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NF_3와 O_2 리모트 플라즈마 노출에 따른 니트릴 가교 과불소고무와 과산화물 가교 과불소고무의 무게 손실과 모폴로지 특성

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Weight Loss and Morphology of Nitrile Curable PFE and Peroxide Curable PFE after Exposing to NF_3 and O_2 Remote Plasmas

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초록: 니트릴 가교 과불소고무와 과산화물 가교 과불소고무의 내플라즈마 특성을 평가하기 위해 고온상태에서 NF_3, O_2 리모트 플라즈마에 노출된 과불소 고무 재질의 오링(O-ring)에 대해 각각의 무게 손실 및 표면 특성을 확인하였다. 이를 위해 컴파운드는 반도체 및 LCD 생산라인에서 적용되고 있는 오링/씰 제조를 위한 전형적인 처방에 맞춰 설계하고 오픈 롤을 사용하여 혼련작업을 실시하였으며, 이후 열프레스로 작업한 후 오븐을 이용한 후가교 공정을 거쳐 최종 오링 형태로 제조하였다. 가교된 과불소고무 오링을 고온 플라즈마 환경에 노출시킨 후 무게 감량 및 표면 특성 변화를 전자 저울 및 주사전자현미경을 사용하여 관찰하였다. 그 결과, 과불소고무의 가교타입, 필러 시스템, 플라즈마의 종류에 따라 무게 손실과 표면 상태의 변화가 상당한 수준으로 발생되는 것을 확인하였다.

Abstract: The plasma resistances of nitrile curable perfluoro elastomer (NT PFE) and peroxide curable PFE (PO PFE) after exposing to NF_3 and O_2 remote plasmas were investigated by analyzing weight loss and morphology of O-ring made of PFE. The compounds were designed following the typical formulations of O-ring/seal which were applied in semiconductor and LCD production site. They were blended by an open roll mill, and then, O-ring was finally made by hot press molding and oven curing. The weight loss was calculated and morphology was observed for each atmosphere and temperature by a digital weighing machine and SEM. As results, it was confirmed the weight loss and related morphology were meaningfully different according to the cure type of PFE, filler system, and the species of remote plasma.

Keywords: perfluoro elastomer, plasma resistance, remote plasma, weight loss, morphology.

Introduction

Perfluoro elastomers (PFE), a fully fluorinated class of elastomers, are very useful raw material for making packing components, such as valve, O-ring, and gasket which is used in semiconductor and LCD manufacturing process.[1,2] PFE products are varied by harsh environments, such as operating temperature (upper use temperature), chemical environment, plasma species and concentrations, and etc. Semiconductor fabricators have found that plasma is a very powerful tool for etching, chemical vapor deposition and stripping because all materials are consumed in plasma and it can increase reactivity. Seals made from fluorinated elastomers are used in these processes because of their exceptional resistance to aggressive media. Despite these superior properties of sealing components, prolonged exposure to plasmas can degrade their surface resulting in particulate contamination before sealing functionality is lost.

The ideal seal for plasma applications, therefore, would resist surface degradation and maintain its functionality.[3,4] Nevertheless, the academic and industrial approach is not common[5] because it is hard to evaluate the properties and performances in lab. scale, and the price of raw material is very expensive. As

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the wafer size is bigger and bigger in semiconductor production line, the performances and durability of packing (O−ring, seal, gasket) products is much more emphasized. But it is hard to find out the evaluation tool in laboratory scale for simulating the real operating conditions. The plasma and temperature resistance are very important in the usage of PFE packing products and it should be evaluated before installation.

This paper is designed to suggest the evaluation tool for PFE products, especially, in remote plasma and high temperature conditions for NT PFE and PO PFE which are major material in high temperature and/or plasma conditions in vacuum.[5−8]

In order to investigate the remote plasma resistance and temperature resistance of PFE, we evaluated the weight loss and carried out the surface analysis using SEM (scanning electron microscope) after exposure in diverse gas and temperature conditions.

Experimental

The O−rings made of NT PFE (3M Dyneon PFE 131TX and 132TBX) and peroxide curable PFE (3M Dyneon PFE 80X) were prepared with their typical formulations and under processing conditions. Table 1 lists the materials evaluated in this experiment. NT PFE 1 was just raw gums consisted of TFE (tetrafluoroethylene) and PMVE (perfluoro methyl vinyl ether), but NT PFE 2 contains originally fluorine fillers in it. The specimens were prepared by adding carbon black, silica, and $BaSO_4$ to make a compound, if needed, and then, it was blended using 8” roll mill and O−ring was made using hot press (1st cure) and hot oven (2nd cure). NT PFE O−ring was 1st cured at 180 ℃ for10 min. and 2nd cured at 250 ℃ for 24 hrs. PO PFE was 1st cured at 180 ℃ for 10 min and 2nd cured at 230 ℃ for 16 hrs following supplier’s processing recommendation in order to make the products show the best performance. Figure 1 shows the shows the classified O−rings for the test. Weight loss calculation after exposing remote plasma and morphology comparison using SEM−EDS were performed in order to compare the relative performance of each O−ring at elevated temperatures. Table 2 lists the remote plasma source and its conditions in this experiment, Figure 2 shows the schematic diagram of remote plasma equipment. The reaction chamber system equipped with a toroidal type remote plasma generator (RPG) and associated diagnostic tools. The reaction chamber was evacuated down to approximately 1 Torr using a pumping system combined with a booster and a dry pump which was purged by N_2 gas flow. The inductively coupled toroidal−type RPG (New Power Plasma Co., Korea) used in this experiment is powered by a power source with an output power of 10 kW and a frequency of 400 kHz. In this technology, the power is delivered to the reaction tube that surrounds the ferrite core. The plasma generated inside the reaction tube acts as a secondary winding of a transformer circuit that couples electromagnetic energy directly into the reaction tube. During the generation of the plasma, the power delivered to the source is automatically

Table 1. The Classified O-Rings for the Test

Materials	Filler system	Cross−linking system
NT1 natural	FP[a]	Nitrile
NT1 white	FP/Silica	Nitrile
NT2 natural	None	Nitrile
NT2 white	Silica	Nitrile
PO white	Silica, $BaSO_4$	Peroxide
PO white	Carbon black	Peroxide

[a]FP: Fluoropolymer(organic filler) is contained in PFE.

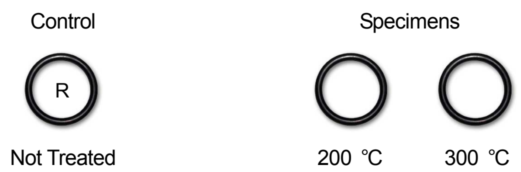

Figure 1. The classified O−rings for the test.

Table 2. Remote Plasma Source and Conditions

Classifications	Conditions
Source	Toroidal−type remote plasma source
Atmosphere	O_2, NF_3, NF_3+O_2
Flux	1000 sccm
Wafer size	4 Inch
Pressure	1 Torr
Test temp.	200 ℃, 300 ℃
Duration	30 min

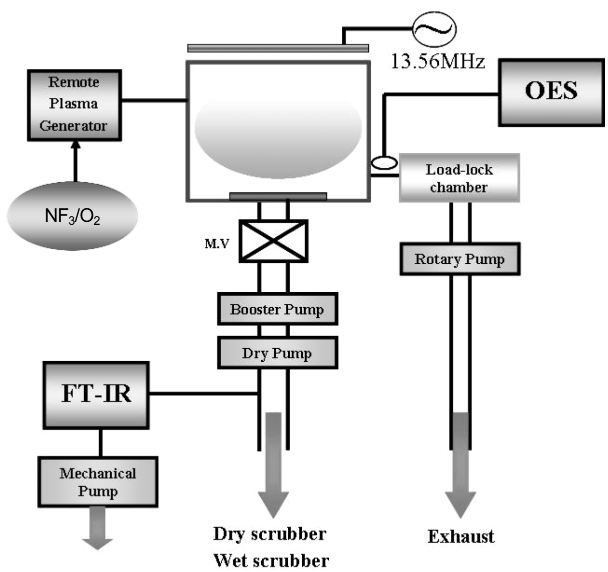

Figure 2. Schematic diagram of remote plasma equipment.

adjusted, depending on the total flow rate of the input gas. The remote plasma source used in this experiment was shown to be very effective in dissociating the reactive gas molecules. The radical species generated by the remote source were injected through an alumina (Al_2O_3) injector situated at the bottom of the reaction chamber.[8]

Results and Discussion

In general, most of engineers work in semiconductor and LCD manufacturing process require the packing components which have the durability, such as long life without crack, low particle generation, low weight loss, and etc. Most of all, it is known that weight loss and particle generation are most important issues because they are directly related with the productivity in the production line. Therefore, this study focuses on the weight loss and surface change after harsh and intensive remote plasma treatment at high temperatures for simulating the environment of real production line.

Weight Loss Results.

O_2 Remote Plasma Exposure: Figure 3 and Figure 4 compares the weight loss of the various specimens evaluated after being exposed to O_2 remote plasma, at 200 and 300 ℃. O_2 remote plasma is popular atmosphere in semiconductor processing, especially in CVD (chemical vapor deposition) process. Test was performed for every specimens and some general observations can be made. It showed slight weight loss difference between each specimens at 200 ℃, but at 300 ℃, NT PFE showed excellent weight loss values compared to PO PFE and NT1 natural showed best performance. From this result, It can be inferred that NT PFE would be more effective product which can resists in harsh O_2 atmosphere.

NF_3 Remote Plasma Exposure: Figure 5 and Figure 6 compares the weight loss of the various specimens evaluated after being exposed to NF_3 remote plasma, at 200 and 300 ℃. It showed slight weight loss difference between each specimen at 200 and 300 ℃. Regardless of the species of PFE cure type, weight loss values were almost similar. From this result, It can be inferred that PO PFE and NT PFE is not sufficient material by itself in NF_3 atmosphere.

O_2/NF_3 Remote Plasma Exposure: Figure 7 and Figure 8 compares the weight loss of the various specimens evaluated after being exposed to NF_3 remote plasma, at 200 and 300 ℃. PO PFE showed the lowest weight loss value at 200 ℃, but the highest at 300 ℃. On the contrary to that, NT PFE just showed slight increase of weight loss value as the temperature is going on from 200 to 300 ℃. It can be expected that NT PFE has a probability to meet in this kind of mixed remote plasma atmosphere from this result.

Surface Analysis Results: The SEM image was observed in diverse magnitude, but in this paper, 2000 times magnification

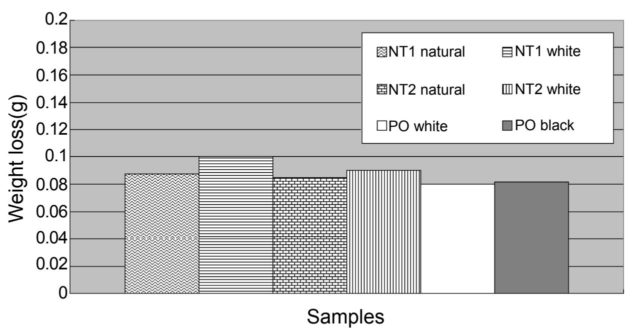

Figure 3. Comparison of weight losses after exposing to O_2 plasma at 200 ℃.

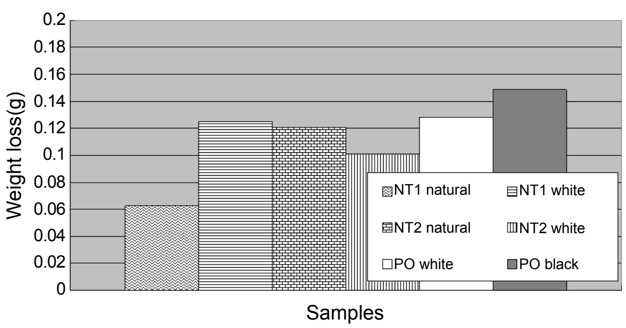

Figure 4. Comparison of weight losses after exposing to O_2 plasma at 300 ℃.

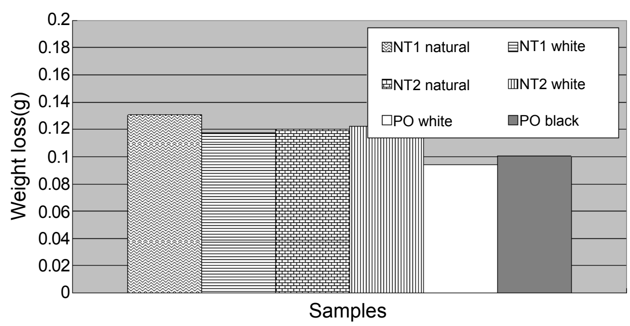

Figure 5. Comparison of weight losses after exposing to NF_3 to plasma at 200 ℃.

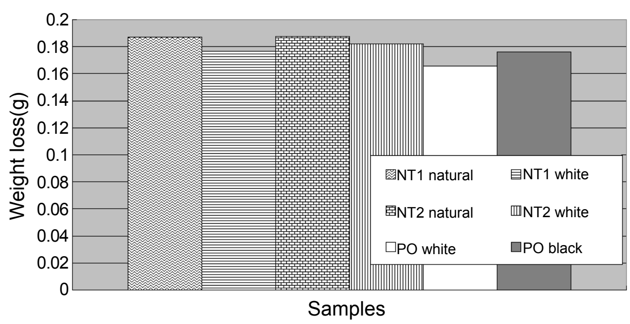

Figure 6. Comparison of weight losses after exposing to NF_3 to plasma at 300 ℃.

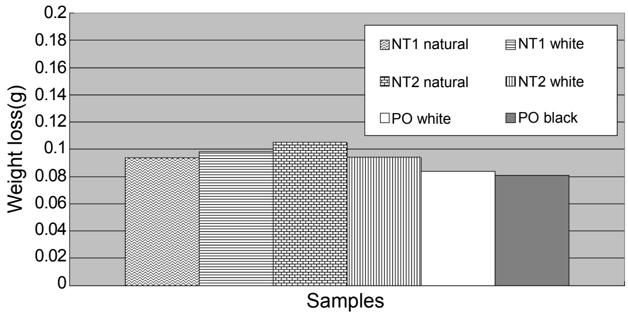

Figure 7. Comparison of weight losses after exposing to O_2/NF_3 plasma at 200 ℃.

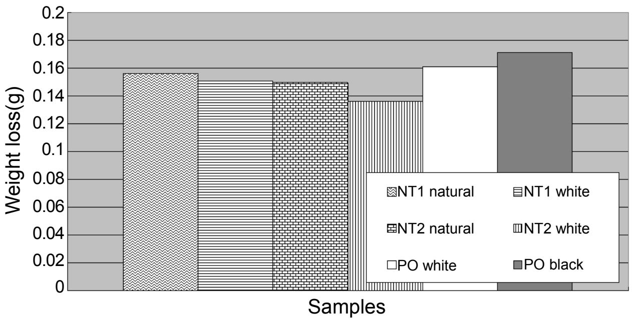

Figure 8. Comparison of weight losses after exposing to O_2/NF_3 plasma at 300 ℃.

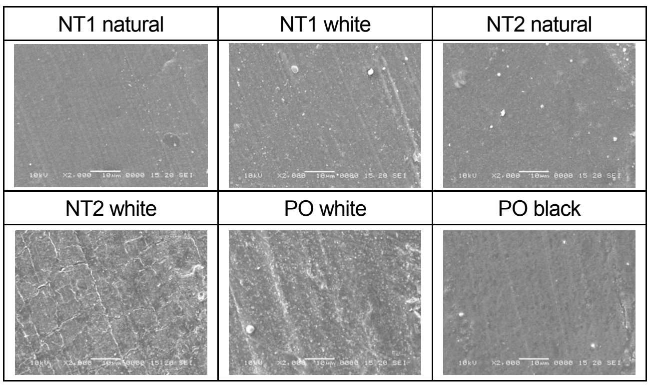

Figure 9. Surface morphologies by SEM analysis after exposing to O_2 plasma at 200 ℃.

was preferred because it showed the surface change exactly, such as initiation and propagation of crack in detail after remote plasma exposure. In addition to that, EDS (energy dispersive X-ray spectrometer) analysis was also executed in order to check the change of chemical elements of each samples before and after exposing remote plasmas.

Surface Morphologies after O_2 Remote Plasma Exposure: Figure 9 and Figure 10 compares the surface morphology of the various specimens evaluated after being exposed to O_2 remote plasma, at 200 ℃ and 300 ℃. All specimens showed clean surface morphology at 200 ℃ even though it was exposed to O_2 remote plasma, especially NT1 natural was

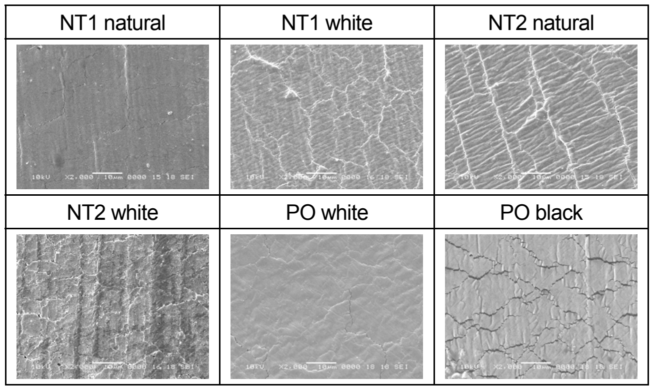

Figure 10. Surface morphologies by SEM analysis after exposing to O_2 plasma at 300 ℃.

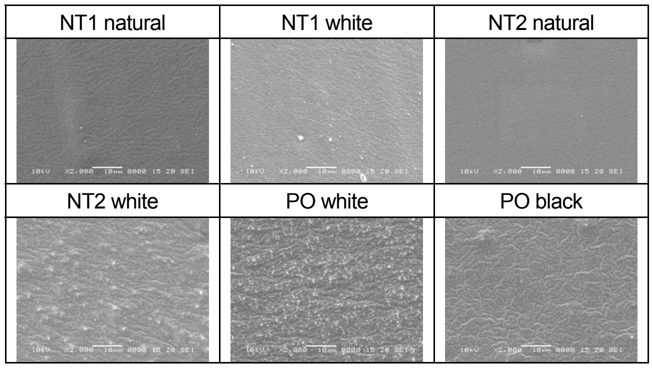

Figure 11. Surface morphologies by SEM analysis after exposing to NF_3 plasma at 200 ℃.

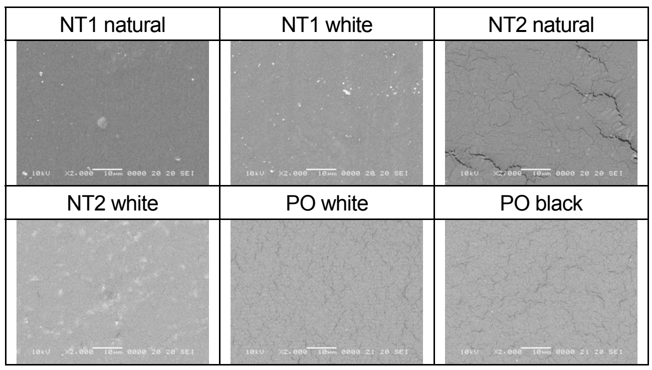

Figure 12. Surface morphologies by SEM analysis after exposing to NF_3 plasma at 300 ℃.

most excellent surface smoothness. But as the temperature was increased, the difference between specimen were evident. NT1 natural was very clean, but all other specimen showed deterioration, especially PO black showed many cracks from the surface. From this result, it can be inferred that the NT PFE product based on non-filler system would be more effective at O_2 remote plasma condition.

Surface Morphologies after NF_3 Remote Plasma Exposure: Figure 11 and Figure 12 compares the surface morphology of the various specimens evaluated after being exposed to

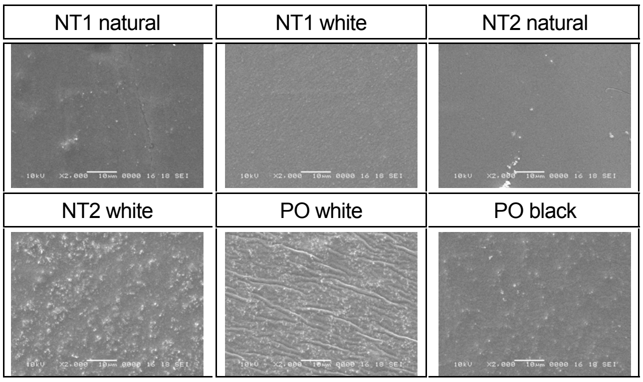

Figure 13. Surface morphologies by SEM analysis after exposing to O_2/NF_3 plasma at 200 ℃.

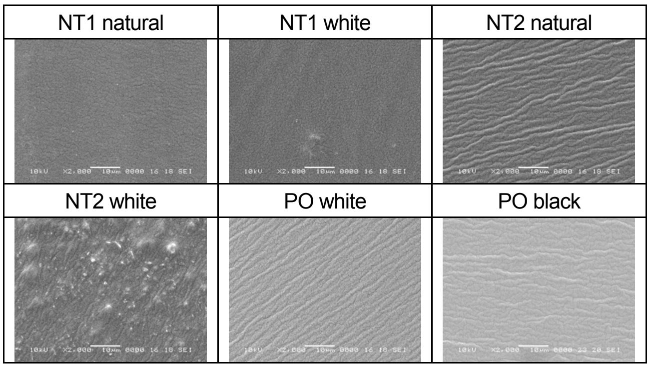

Figure 14. Surface morphologies by SEM analysis after exposing to O_2/NF_3 plasma at 300 ℃.

NF_3 remote plasma, at 200 and 300 ℃. NT1 natural, NT1 white, and NT2 natural showed clean surface, but NT2 white, PO white, and PO black showed the initiation and propagation of crack. NT1 natural, NT1 white, and NT2 white still showed clean surface even at 300 ℃, but NT2 natural and PO PFE showed the initiation and propagation of crack. From this result, it can be inferred that the NT PFE product based on non-filler system would also be more effective at NF_3 remote plasma exposure like O_2 remote plasma condition.

Surface Morphologies after O_2/NF_3 Remote Plasma Exposure: Figure 13 and Figure 14 compares the weight loss of the various specimens evaluated after being exposed to NF_3 remote plasma, at 200 and 300 ℃. In the mixture of O_2/NF_3 (1:1) remote plasma conditions, NT PFE showed the superior surface properties compared to PO PFE. Especially, NT1 PFE showed the best performances against O_2/NF_3 (1:1) remote plasma, not only at 200 ℃ but also at 300 ℃. Compared to 200 ℃ experiment, NT2 PFE showed the initiation of crack phenomena from the surface. Alike as O_2 and NF_3 remote plasma exposure, it can be inferred that NT PFE product based on non-filler system would be more effective at O_2/NF_3 mixed remote plasma exposure.

The Change of Chemical Elements before and after Exposing Remote Plasma. All PFE products are mainly composed of carbon (C), fluorine (F), oxygen (O), and contains small amounts of silica (Si), barium (Ba), titanium (Ti), and etc. By EDS analysis, we could find out the change of elements for each samples, that is, the amounts of oxygen elements were increased, however, the amounts of carbon and fluorine elements were decreased. As the propagation of crack is going on much, the loss of carbon and fluorine elements were increased and it means plasma exposure at high temperature cause the dissociation of C-F bond, the degradation and oxidation for PFE products.

Conclusions

Among the PFE products evaluated, those having a nitrile crosslinking system are more stable than peroxide crosslinking system against remote plasma resistance and high temperature. The O-ring made of NT PFE shows very slight weight losses after harsh plasma treatment, and even under high temperature compared to PO PFE. Especially NT PFE product based on non-filler system shows the stable performances all conditions evaluated in this paper, it can be expected that it will be a effective material in semiconductor and LCD manufacturing process conditions, especially at O_2, NF_3, and O_2/NF_3 mixed remote plasma exposure.

By surface analysis using SEM, we can infer NT PFE also shows extremely restrained particle generation and preserved smoothness of the surfaces even under high temperature. NT PFE shows outstanding plasma resistance for weight loss and surface morphology, especially, in the condition of O_2.

From the experiments, the O-ring made of NT PFE is not damaged by O_2 and/ or NF_3 remote plasma generated by remote plasma source and we found out the possibility of remote plasma system in laboratory, as a simulation tool, which can be applied to evaluate the durability and the performance of packing products used in semiconductor and LCD manufacturing process.

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