given by the formulation A_2 after 12 passes. For other formulation maximum gel remains 84–92%. The gel content of the formulation with the monomer TPGDA are lower than those of the formulations containing monomer TMPTA in equal percent at the same UV doses. The diluent's monomer TMPTA is already found to play a good role in creating better crosslinking density at the surface as manifested by the highest PH.[18]

Investigation of the coated paperboards

Paperboards were coated with the formulated solutions (A_1–A_6) and cured under UV radiation at different intensities. After 24 h of UV radiation the cured surface were subjected to various characterization tests in order to asses the quality of the coated paperboards.

Tensile strength

The enhancement of tensile strength after treatment with different polymeric formulations is expressed by tensile strength factor (T_f). The T_f values are graphically shown in Figure 3 against number of passes. The tensile strength of the coated surface increases with the increase of UV doses, represented by number of passes. Most of the coatings show maximum tensile strength after 12 passes. Tensile strength of the coated sample decreases as the radiation doses increases after optimum passes of UV radiation. It is observed that the highest tensile strength enhancement (T_f = 4.25) was obtained for the samples treated with formulation A_2 at the 12th pass of radiation. With other formulations tensile strength does not increase so sharply as on formulation A_2. The lowest tensile strength was offered for the samples treated with formulation A_6. The mechanical properties of UV-cured substrate are governed by the various factors like number of double bonds,[19] and the shape and size[20] of multifunctional monomers. TMPTA-containing formulations (A1–A3) produced the higher and TS than that of TPGDA-containing formulations (A4–A6) it might be possible that TMPTA is more effective in producing a slightly denser network than TPGDA having the lower unsaturation. TMPTA increases the radical–radical terminations and hence decreases the extent of scission reactions and oxidation.[17] As TMPTA concentration is increased, there is the consequence of a faster rate of formation of the three-dimensional network structures causing restricted mobility.[21]

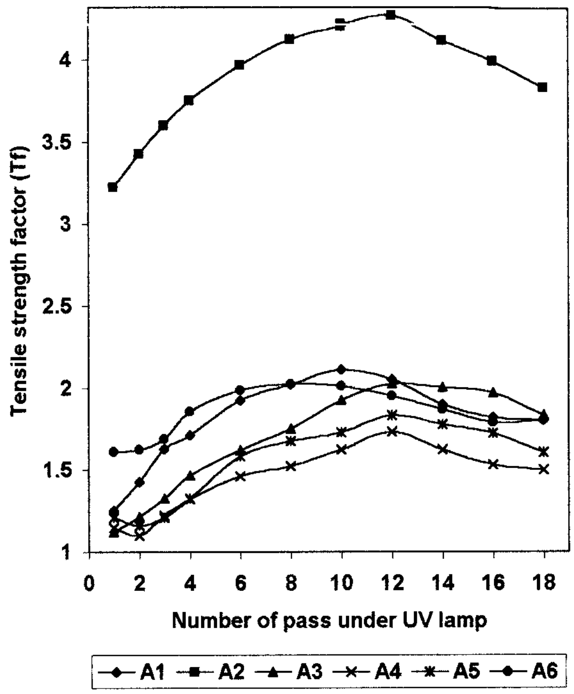

Figure 3 Tensile strength (T_f) of coated paperboards against the intensities of UV radiation.

Elongation property

Since paperboards are mainly used in packing purposes, it is good to have paperboard that possesses extra stretching ability. Paperboard is not known to have high elongation like the elastic polymer, but it is possible to elongate the coated paperboards. Enhancement of elongation of the coated paperboard is manifested by elongation factor (E_f). The values of E_f are plotted in Figure 4 against the number of passes under UV radiation. It is observed that stretching ability of the coated paperboard has been increased between 50 and 140% as a result of UV-cured coatings. The highest elongation was obtained for formulation A_2 followed by formulations A_1 and A_5.

Pendulum hardness (PH)

PH is another important property for coated paperboards and it is related to the crosslinking density on the cured surface. The results of PH are graphically presented in Figure 5 against number of passes. The increase in PH with the increase of UV doses manifests the crosslinking. However, after maximum PH, higher dose causes the reduction of values and this decrease could be caused due to the degradation of the poly-

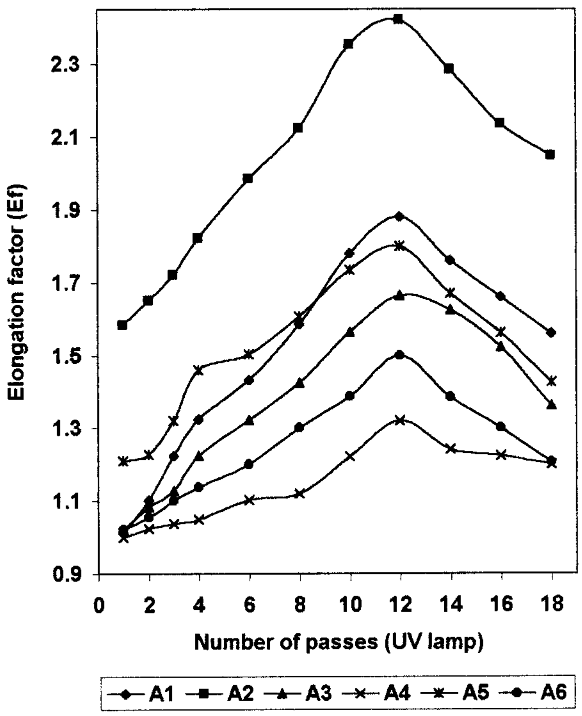

Figure 4 Elongation property (E_f) of coated paperboards against the intensities of UV radiation.

mer. The pendulum hardness value (25%) was obtained by the formulation A_2 at the 12th pass of radiation followed by the formulation A_5 (19%). The lowest PH was observed for formulation A_6.

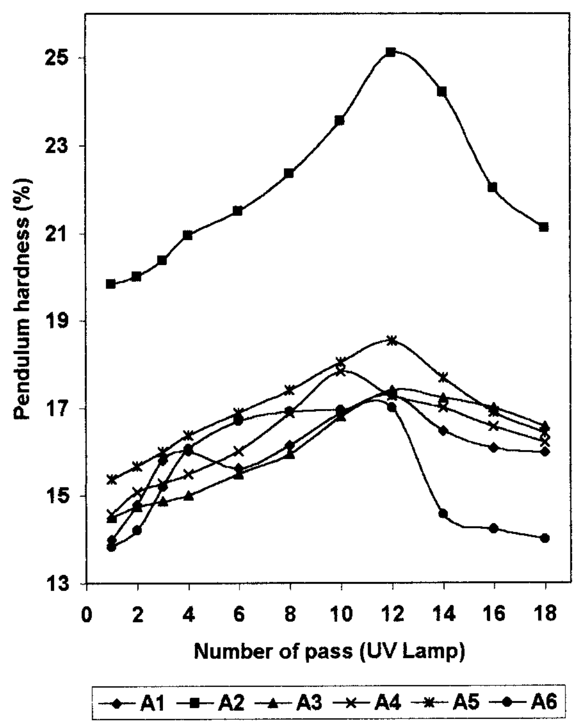

Figure 5 Pendulum hardness of coated paperboards against the intensities of UV radiation.

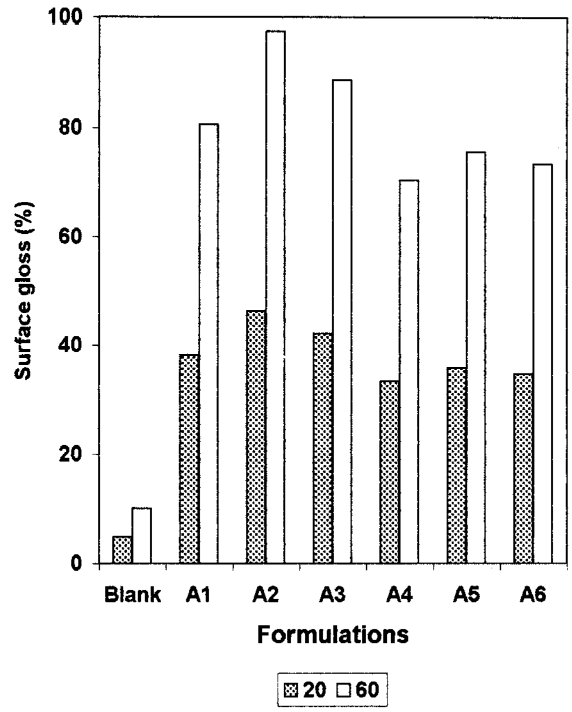

Figure 6 Surface gloss at 20° and 60° angles of coated and uncoated paperboards against different formulations.

Surface gloss

Quality of surface coating can be roughly estimated with visual observation. Gloss determination of the coating is an index of such estimation, which is the reflection of light from the coating at certain angle with the vision. Gloss was determined at two angles 20° and 60° of the plane of the coated and uncoated surfaces. Gloss determination at a 60° angle is generally higher than that at 20° angles. It was from the previous experiment that 12 passes under UV radiation gives the highest values in most of the cases, so gloss was determined for all the formulations that were cured at 12 passes. Results of surface gloss values for coated and uncoated samples are plotted in Figure 6. The highest gloss is obtained by the formulation A_2 at both angles (20° = 46% and 60° = 97%) containing monomer TMPTA (18%) followed by the samples treated with the formulation A_3. The coating obtained from formulation containing monomer TPGDA registered the minimum gloss than that from containing TMPTA.

Adhesion property

Adhesion is a test that applies to certain force to pull out the coating from the surface of the paperboards. If a coating is loosely bound with the substrate surface, then it can be easily pulled off by applying a small peeling force and vice versa.[17] The results of adhesion force in N/mm^2 are shown Figure 7. The coating

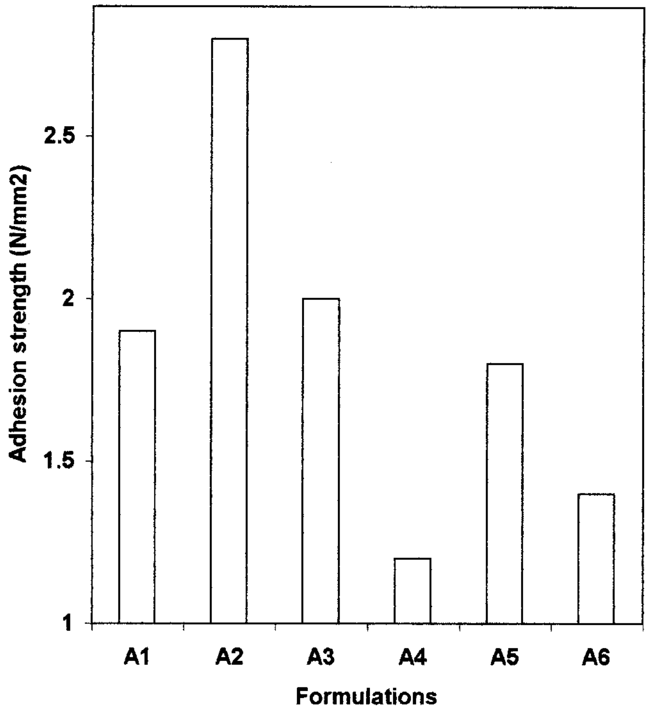

Figure 7 Adhesion strength in N/mm^2 of coated paperboards against different formulations.

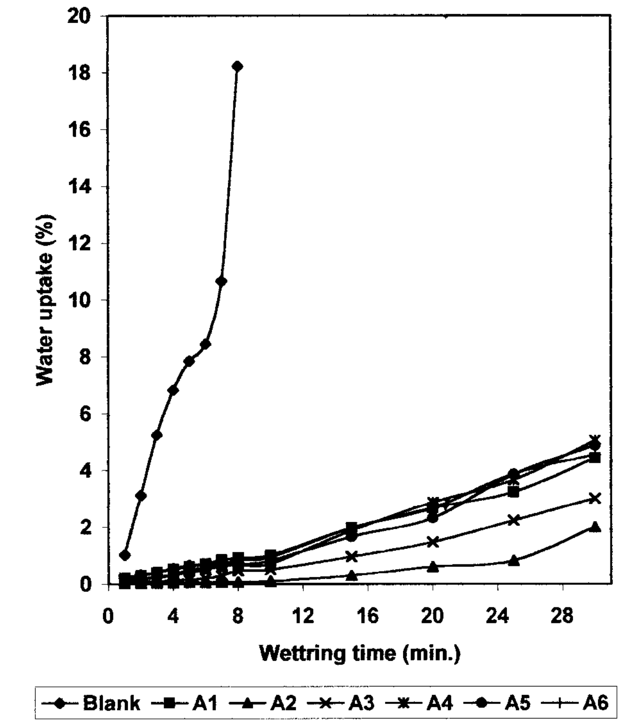

Figure 9 Water uptake of coated and uncoated paperboards against wetting time in minutes.

obtained from formulation A_4 shows the lowest adhesion strength (1.2 N/mm^2), which contains 8% TPGDA. The formulation containing TMPTA shows higher adhesion values to that containing TPGDA. The highest adhesion value (2.8 N/mm^2) was observed for formulation A_2 followed by formulation A_3.

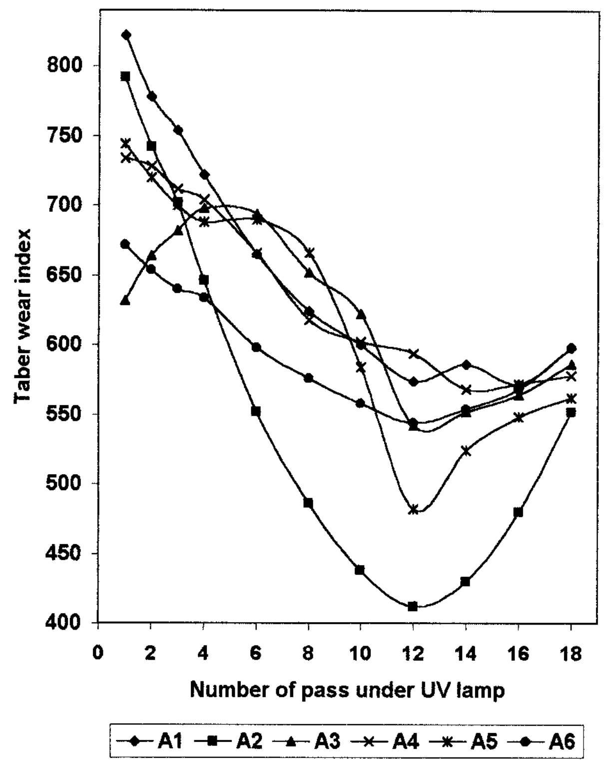

Figure 8 Abrasion resistance property (Taber wear index) of coated paperboards against the intensities of UV radiation.

Abrasion property

Abrasion is another important property, in the sense that paperboards are normally used for packing purposes. If the wearing resistance is high, the products are considered to be more durable and can last longer. The wearing resistance of the coated paperboards was determined by the application of taber abrasion test through weight loss method. Taber wear index values are graphically plotted in Figure 8 against the number of passes under a UV lamp. It is observed that taber index value decreases with increasing radiation doses up to 12 passes after that taber index values are increased. This figure reveals that the abrasion resistance is obtained after 12 passes of radiation. The lowest taber index value (412) is obtained by formulation A_2 at the 12th pass followed by the formulation A_5 (482) at the same UV intensities.

Water uptake

The extent of water uptake exhibited the increase in weight of the paperboards due to water absorption by putting a drop of water on the coated and uncoated paperboard surfaces. The wetting time period was 1–30 min. The results are depicted as water uptake (%)

in Figure 9. It is observed that there is very little uptake of water by each of the coated paperboards, whereas uncoated paperboard soared in water absorption to 18% in 8 min. The differences of water uptake are very small among the coated materials. The highest water absorption (5%) was obtained from formulation A_4 containing 8% TPGDA and the lowest water absorption value (2%) after 30 min was obtained for the samples treated with the formulation A_2 containing 18% TMPTA. These demonstrate that the coating found from A_2 was more uniform and compact.

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