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Simple and cheap process for protecting polycarbonate from wiping

ABSTRACT

Polycarbonate (PC) is very sensitive not only to scratching but also to even wiping with textiles or non-wovens. It can be a serious problem just to handle PC in production such that the integrity of the surface is kept. We report on a new process for rendering PC resistant to small scratches by wiping and similar procedures. For this, a very thin base coat from silicon dioxide is deposited by some low pressure or atmospheric plasma. Subsequently, a slippery polymer such as an easy-to-clean material is deposited on the surface. It was found that this results in significantly reduced scratching of PC surfaces upon wiping by a stroke tester with a felt disc. In addition, the resistance to a hardness pencil was also increased.

INTRODUCTION

The optical quality, maybe just the appearance, of plastic parts can suffer seriously from even very small scratches. These may be caused by even gentle friction of these parts to any other material. Hence, it can be difficult to handle polycarbonate (PC) parts just from one end of production to the other. For solving this problem, PVD [1,2] and PECVD [3] of silicon dioxide protective coatings has been proposed and demonstrated successfully[4-6] . However, the related cost is significant and was mostly found to be prohibitive because of too low deposition rates and expensive equipment. Here, we report on an efficient and new process combination to overcome this by combining a very thin silicon dioxide (“SiOx”) layer and an easy-to-clean deposit.

EXPERIMENTAL

Substrate materials

Plates of two different polycarbonates, PC, (Makrolon 2407 by Bayer and Lexan DMX 1435 from Sabic) were used as received without further pretreatment.

SiOx coating

Polycarbonate was coated silicon dioxide film at a thickness of approximately 2.5 µm from a non-thermal, RF-driven quartz capillary atmospheric plasma source with 10 jets as described in [7] by scanning the substrate with an automatic x/y mechanism. Octamethylcyclotetrasiloxane (OMCTS) and oxygen were used as feed materials in a mixing ratio of 1:10. The deposition rate for good coatings was approximately 1 nm /s.

Fig. 1: Atmospheric plasma jet array used for this work.

In another series of experiments, the SiOx was deposited onto PC Lexan DMX 1435 in a commercial barrel-type plasma reactor (built by plasma electronic, Filderstadt, in 1991) with a volume of approx. 10 l. A mixture of tetramethyldisiloxane (TMDSO) and oxygen (1:4) was fed in to a pressure of 0.5 mbar. The RF (13.56 MHz)- power was 50 W. Deposition time was 5 min for the start. The deposition rate was determined from the step height on a witness glass slide using a surface profiler (Dektak 3ST, Veeco) to be approx. 4 to 12 nm/min in one run.

Deposition of easy-to-clean material:

An easy-to-clean material (ETC 1 from Surface Chemistry, 61194 Niddatal, Germany) was evaporated in a vacuum oven from a porous brass tablet put into a thermal boat evaporator (heated up to 380°C) at an oven and substrate temperature of 70°C on the plate.

Test procedures:

For investigating the <u>wipe resistance</u>, the samples were abraded with a woollen, disk-shaped piece of felt (10 mm diameter, hardness H1 according to the German standard DIN 61200) using a commercial stroke tester (Karl-Fischer Maschinenbau). The felt disk was replaced by a new one for each measurement. After wiping, the samples were cleaned with a cloth and inspected similarly to German standard DIN 53218 from a distance of 30 cm at an angle of 10 to 90°perpendicularly to the stroke direction using a mirror. The illumination (Pantone Color Viewing Light from JUST Normlicht) was standard light D65 as a daylight equivalent and A (incandescent lamp) according to German standard DIN 5033 part 7, respectively. The number of strokes and the load on the felt disc were increased stepwise and the test procedure stopped as soon as scratches became visible. The test result is defined by the last step that was reached before scratches appeared.

Level	Number of strokes	Load in N
K1	1.000	1
K2	10.000	1
K3	30.000	1
K4	1000	2
K5	10.000	2
K6	30.000	2
K7	1.000	4
K8	10.000	4
K9	30.000	4
K10	30.000, no damage	4
K11	1.000	8
K12	10.000	8
K13	10.000, no damage	8

Table 1: Definition of different levels of wipe resistance after stroke testing

Fig. 2. Stroke tester for wipe testing

The scratch resistance was determined with a hardness test pen supplied by Erichsen, Hemer, Germany (fig. 3). The tip (diameter: 1mm, similar to ISO 1518) of this ball-pen shaped instrument is loaded by a spring .The preload of the spring can be adjusted from 0 to 20 N. By this, the force pressing the tip to the surface is defined when passing the tip perpendicularly across the surface over 10 mm. During the procedure, the preload of the spring is increased stepwise by 1 N each step for another run on a new surface area. After each pass the surface was cleaned with a cloth and inspected as above. The test result equals the preload of the spring that caused the first visible track on the polymer.

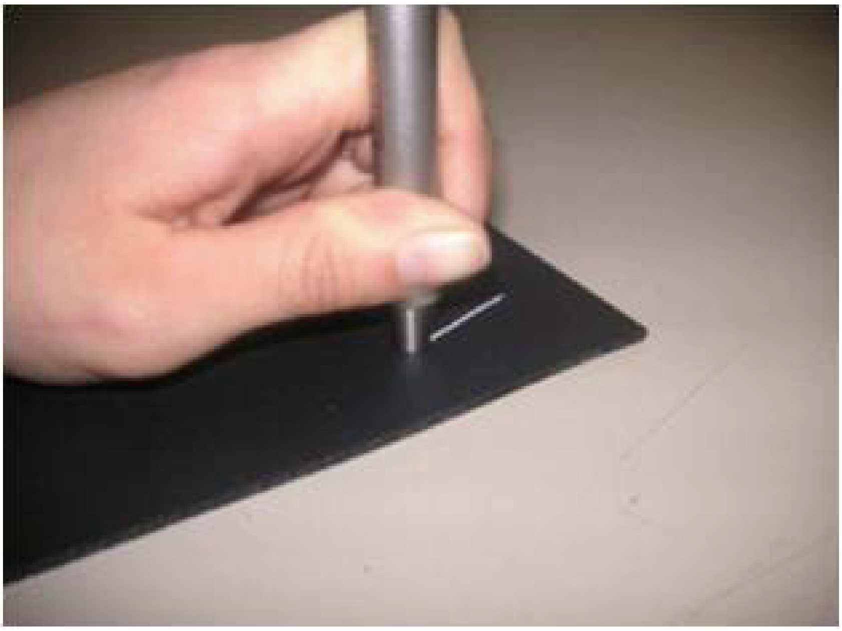

Fig. 3: hardness pen for scratch testing

RESULTS

	Wipe testing, stroke tester		Scratch testing, hardness pen	
	A (incandescent lamp)	D65 (daylight equivalent)	A (incandescent lamp)	D65 (daylight equivalent)
PC Makrolon 2407(Bayer), untreated	K1	K1	3N	3N
<5 nm SiOx + ETC1	K13	K13	2N	2N
20 nm SiOx + ETC1	K1 K1	K1 K1	5N 5N	5N 5N
100 nm SiOx + ETC1	K1 K1	K1 K1	5N 4N	5N 3N

Table 3: Atmospheric pressure plasma deposited SiOx with ETC1 impregnation; wipe and scratch testing results on PC Makrolon 2407 from Bayer

	Wipe testing, stroke tester		Scratch testing ,hardness pen	
	A (incandescent lamp)	D65 (daylight equivalent)	A (incandescent lamp)	D65 (daylight equivalent)
PC Lexan DMX 1435 (Sabic),untreated	K1	K1	9N	9N
2500 nm SiOx by atm. plasma	K11	K11	7N	7N
40 nm SiOx + ETC1	K12	K12	13N	13N
80 nm SiOx + ETC1	K7	K7	4N	7N
160 nm SiOx + ETC1	K12	K12	10N	11N
320 nm SiOx + ETC1	K1	K1	8N	8N
ETC1 only	K1	K1	13N	14N

Table 3: Low pressure plasma SiOx with ETC1 impregnation; wipe and scratch testing results on PC Lexan DMX1435 from Sabic

DISCUSSION

Comparison of the untreated substrate materials reveals that both of them are very sensitive to wiping (level K1 in the wipe test) but that they are withstanding different loads of the Erichsen hardness pen, Makrolon (3N) being more sensitive than Lexan (9N). In other words, there is no correlation between the pencil hardness and the wipe test. Some error possibility was found in the stroke tester related to the mounting of the felt disc. Little deviations in the test results under different light conditions were found but not enough to explain the divergence of wipe and scratch test results. Therefore, it can be assumed here that resistance to wiping as tested by the stroke tester and resistance to scratching by the hardness pen are different properties of the material.

The Makrolon appears to be not very resistant to neither wiping nor scratching. The material gained substancially in wipe resistance (from K1 to K13) by a treatment comprising a very thin(<5nm) SiOx coating by atmospheric plasma plus the easy-to-clean impregnation. The scratch resistance was not improved in parallel but slightly decreased by the same treatment from 3 to 2 N.

The Lexan was found to be more resistant to the scratch test than the Makrolon. An approx. 2.5 µm thick SiOx coating by atmospheric plasma increased wiping resistance from K1 to K11 but decreased

scratch resistance from 9 to 6 N. The tip of the hardness pen may have broken through the SiOx and the debris may have caused damage when moving the instrument.
An even better resistance against wiping was achieved with a 40 nm thick SiOx coating plus the ETC material, namely K12 and 13N. Similar results were found for 160 nm SiOx thickness but not for 80 nor 320 nm. So, the role of the SiOx thickness remains somewhat unclear. This may be a consequence of the inhomogeneous deposition rate within the reactor.
In a control experiment, the ETC1 was evaporated onto the Lexan directly, without any underlying SiOx. The wipe test ended on level K1 whereas the hardness pen went up to 13 and 14N, respectively. The latter result underlines the role of the ETC material (maybe, some lubricating effect) but has no technical meaning as the ETC material is wiped off rather soon.

Generally, the correlation of SiOx film thicknesses with the test results is not clear. In the light of earlier work on SiOx film properties [8] it would be helpful to keep the SiOx film properties under control. In this work, three different modifications of SiOx were found depending on parameter constellations showing spherical particles, compressive stress or neither of those.

CONCLUSION

It was shown that the resistance of polycarbonate Lexan DMX 1435 to wiping by a stroke tester can be improved significantly by some 2.5 μm thick SiOx coating deposited with an array of non-thermal atmospheric plasma jets. However, similar wipe resistance was found after low-pressure plasma deposition of much thinner films in combination with an easy-to-clean material.Very good wipe resistance was also obtained on polycarbonate Makrolon 2407 after atmospheric plasma deposition of a very thin (<5nm) SiOx film. Such thin films can be deposited within seconds even under the conditions of a localized atmospheric plasma jet arrangement. The time limiting step for now is the deposition of the easy-to-clean material in a simple vacuum oven taking a couple of minutes. Integration of this process into a low-pressure plasma device is simple. The data are not fully complete nor conclusive yet but the effect and its benefit are evident. More work needs to be done on the role of the easy-to-clean material and to identify the effect of SiOx properties on the resulting wipe and scratch resistance. A very good basis for this is the detailed work on parameter dependence of SiOx film properties [8].

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