

## Novel Method to Protect Electronics Devices from Electrostatic Charging using Electrostatic Series of Polymers

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Polymers are used as indispensable materials in the electronic industry for their insulating properties. On the other hand, the insulators are known to develop electrostatic charges which can damage electrical components upon discharge. This is a serious problem when one considers that polymers are used as packaging materials for almost all electronic devices. The problems caused by the electrostatic charging have been magnified as the size of the electronic devices decreases. In the serious cases, electronic devices are rendered unusable by the electrostatic charge occurring between the surface of the devices and the packaging polymers. For example, according to “Charged Device Model”,<sup>1</sup> the electrostatic charging induces high voltage current that causes meltdown of the wire existing inside of the devices. In manufacturing for electric devices, small and light chip devices stick on the cover tape of container when the cover tape is opened by a machine.

Elimination of electrostatic charge by grounding and ionizers are insufficient methods, since electrostatic charging occurs constantly between two contacting surfaces. The process of electrostatic charging produces equal and opposite charges on the surfaces of dissimilar materials upon separation from contact. An empirical electrostatic series of polymers is well documented.<sup>2–6</sup> When material “A” is contacted then separated from material “B”, an electrostatic charging is observed and ranked by an empirical electrostatic series. The electrostatic series ranks the polymers in the order of the relative polarity of the charge acquired from positive to negative such as nylon and halogenated polymers, respectively. The higher ranked materials will acquire a positive charge when contacted with a material at a lower rank along the series. It is noteworthy that these simple phenomena have not been applied to minimize charging at the interface of polymeric materials so far. Thus, it is possible to mitigate electrostatic charging if we can minimize distance of the rank in electrostatic series between the contacting two materials.

Poly (vinylidene difluoride) (PVDF) is known to have good chemical resistance and thermal stability. Additionally, its adhesion to metal can be improved by blending with 5–25 wt % of poly(methyl methacrylate) (PMMA). The PVDF/PMMA polymer blend system is a rare case in which two polymers

are miscible at the molecular level in the glass state in spite of substantially different structures.<sup>7–12</sup> It is reported that PVDF crystallize with annealing the polymer blends, and then these two phases are separated each other. From the electrostatic series, PVDF acquires a negative charge while PMMA acquires a positively charge, and are located far apart from each other.

In this paper, the electrostatic charging characteristics of PVDF/PMMA polymer blends were investigated, and we present the first report for a simple method to control rank of the electrostatic charging, and we can adjust the rank of electrostatic series between the surfaces of the devices and the packaging polymer. By controlling the electrostatic rank, electric devices can be protect from the damage occurred by incidental electrostatic charging during processing.

### EXPERIMENTAL

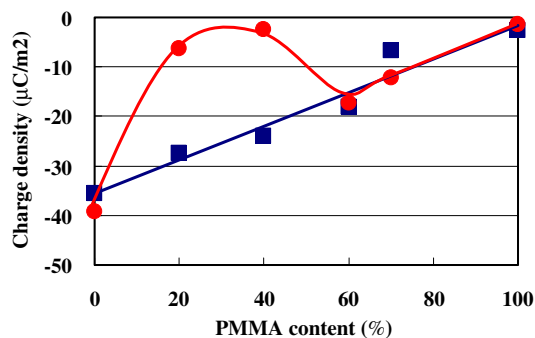
#### Film Preparation

PVDF was obtained from Ausimont MP-10, and PMMA from Mitsubishi Rayon Acrypet MF. The film samples were prepared by pressing at 200 °C after the PVDF and PMMA were extruding at each mixing ratio. The thickness of the films was 140 μm. The quenched samples were prepared by cooling in water immediately after pressing. The annealed samples were prepared from the quenched samples by annealing at 120 °C for ten or more days.

#### Measurements

The charging characteristics of the sample were measured by using a modified cascade method.<sup>13,14</sup> All film samples were equilibrated at 25 °C, 50%RH for at least 12 hr prior to measuring. The film sample was fixed onto the surface of an inclined metal plate with a metal cover. Ten grams of copper beads with an average diameter of 500 μm were dropped onto the film from a hopper. The beads slid and/or rolled down the surface of film sample generating friction and/or contact charging, then collected in a Faraday cage. The total amount of the charge generated on the copper beads was measured by a nano-coulombmeter (Monroe Electronics Ltd). The charge

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**Figure 1.** Correlation of charging density and PMMA content of PVDF/PMMA polymer blends; (■) quenched sample; (●) annealed sample.

density was calculated by dividing the total charge by the area of the surface copper beads touched.

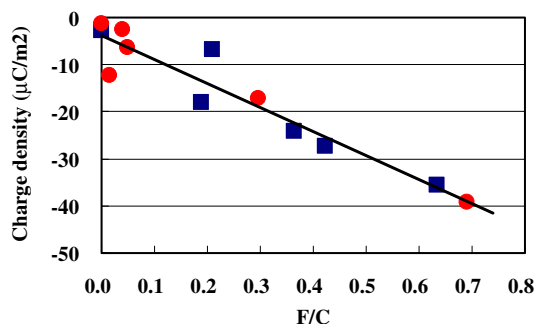
Atomic analysis of sample surface was performed using X-ray photoelectron spectroscopy (XPS, ESCA-5500MC/PHI). A typical operating condition was 14 kV and 200 W for an Al X-ray source. Photoelectron collection was at 65° angle normal to the sample surface.

## RESULTS AND DISCUSSION

Charging characterization of the PVDF/PMMA polymer blends indicates a net negative charge against copper for all compositions. (Figure 1) As the PVDF content increased the polymer blends exhibited a large negative charge consistent with the electrostatic series. The composition to charging density had a linear relationship for the quenched samples. However, the annealed samples deviated significantly from the linear relationship when the PMMA content was between 20 and 40 wt %. The linear relationship of the quenched sample composition can be used to control charge density. Although these behaviors seem intuitive, the present study is the first report describing this simple relationship.

Crystallization of PVDF has been discussed in the literature.<sup>7</sup> As a semi-crystalline polymer, annealing promotes PVDF crystallization. Since the behavior of the quenched and annealed samples is significantly different, crystallization is a potential source for this difference. It was reported that the heat of fusion of the quenched samples deviates significantly from the linear relationship for blend compositions. However, the annealed samples maintain a linear relationship throughout all blend compositions.

Electrostatic charging is a surface to surface interaction, so it is reasonable to assume that the chemical composition at the surface has the largest influence this phenomenon. Fluorine content can be solely attributed to PVDF in the blend films. F/C ratio correlates directly to the PVDF content at the surface. Although the F/C ratio decrease linearly with the PMMA content of the quenched samples, the ratio of the annealed samples deviate from the linear relationship. Especially, the F/C ratio on the surface in the region of the PMMA content



**Figure 2.** Correlation of charging density and F/C ratio of the surface of PVDF/PMMA polymer blend films; (■) quenched sample; (●) annealed sample.

between 20 and 40 wt % decreased down close to the value of the PMMA content 100 wt %. This indicates that significant crystallization of PVDF proceeded in bulk, when PVDF is the major component. Therefore, PVDF molecules on the surface moved into bulk for crystallization and PMMA molecules are excluded from the crystallites to the surface. On the other hand for samples with PMMA content over 60 wt %, the crystallization of PVDF is suppressed by PMMA and the polymer ratio on the surface did not change remarkably by annealing.

The charge densities were plotted against the values of F/C ratio as shown in Figure 2. F/C ratio correlated well regardless of preparation conditions. Since the F/C ratio indicates the ratio of PVDF and PMMA very near the surface, it was concluded that the electrostatic charging characteristics were proportional to the polymer ratio on the surface of the polymer blends.

This important observation allows the electrostatic charging characteristics to be easily controlled by changing the ratio of polymers on the surface. By using this technique, the difference of the charging density between the surfaces of the packaging polymers and small electronics devices can be minimized to prevent damage by the electrostatic charging.

## REFERENCES

1. B. A. Unger, *IRPS, 19<sup>th</sup> Annual. Proc.*, **4**, (1981).
2. A. Coehn, *Ann. Phys.*, **64**, 217 (1898).
3. S. P. D. Hersch and J. Montgomery, *Text. Res. J.*, **25**, 279 (1955).
4. J. Henniker, *Nature*, **196**, 474 (1962).
5. C. K. Adams, "Nature's Electricity, 63," Tab Books, Blue Ridge Summit, PA, 1987.
6. A. F. Diaz and R. M. Felix-Navarro, *J. Electrostat.*, **62**, 277 (2004).
7. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
8. J. S. Noland, N. N.-C. Hsu, R. Saxon, and J. M. Schmitt, *Adv. Chem. Ser.*, **99**, 15 (1971).
9. D. R. Paul and J. O. Altamirano, *Adv. Chem. Ser.*, **142**, 142 (1975).
10. D. J. Hourston and I. D. Hughes, *Polymer*, **18**, 1175 (1977).
11. E. Roerdink and G. Challa, *Polymer*, **21**, 509 (1980).
12. J. H. Wendorff, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 439 (1980).
13. H. W. Gibson, *J. Am. Chem. Soc.*, **97**, 3832 (1975).
14. H. Takeda and Y. Murata, *Jpn. J. Appl. Phys.*, **35**, 4791 (1996).