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Investigation of Properties of Fluorine Containing Hybrid Coatings Intended for Use in Printing

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The aim of this study is to investigate the effect of fluoro-silane content on a UV curable hybrid polymer applied on unsealed test charts. Silane terminated oligomer was obtained by the reaction of diethylene glycol and 3-isocyanatopropyltrimethoxysilane. Inorganic part was obtained by hydrolysis and condensation reaction of silane-terminated diethylene glycol, 1H,1H,2H,2H-perfluorooctyltriethoxysilane and 3-(trimethoxysilyl)-propylmethacrylate. Organic part consists of UV curableres in and 1,6-hexanedioldiacrylate. Hybrid coating formulations were prepared by adding previously prepared inorganic part into organic part in predetermined ratios. The abrasion resistance, static-kinetic friction coefficient, gloss and tape adhesion properties were characterized. It was found that fluoro-silane content has the main effect on the tested parameters. The resultant coatings have a high gloss endurance and high abrasion resistance and therefore they would keep the visual appearance of printed surfaces in the original condition during long periods of time.

Keywords: Organic-inorganic hybrids, UV curable, Sol-gel, Fluoropolymer.

INTRODUCTION

The UV-curing technique depends on the polymerization of a multifunctional system induced by an incident UV radiation to have a three-dimensional network. One of the main advantages of these systems is that the oxygen inhibition of free radical polymerization is greatly reduced, thus obtaining higher photopolymerization rates and conversions, as well as reduced costs by eliminating nitrogen blanketing normally used in radical photopolymerization processes. The reaction permits to transform at room temperature in a fraction of a second, a liquid system into a solid[1,2]. UV-curing is widely applied in many fields ranging from dentistry to printing.

In printed media, lacquer printing is needed for the purposes of high gloss, protection from friction and durability of print. UV curable lacquers have many advantages such as low energy cost, high solids content, low volatile organic content, low investment and production cost, quality products and no harmful effects for health and environment[3-5].

The technique based on UV-curing has also been widely used in sol-gel processing of hybrid coatings having photopolymerizable organic functionalities[6-9]. Hydrolysis and condensation reactions of the inorganic part and photopolymerization of the organic moieties lead to glassy behaviour for the resultant material at room temperature[10,11].

Hybrid organic-inorganic materials can be defined as nanocomposites made of organic-inorganic components on a nanometric scale. Organic-inorganic hybrids are developed from the idea of unifying on a nanometric scale the domains of organic and inorganic components. This scale of unification results a type of material that assumes a character that is a "hybrid" between the two chemical properties. It is well known that hybrid materials have excellent mechanical properties, especially hardness and wear resistance, as well as an outstanding chemical stability against atmospheric effects. The development of these multi-functional advanced materials has a substantial effect on future applications in areas like high performance protective coatings, optics, electronics, mechanics, membranes, sensors and catalysis[12,13].

Several hybrid UV-curing systems using mixtures of acrylates and epoxides[14,15], vinyl ethers[16] or oxetanes[17] were recently developed. UV-curable lacquer systems are modified by a variety of different monomer groups. Modification of UV-curable systems by the introduction of fluorosilane structures is one of the ways resulting in synergistic effects[18]. With this method it seems possible to combine the properties of these molecules and the advantages of the UV curing technology, leading to cured products with outstanding properties[19].

The use of fluorinated monomers and oligomers for coatings is very attractive due to the peculiar characteristics given by the presence of fluorine: hydrophobicity, chemical stability, atmospheric resistance, good release properties, low coefficient of friction, water impermeability and low refractive index[20-24]. Different fluorinated monomers are already used in many coating applications[25,26].

In this study, UV lacquer containing fluorinated methacrylate functional oligomers with various hybrid formulations were applied on cardboards. Physical and chemical characterizations were performed on coatings as well as free films.

EXPERIMENTAL

UV curable resin (code 11173) was obtained from Frimpeks, Turkey. This is believed to be a polyether acrylate based resin. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (97 %) was purchased from ABCR. 3-Isocyanatopropyltrimethoxysilane (95 %) (ICPTMS) and diethylene glycol (≥ 99.5 %) (DEG) were supplied by Sigma Aldrich. Dibutyltindilaurate (Sigma Aldrich) was used as a catalyst. 3-(Trimethoxysilyl)propyl methacrylate (98 %), 1,6-hexanedioldiacrylate (reactive diluent), 1-hydroxy-cyclohexyl-phenyl-ketone (photoinitiator, Irgacure 184) and *p*-toluenesulfonic acid (PTSA) were obtained from Sigma Aldrich. Unsealed test chart (Form N2A type) used as printing material supplied by Leneta.

Synthesis of silane-terminated diethylene glycol: 10 g of diethylene glycol was charged to a 100 mL three-necked round bottom flask that fitted with a thermometer pocket, water condenser and a magnetic stirrer. 46.618 g of 3- isocyanatopropyl trimethoxysilane was slowly added to the reaction flask. Dibutyltin dilaurate was added to the reaction flask as a catalyst, at a concentration of 0.5 %. A schematic representation of this reaction is shown in Fig. 1. The temperature was raised to 60 °C and the mixture was stirred for 8 h. Completion of the urethane reaction was confirmed by the disappearance of the characteristic -NCO peak at 2275 cm^{-1} in the FT-IR spectrum (Fig. 2).

Synthesis of fluorinated methacrylate functional oligomers: A 250 mL three necked round bottom flask equipped with a magnetic stirrer, a dropping funnel and a nitrogen inlet was charged with 0.094 mol 1H,1H,2H,2H-perfluorooctyl triethoxysilane (PTES), 0.282 mol of 3-(trimethoxysilyl)propyl methacrylate (MEMO) and 0.094 mol silane-terminated diethylene glycol (STDEG). Ethanol was added to the reaction mixture. The mixture was then homogenized by mixing with a magnetic stirrer. The water/silicone ratio was calculated as r = 3 and the calculated amount of water added to the mixture. 0.1 % of *para*-toluene sulfonic acid as catalyst was added to the above mixture. The mixture was stirred for 8 h at room temperature with a magnetic stirrer. A schematic representation of this reaction is shown in Fig. 3.

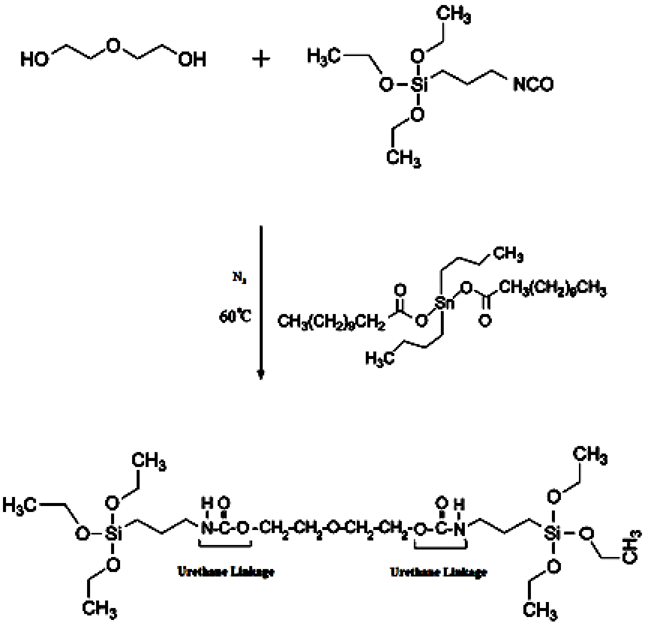

Fig. 1. Synthesis of silane terminated diethylene glycol

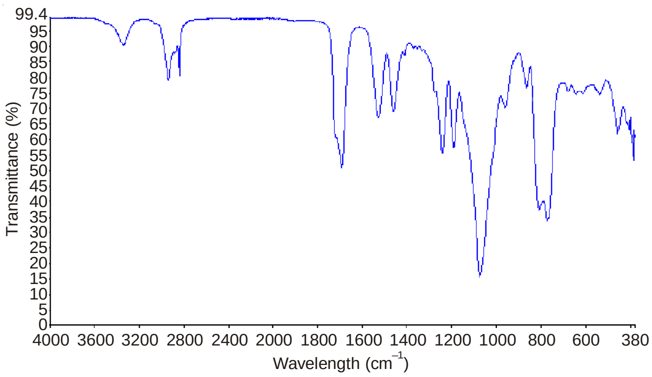

Fig. 2. FT-IR spectrum of silane terminated diethylene glycol

Preparation of hybrid coatings: As shown in Fig. 4, hybrid coating formulation was prepared by adding inorganic part to organic part in predetermined (2.5 %, 5 %, 7.5 % and 10 % by weight) ratios. Organic part of formulation is composed of an UV resin (Frimpeks-11173) and a reactive diluent (HDDA). Formulation of hybrid coatings was given in Table-1. A 3 % (by total weight) photoinitiator was added to each of the hybrid formulations. Each formulation was stirred until all the components were miscibilised completely. The efficiency of mixing was judged by the amount of cloudiness visible during the mixing. Hybrid formulations were heated at 35 °C in a vacuum oven for about 5 min to remove the trapped air formed during the mixing procedure. These solutions were then applied on the opaque paper by using a K-bar coater. The

TABLE-1
COMPOSITION OF HYBRID COATINGS

Notation	Organic part		Inorganic part			Photoinitiator
	Frimpeks-11173 (wt %)	HDDA (wt %)	PTES (wt %)	MEMO (wt %)	STDEG (wt %)	Irgacure 184 (Total wt %)
HF-0	80	20	-	-	-	3
HF-2.5	78	19.5	0.720	1.052	0.728	3
HF-5.0	76	19	1.440	2.102	1.458	3
HF-7.5	74	18.5	2.160	3.154	2.186	3
HF-10.0	72	18	2.880	4.204	2.916	3

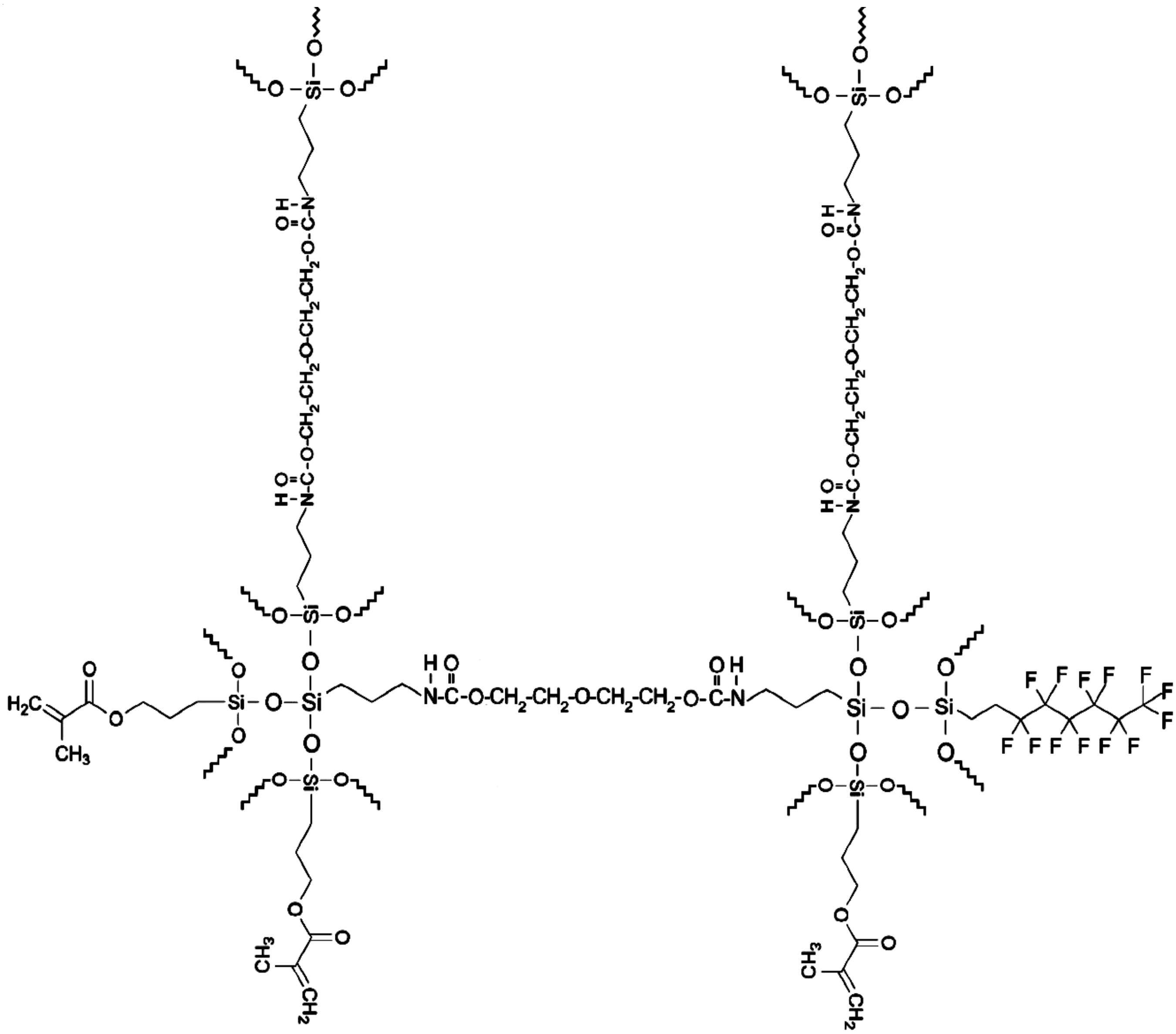

Fig. 3. Schematic representation of reaction of fluorinated methacrylate functional oligomers

obtained coatings were cured by a Raycon-UV drying system with a medium pressure mercury lamp (150 W/cm, λ_{max}: 320-390 nm), the speed of conveyor belt was 2 m/min.

Free films were prepared by pouring the UV curable hybrid formulations into a Teflon® mold with dimensions 10 mm × 80 mm × 1 mm. These free films were cured by passing the Teflon mold through the UV drying system under similar conditions applied to that of coatings.

Characterization: The FT-IR spectrum of the silane-terminated diethylene glycol was recorded on a Shimadzu 8300 FT-IR spectrophotometer. Soluble gel content of the UV-cured free films was extracted by Soxhlet extraction method for 8 h using pure acetone. Insoluble gel fraction was dried in vacuum oven at 40 °C to constant weight and the gel content was calculated. Thermogravimetric analysis (TGA) of the UV-cured free films was performed using a Perkin Elmer thermo-gravimetric analyzer. The tests were run from 30 to 800 °C with a heating rate of 20 °C/min under an air atmosphere. DSC analysis of the hybrid films was performed with Perkin Elmer DSC equipment. The tests were run from 20 to 220 °C with a heating rate of 10 °C/min under N_2 atmosphere. The fracture surface of the free films was examined on JOEL JSM-5910 LV SEM equipment. Elemental concentration of silicone, fluorine, carbon and oxygen atoms was determined with an Oxford Instruments-INCA energy dispersive spectrum (EDS) system. The abrasion resistance of coated surfaces was determined by using a Radian Rub Tester according to ASTM D5264.The surfaces of coated paper and cardboard were rubbed with each other 1000 times and then the surface abrasion was investigated. Static and kinetic friction coefficients of coated papers were determined by using the Lloyd FT1 friction tester according to standard TAPPI T549 and sled weight used was 200 g. Water contact angles were measured by using a Krüss DSA-2 goniometer. The volume of droplets was controlled to be about 5 μL. Gloss of the coated surfaces was measured by using a BYK-Gardner Glossmeter at angles of 20° and 60°. Adhesion of coatings was determined through a tape adhesion test according to ASTM D-3359 standard by using a TESA™ 4124 tape.

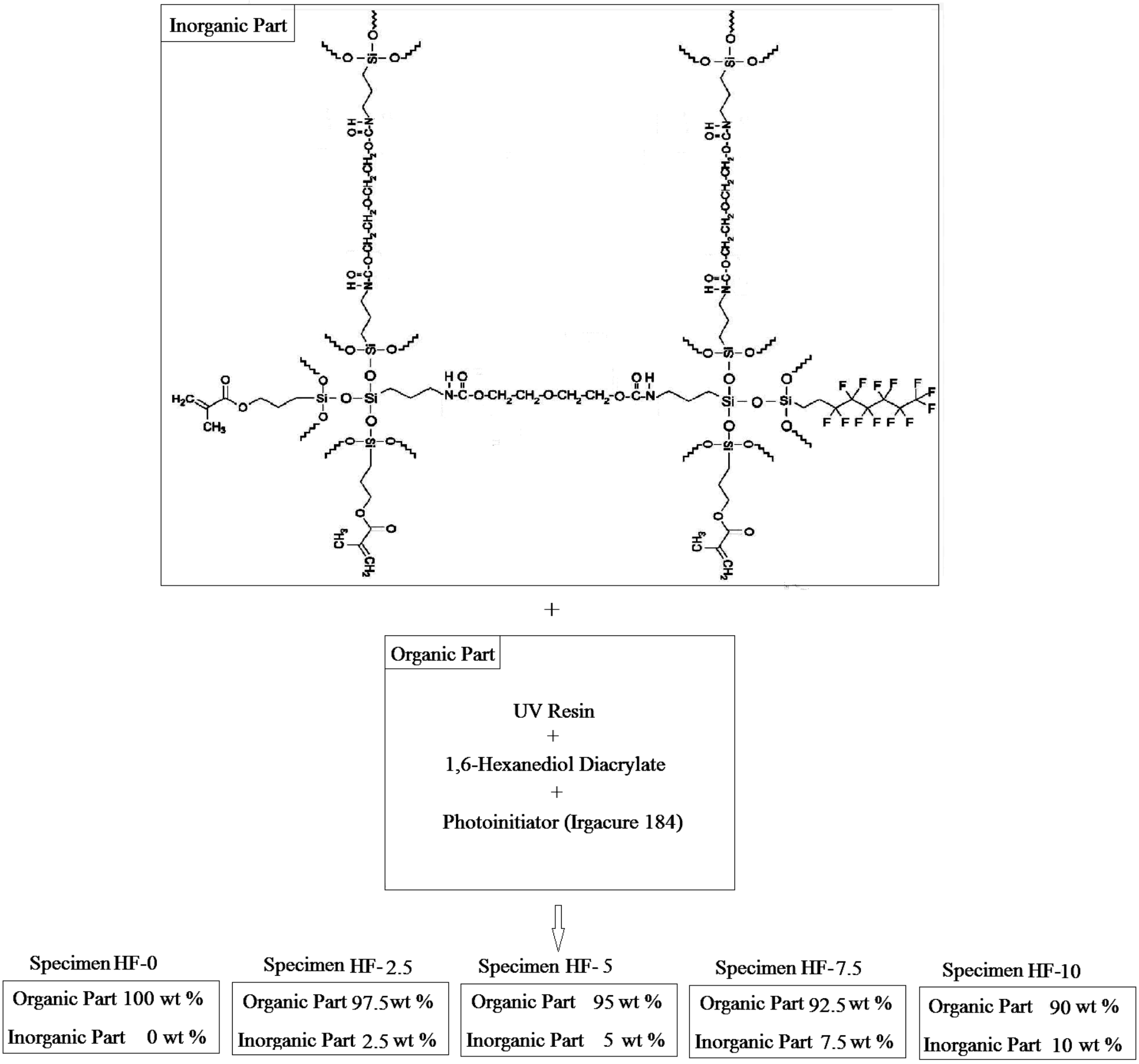

Fig. 4. Schematic representation of preparation of the hybrid coating formulations

RESULTS AND DISCUSSION

UV curable lacquer was modified by adding the previously synthesized inorganic part in different ratios. In the first stage of the synthesis of the inorganic part, silane terminated diethylene glycol was synthesized by reacting diethylene glycol with 3-isocyanato propyl trimethoxysilane at 80 °C in the presence of dibutyltin dilaurate. In the second stage of the synthesis of the inorganic part, fluorinated methacrylate functional oligomer was prepared by reacting 1H,1H,2H,2H-perfluorooctyl triethoxysilane, 3-(trimethoxysilyl)propyl methacrylate and silane-terminated diethylene glycol together. Hybrid formulations containing fluorinated methacrylate functional oligomer were coated on test paper by a K-Bar applicator. Coated samples and free films with 5 different compositions were prepared and their physical and chemical properties investigated. All the resultant formulations had visually clear appearance.

The results of gloss measurements were presented in Table-2. As can be seen from the table, the addition of fluorinated methacrylate functional oligomer did not have a considerable effect on the gloss values.

With the increasing fluorinated methacrylate functional oligomer content, the viscosity value of the resultant mixture decreased to 147 mPa·s from a starting value of 198 mPa·s due to the low viscosity value (73 mPa·s) of the fluorinated methacrylate functional oligomer.

In tape adhesion tests all the formulations resulted in a good adhesion on white paper whereas on black paper only the HF-10 hybrid had a good adhesion. With the increasing fluor content, the hybrid solutions lose their transparency and become cloudy. However, with the increasing fluor content, the adhesion becomes better in the case of black paper. The level of adhesion changes from bad to medium and to good. In UV curing of coatings, the colour of the substrate is very

TABLE-2
SOME OF THE PHYSICAL PROPERTIES OF COATINGS

Notation	Gloss		Visual appearance	Tape adhesion		Contact angle
	20°	60°		White paper	Black paper	
HF-0	94.1	75.8	Transparent	Good	Bad	75.54
HF-2.5	94.3	77.2	Transparent	Good	Bad	82.98
HF-5.0	94.8	77.9	Transparent	Good	Medium	83.93
HF-7.5	94.1	74.7	Transparent	Good	Medium	87.82
HF-10.0	93.7	73.4	Transparent	Good	Good	91.62

important since it affects the UV curing chemistry. Therefore, one must be careful with colours that have absorption in the ultraviolet region as they cause reduction in the amount of UV energy that can reach the chemistry. The process of UV chemistry can only work if it can have enough UV energy. Colours that absorb UV energy prevent energy from reaching the chemistry. It is well known that yellows, reds, blacks and some metallics are more problematic than other colours[27]. In our case, the surface of the black paper will inevitable absorb the UV substantially. So, the remaining UV will not cause enough reaction to proceed the chemistry. With the increasing fluor content, the hybrid solutions lose their transparency and become cloudy, the UV can not totally reach on the black surface and stay within the coating solution to affect the reaction. Accordingly, the reaction can find enough UV to proceed the chemistry.

The water contact angles were measured to determine the relative wettabilities of the coated surfaces. Photographs of water drops on the coated surfaces were shown in Fig. 5. The measured values of water contact angles were presented in Table-2. With the 2.5 % addition of fluorinated methacrylate functional oligomer, the value of water contact angle increased from 75.54° to 82.98°. With the further addition, the value of the contact angle started to increase and at a 10 % addition it reached a water contact angle value of 91.62°. This increase is due to the presence of fluorinated segments on the coated surfaces[28]. If a surface is hydrophobic, the contact angle will be larger than 90°. In this study, the measured value of water contact angle is higher than the 90° for HF-10 samples, therefore the obtained surfaces can be accepted as slightly hydrophobic.

The results of static and kinetic coefficients of friction measurement values for coated surfaces were presented in Table-3. As expected, both static and kinetic coefficients of friction values decreased with the increasing content of fluorinated methacrylate functional oligomer in the coating material. This decrease is also caused by the presence of fluorinated segments on the coated surfaces. Fluorinated segments have an effect on the surfaces nearly similar to that of the fluoropolymers.

TABLE-3
VALUES OF COEFFICIENT OF FRICTION
ON THE COATED SURFACES

Notation	Static coefficient of friction	Kinetic coefficient of friction
HF-0	0.223	0.067
HF-2.5	0.221	0.062
HF-5.0	0.212	0.044
HF-7.5	0.194	0.023
HF-10.0	0.116	0.004

The photographic images of rub tested surfaces were shown in Fig. 6. Uncoated parts of the cardboards exhibited a rapid surface abrasion whereas the coated regions exhibited a

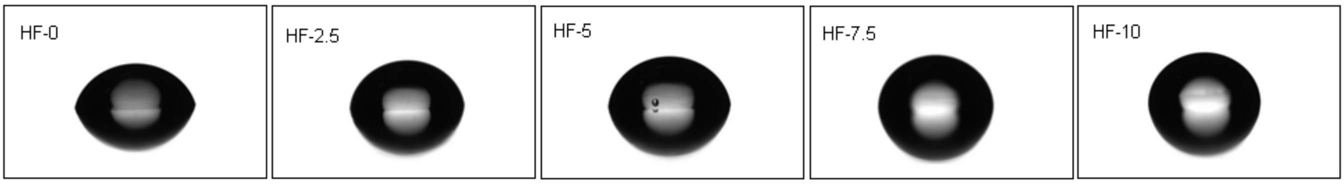

Fig. 5. Images of water contact angles measured on coated paper surfaces (a) HF-0 (b) HF-2.5 (c) HF-5 (d) HF-7.5 (e) HF-10

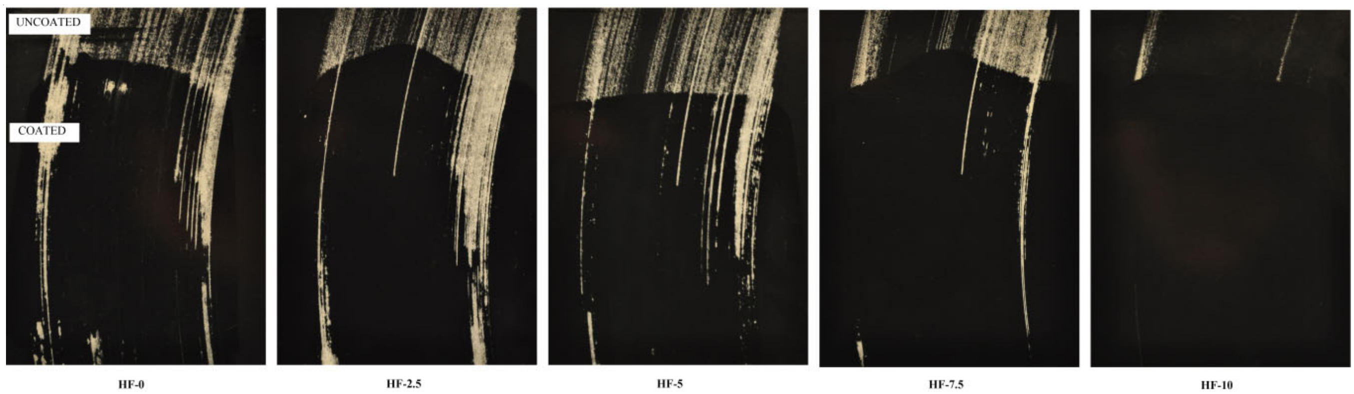

Fig. 6. Photographic images of rub tested surfaces. The upper parts of the cardboards are in uncoated condition

slow surface abrasion. It was observed that the amount of abraded surface decreased with the increasing fluorinated methacrylate functional oligomer content and at a content of 10 % there was no abrasion loss.

DSC thermograms of the samples of free films were given in Fig. 7. It was observed that HF-0 has a higher glass transition temperature (T_g = 168 °C) than HF-10 (158.3 °C). The values of glass temperature (T_g) of the HF-0 samples decreased with the increasing content of hybrid oligomer. The T_g values depending on the percentage amount of fluorinated methacrylate functional oligomer were also given in a column fashion in Fig. 8. The change in the T_g values can be attributed to the presence flourinated segments. Similar behaviour was also observed in other fluorinated-side-chain polymer systems[29,30]. The increase in the content of fluorinated side chains of the HF samples causes an increase in the free volume of the backbone domains. From a molecular dynamics perspective, it is presumed that motions that are related to the backbone are not hindered leading to decreased glass temperature.

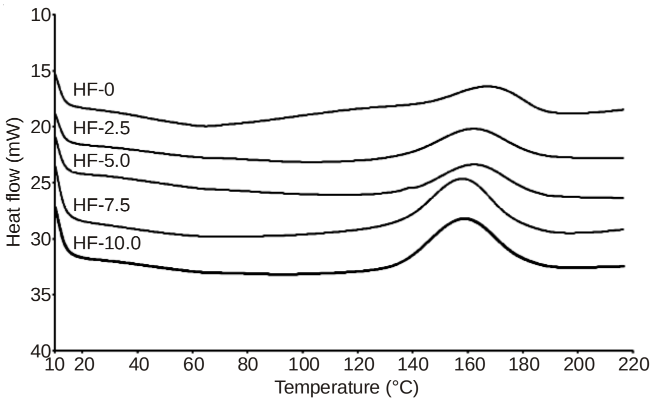

Fig. 7. DSC curves of free hybrid films

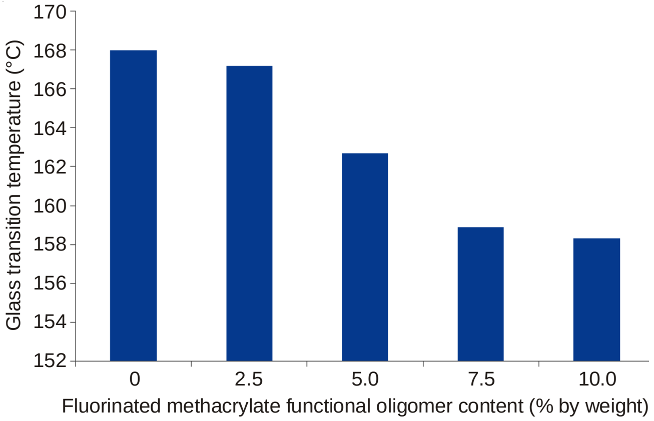

Fig. 8. Change of glass transition temperature with the percentage amount of fluorinated methacrylate functional oligomer

Thermo-oxidative stability of the free hybrid films was investigated by TGA analysis. The thermograms of the free hybrid films in air atmosphere are shown in Fig. 9. From the Fig. 9 it can be seen that the 1st. decomposition temperature for all of the hybrid materials was about 350 °C. The presence of the fluorinated methacrylate functional oligomers is believed to increase the thermal stability of the hybrid materials. There is a direct relation between the char residue and SiO_2 and fluorine content in the hybrid system.

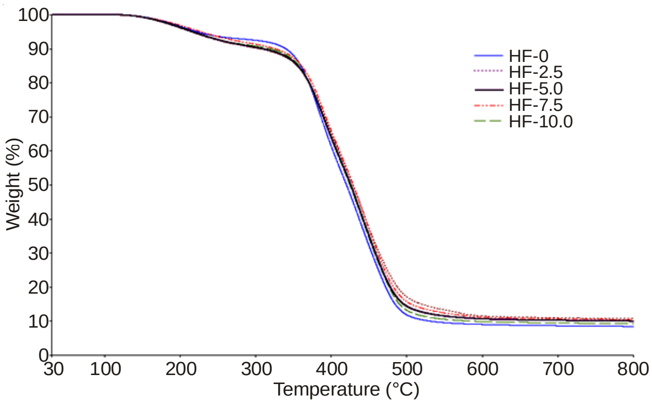

Fig. 9. TGA thermograms of free hybrid films

SEM images of fracture surfaces of free films of control (HF-0) and HF-7.5 samples are presented in Fig. 10a and 10b. Both images reveal that fracture occurred in a brittle manner. Fig. 10b shows the homogeneous dispersion of added inorganic phase in organic main structure.

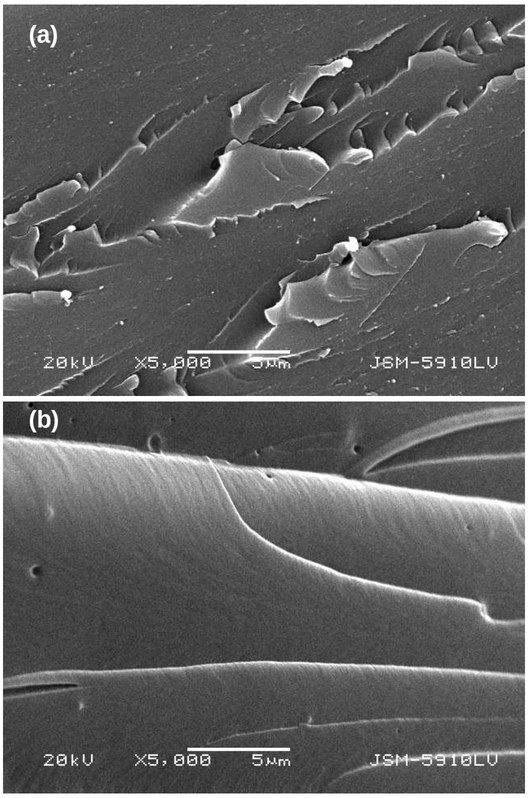

Fig. 10. SEM images of fracturesurfaces of (a) HF-0 (b) HF-7.5 samples

Elemental analysis of HF-7.5 sample was investigated by SEM–EDS analysis. SEM–EDS spectrum of HF-7.5 sample taken from fracture surface was presented in Fig. 11. SEM-EDS elemental analysis results were also presented in Table-4 as mass percentage of silicon. The EDS spectrum reveals the presence of carbon, oxygen, flourine and silicon and also the element gold that was deposited on the sample surface. The percentage of elements is used for the determination of semi-quantitative composition of the sample excluding gold. The presence of silicon confirms the effective incorporation of the inorganic precursor to the system.

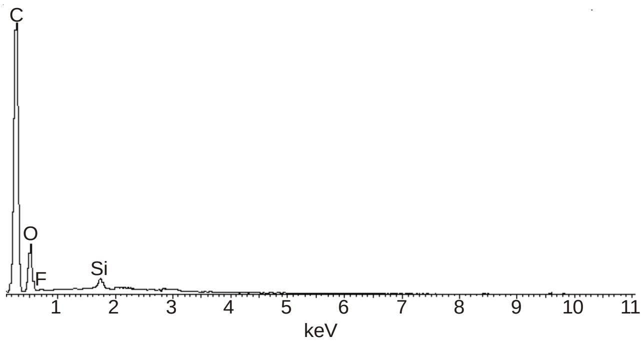

Fig. 11. SEM–EDS spectrum of HF-7.5 sample taken from fracture surface

TABLE-4
SEM-EDS ELEMENTAL ANALYSIS FOR HF-7.5 SAMPLE GIVEN AS MASS PERCENTAGE OF SILICON

Element	C	O	F	Si	Total
Element percentage	66.16	32.95	0.20	0.68	100.00

Conclusion

Surface characteristics and thermal properties of fluorinated methacrylate functional oligomer added Frimpex 11173 UV resin coatings were investigated. From the results it can be concluded that hybrid coatings can be used as UV lacquer in the printing sector for the cover pages of books, magazines, label printings and catalogues, *etc*. It was found that these coatings have a high gloss endurance and high abrasion resistance. These properties would keep the visual appearance of printed surfaces in the original condition during long periods of time.

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