Hard Coat Layers by PE-CVD Process for the Top Surface of Touch Panel

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Abstract. In order to protect surface from damages, the high pencil hardness and the high abrasion resistance are required for the hard coat layers on polyethylene telephthalate (PET) films for the application of touch panel surface. We have already found that the UV-curing-hard-coat-polymer (UHP) coated PET films show the poor abrasion resistance, while they have the high pencil hardness. It reveals that the abrasion resistance of hard coat layers of the UHP is not simply dependent on the pencil hardness. In this work, we have studied to improve the abrasion resistance of SiOC films as hard coat layers, which were formed by PE-CVD process on UHP coated PET. The abrasion resistance was evaluated by Taber abrasion test. PE-CVD hard coat layers which formed on UHP coater PET films have showed the better abrasion resistance and have the possibility of substitution to the thin glass sheets for touch panel application.

1. Introduction

Recently, a mobile application, such as the smart phone, the tablet and E-paper, is in fashion. The touch panel is used for input-device. A glass sheet is used in the surface of the screen to protect it against the scratch by fingers and stylus pens. However, the glass sheet is poor physical damage, so that it needs the substitution to the glass sheet. The substitution to the glass sheet for the top cover of a touch panel is required in the mobile application. One of candidate of the substitution material is the transparent plastic films because of their flexibility. The plastic film requires the hard coat layer to obtain high abrasion resistance, because the surface of it has the poor abrasion resistance. Therefore, the protective layer on the surface of the plastic film is required to protect any physical damage. One of the protective layers is the UV-curig-hard-coat-polymer (UHP), which satisfies some of the physical damage, but they have not enough abrasion resistance. The hard coat layers formed by CVD process have various kinds of layers, for example, SiO_2, SiOC [1-3], TiO_2 [4, 5], DLC (Diamond like carbon) [6, 7, 8] are known as protective layers. It is well known that the SiOC layers coated with polymer hard coat layers are already used for the top coat of the transparent polycarbonate (PC) windows for actual automobile application, because they have the high abrasion resistance. The specification of the abrasion resistance for automotive windows is defined as the delta haze of the surface after Taber abrasion tests should keep less than 10% in delta haze in ECE R43[9]. The SiOC layers on PC (polycarbonate) sheet meet this criterion. The SiOC layers by CVD process is also expected for the hard coat layers of plastic films for the surface of touch panels. In this work, we have studied the abrasion resistance of hard coat layers by CVD process on UHP coated PET films.

2. Experimental

The structure of hard coat films is shown in Figure 1. The SiOC layers were formed by PE-CVD process on the UHP coated PET films using Roll-to-Roll PE-CVD equipment illustrated in Figure 2. Hexametyldisiloxane (HMDSO) and O_2 were used as the precursor and reactive gases, respectively. The flows of each gas were controlled using mass flow controllers. After the initial evacuation less than 10^{-3} Pa, the SiOC layers were deposited under conditions summarized in table 1. The thickness of the SiOC layers was measured by a surface profiler (P-6, KLA-Tencor). The UHP was used silicon-containing acrylic polymer. PET film (Teijin DuPont Film, Thickness: 188μm) is used as the substrate. The silicon containing acrylic polymers were dried at 80 deg.C in air, and then cured by UV irradiation unit (UC-1501, HOYA-SCHOTT) at 600mJ/cm^2. The thickness of the UHP was about 3μm. The abrasion resistance properties of the hard coat PET films were investigated by delta haze. The delta haze is increment of the haze after the Taber abrasion test using Taber abrasion tester (YASUDA SEIKI SEISAKUSHO Ltd.). The wheels of the Taber tester were used CF-10F, and the load of the wheels was 4.9N [10]. The haze was measured by haze mater (NDH4000, NIPPON DENSHOKU). Compositions of the SiOC layers ware evaluated by X-ray photoelectron spectroscopy (ESCA 5800, ULVAC PHI). The surface of SiOC hard coat layer after the test was observed by a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi).

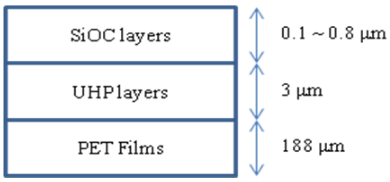

Figure 1. Structure of hard coat films.

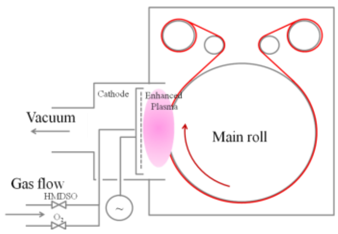

Figure 2. Schematic view of Roll-to-Roll PE-CVD coater.

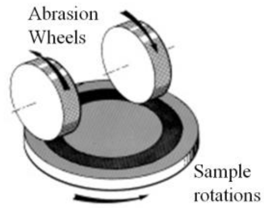

Figure 3. Schematic view of Taber abrasion tester.

3. Results and discussion

Figure 4 shows the appearance of the UHP coated PET film (a) without and (b) with SiOC hard coat layer after Taber abrasion test at 500 cycles. The surface of UHP coated PET is markedly damaged by the abrasion wheels, while the surface of SiOC layers on the UHP coated PET is not markedly damaged. Changes of haze value before and after Taber abrasion tests of the SiOC layers with 400nm thick on the UHP coated PET films and UHP coated PET films shown in Figure 5. The haze value of UHP coated PET rises drastically from 0.6% to 45% with increasing number of cycles in abrasion test from 0 to 500 cycles. On the other hand, the haze value of the SiOC hard coat layers on the UHP coated PET rises gradually from 0.76% only to 4.0%. It means that the SiOC coated films with 400nm thick has very high abrasion resistance. The pencil hardness of both hard coat layers showed the same value, 2H pencil hardness. These results indicate that the Taber abrasion resistance of hard coat layers has no explicit correlation with the pencil hardness of the surface.

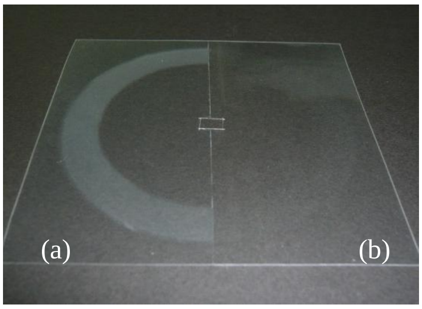

Figure 4. Results of Taber abrasion test. (a): UHP coated PET, (b): SiOC hard coat layers on UHP coated PET.

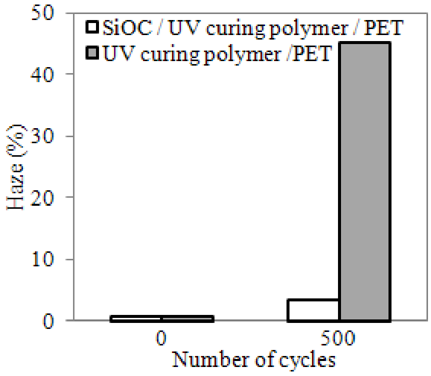

Figure 5. Haze value before after Taber abrasion tests.

The delta haze depends on the thickness of the SiOC layers, as shown in Figure 6. Delta haze decreases a first and shows the minimum value, 4% in 400nm -500nm thick, with increasing the thickness of the SiOC layers.

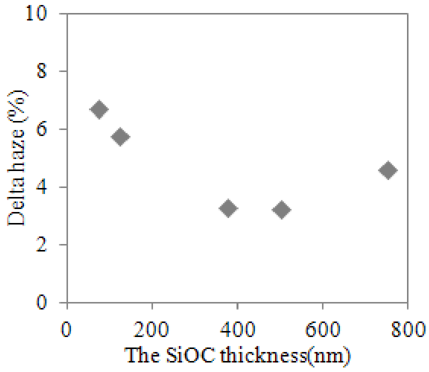

Figure 6. Delta haze vs. thickness of the SiOC hard coat layers.

Delta haze as a function of the amount of HMDSO flow, keeping constant flow of O_2 gas with 100, 350 and 550 sccm are shown in Figure 7. The delta haze of O_2 flow as 350 and 550 sccm in O_2 gas flow exhibit no marked dependence on the HMDSO flow, while delta haze of O_2 flow a 100 sccm keeps stable when HMDSO less than 15 sccm and then it increase, when HMDSO flows exceed 15 sccm. It is expressed in Figure 8, delta haze is re-plotted as a function of flow ratio of HMDSO / (HMDSO + O_2). In Figure 8, the delta haze seems to be almost constant up to 15% in the ratio, and they increases rapidly when the ratio of HMDSO / (HMDSO + O_2) exceed 15%. It seems that the excess HMDSO exist another un-reacted oligomer in SiOC layers, which should show the low abrasion resistance, when ratio of HMDSO / (HMDSO + O_2) exceed 15%.

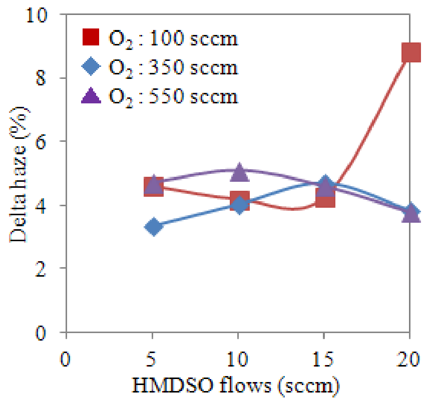

Figure 7. Delta haze vs. HMDSO flow.

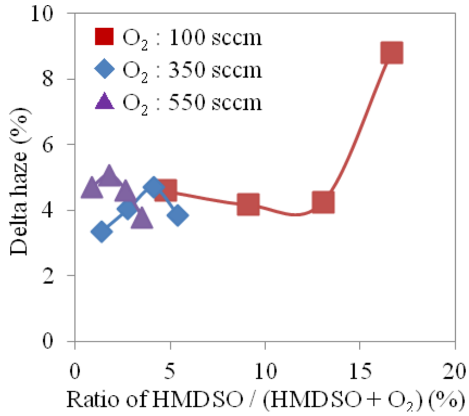

Figure 8. Delta haze vs. ratio of HMDSO / (HMDSO + O_2).

Figure 9 shows the relationship between compositions of the SiOC layers and deposition conditions. The atomic concentrations of carbon in the SiOC layers are increased with increasing the rate of HMDSO / (HMDSO+O_2) during deposition. The atomic concentration of carbon in the SiOC layers depends on the amount of incompletely reacted precursors. It is thought that the SiOC layers which have almost no carbon are formed as inorganic hard materials. Figure 10 shows the relation between the atomic concentration of carbon in the SiOC layers and delta haze. The delta hazes of films at carbon atomic concentration of 10% or lower are almost constant, and they are sharply increased at 20% of carbon atomic concentration.

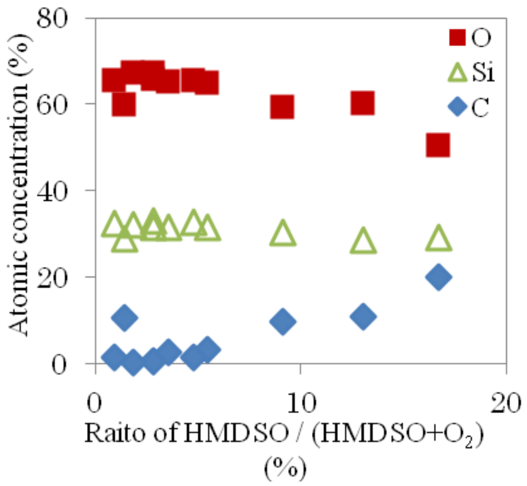

Figure 9. Atomic concentration vs. Ratio of HMDSO / (HMDSO+O_2).

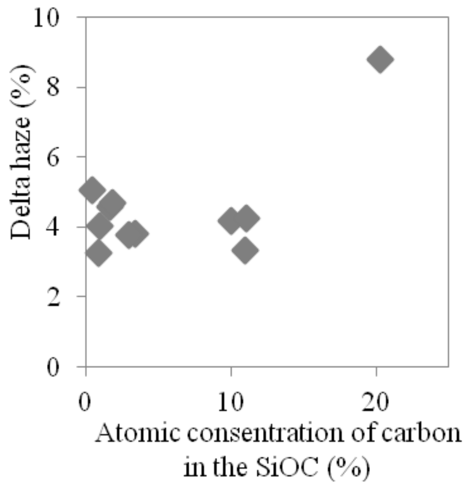

Figure 10. Delta haze vs. Atomic concentration of carbon in the SiOC.

Figure 11 shows the figure plotted the number of cycles to the delta haze. Two different deposition conditions are summarized in table 2. It is thought that the difference of delta haze of the SiOC layers deposited under both conditions in less than 100 cycles in Taber abrasion tests is not important because these results are within the range of variation. It is noted that the SiOC layers deposited under Condition (A), (B) have clear differences in changes of delta haze with increasing the number of cycles. The delta haze of SiOC layers formed under Condition (B) on UHB coated PET slightly depends on the number of cycles and indicates less than 4% even at 500 cycles. On the other hand, in case of Condition (A), the delta haze greatly increases with the number of cycles and reaches to 9% at 500 cycles. It is easily estimated that difference of delta haze of both films will expand wider at 1000 cycles or more. The SEM micrographs of the SiOC and UHP surfaces after Taber abrasion tests at 500 cycles is shown in figure 12. Notation (a), (b) indicate the surface of the SiOC layers deposited under Condition (A), (B), respectively. Notation (c) indicates the surface of the UHP without the SiOC layers. The surface of the SiOC layers deposited under Condition (A) tested after Taber abrasion tests at 500cycles has two clear scratches added to shallow traces, which show 9% in delta haze. On the other hand, it is found that the surface of the SiOC layers under Condition (B) has only shallow traces, so that the delta haze shows 4%. The surface of the UHP has many clear scratches more than these of the SiOC layers deposited under Condition (A), which show 45% in delta haze. These results indicate that the values of delta haze are related to the number of clear scratches on the surface. It is thought that the surface of the SiOC layers, such as inorganic hard material, deposited under Condition (B) has shallow traces by rubbing the surface with sliding taber wheels. On the other hand, the surface of the SiOC layers deposited under Condition (A) which contains some incompletely reacted precursor as organic parts have clear scratches by abrasion by taber wheels. In addition, UHP without SiOC layers, which has more organic behavior compared the SiOC layers deposited under Condition (A) in abrasion, have many clear scratches.

Table 2. Deposition conditions at the SiOC layers formed by PE-CVD process.

Condition	HMDSO flow (sccm)	O_2 gas flow (sccm)	Ratio of HMDSO / (HMDSO + O_2)
A	20	100	16.7
B	10	350	2.7

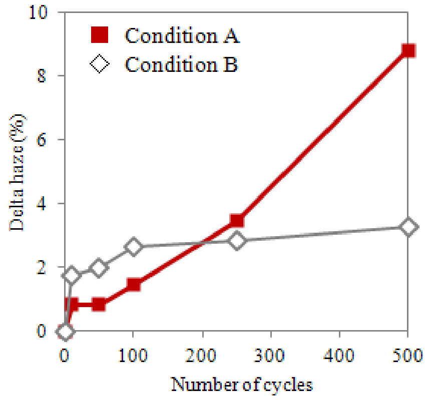

Figure 11. Changes of delta haze vs. Taber abrasion test cycles.

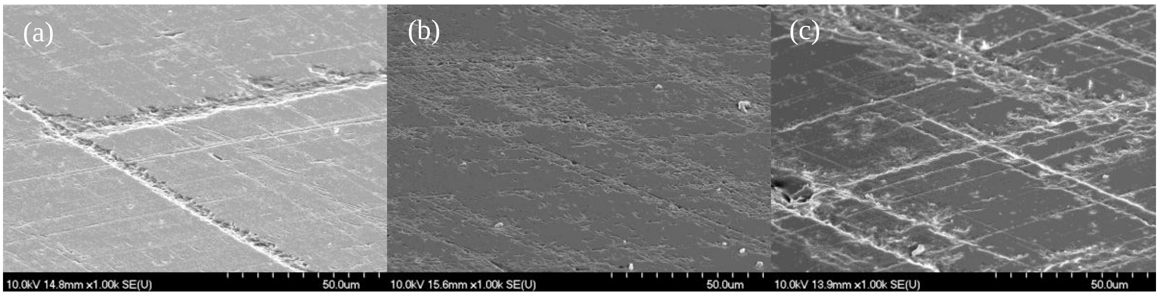

Figure 12. SEM micrographs of the SiOC and the UHP surface after performed Taber abrasion test at 500cycles. (a): The surface of the SiOC layers deposited under Condition (A), (b): The surface of the SiOC layers deposited under Condition (B), (c): The surface of the UHP

4. Conclusion

The SiOC hard coat layers formed by PE-CVD process on UHP coated PET using HMDSO and O_2 gases, in order to add the high abrasion resistance to PET films. The abrasion resistance of SiOC layers on UHP coated PET has been investigated by varying deposition conditions and SiOC thickness. Abrasion resistance has marked dependence on thickness of the SiOC layers and also strongly influenced by depositing conditions. It is clear that the SiOC hard coat layers formed under ratio HMDSO / (HMDSO + O_2) = 2.7% with 400 nm thick should show the excellent abrasion resistance and the delta haze is 4%. The SiOC hard coat layers are expected to have the possibility as a candidate for the substitution to cover glasses for touch panel application.

5. References

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