K.B. Gurbanov

FORMATION OF A CHARGING CONDITION IN POLYMER DIELECTRICS SUBJECTED TO ELECTRICAL EFFECTS

Institute of Physics, Azerbaijan National Academy of Sciences
H. Javid ave. 33, 370143, Baku

1. Introduction

It is known, that the changes of polymer dielectrics properties are closely concerned with their manufacturing technology and, therefore, with their physical and chemical structure. At operation of products in polymer dielectrics its are frequently exposed to effect of the various external factors, such as radiation, mechanical loads, high and low temperatures, strong electrical and magnetic fields, moisture, various kinds of electrical discharge etc. The analysis of literature data about the properties of polymer dielectrics testify that in polymer materials subjected to various external effects the essential changing of their chemical and physical structure and, hence, their basic properties, are observed [I]. Many investigators applying the direct research methods: electrical and optical microscopy [2], X-rays diffraction [3], infrared spectroscopy [4], electron-paramagnetic resonance etc., have rather successfully solved a number of problems concerning with polymer dielectrics properties. In some cases the particular interrelations between the changing of researched objects properties and their structure were convincingly obtained.

However, it is necessary to note that despite of plenty spent researches in this field; the decision of many questions remains open. At many occasions the interpretations of experimental results were not definitive. Absence of conventional classical theoretical works does not allow making the generalizing conclusions.

Above told and also the facts of ongoing the new polymer materials with complex structure and, therefore, with new properties, stimulate the realization of further researches in considered field.

The submitted work is devoted to research of a charging condition formation in the film samples on base of Polyvinylidenfluoride (PVDF) subjected to electrical discharges effects.

The basic purpose of given research is study of basic laws and physical mechanisms of a charging condition formation in linear polymers and compound systems under the strong electrical fields and discharges effects.

2. Experiments and method

The PVDF samples were made under the most various technological conditions, namely: by hot pressing at various pressures, crystallized and subjected to extension at various temperatures, air-hardened and subjected to shrinkage, subjected to recrystallization, containing the some impurities in the structure and also oriented along the axis and being under the constant force.

At the preparing of the samples of compound material formed on a base of PVDF films there is porous adsorbent - KCM mark Silicagel (mainly consisting in silicon dioxide-SiO_2) as filler is used. Some researches on Polythene of high pressure and Nylon samples were carried out.

PVDF as a powder was served an initial material. The PVDF films of (150 – 180) μm thickness were made by hot pressing from melting state at temperature T = (170 – 250)°C under pressure P = (50 – 150) Atm; then samples were hardened at various temperatures. The size of initial powders was within the range of 63 μm.

At the preparing of compound material the filler – special apparatus comminuted Silicagel and in a powder state passed through a sieve for reception the size of 63 μm. The received powder was previously exposed to heating treatment at T = 200°C under the vacuum for 3 hours. Then the PVDF and Silicagel components in a powder state were mixed up in the vibrating mixer at a necessary volumetric proportion, which in our experiments was varied within range of (80 – 99)% PVDF and (20 – 1)% Silicagel.

Received homogeneous powder mixture of components was placed in special pressroom, heated up to temperature T = 170°C and pressed for the time of 3 – 5 minutes. Then the pressure was reduced; the

---

© Гурбанов К.Б., Электронная обработка материалов, 2003, № 4, С. 57–60.

sample was crystallized at various temperatures, which were below the PVDF melting temperature. The samples received by such way represented a films of (150 – 180) μm thickness and size of (50x50) mm^2.

At PVDF and (PVDF+Silicagel) films preparation the crystallization temperature was varied in a wide interval T = (25 – 100)°C.

Effect of mechanical pressure during the some researched materials preparing to their properties at varying of pressure value from 5 up to 150 Atm was carried out.

With purpose of study the charging condition of the film samples prepared under different technological conditions. They were subjected to effect of flame and corona types electrical discharges and thermal polarization in a direct electrical field. The charging condition in samples was revealed by the thermal stimulated relaxation (TSR) method widely used at researches of polymer dielectrics [5]. The TSR method is that a material at first is charged (by means of polarization, corona discharge etc.) and then discharged on the current reading device, simultaneously heating with constant speed of l °C/min. According to TSR current function of time the value of storage charge into material may be determined.

Charging of samples by the flame discharge was carried out at AC voltage U =19 кV, current I = 30 μA, distance between electrodes d = 4 cm. The typical TSR spectrums for a PVDF film treated by flame discharge is shown on Fig. 1, curve 1. The spectrum contains two peaks; the first of them is fixed at T = (95 – 100)°C, the second peak is observed at T = 130°C. Obtained charge density is: $\sigma_f = 8{,}0\cdot10^{-9}$ C/cm^2.

Charging of samples by the corona discharge at negative polarity of coroning electrodes was carried out at $U = 6$ kV, current I = 30 μA during 30 minutes. The typical TSR spectrum for a PVDF film treated by corona discharge of negative polarity is shown on Fig. 1, curve 2. Spectrum also contains two peaks the first of them is fixed at T = (95 – 100)°C, the second peak is observed at T = 135°C. Obtained charge density is: $\sigma_c = 1{,}2\cdot10^{-8}$ C/cm^2. Other kind of materials electrization used in work is polarization in a direct electrical field. The researched sample is displaced between electrodes of the heating device, which is used for TSR spectrum obtaining. There are polarization temperature Tp = 130°C, polarization voltage U_p = 2 kV, polarization time is 1 hour.

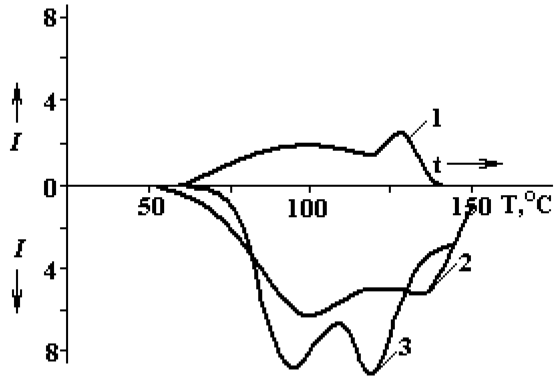

Fig.1. TSR spectra at PVDF films electrization: 1– flame discharge; $I\cdot10^{12}$ A; 2 – corona discharge of negative polarity; $I\cdot10^{12}$ A; 3 – polarization in a direct electric field; $I\cdot10^{11}$ A;

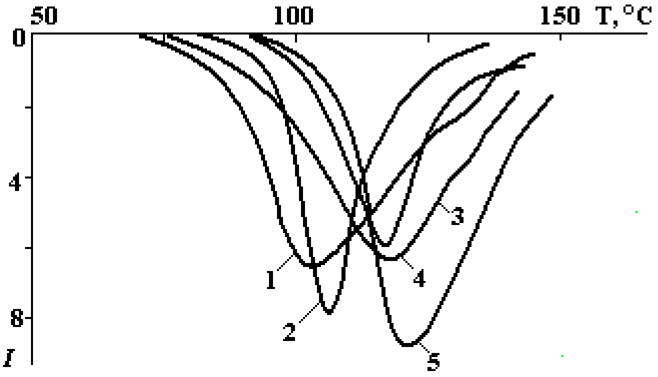

Fig.2. PVDF depolarization heat patterns set for various values of electrization temperature; 1 – 25°C; 2 – 50°C; 3 – 70 °C; 4 – 100°C; 5 – 130°C; $I\cdot10^{11}$A

After exposure for a time of 1 hour the heating of a sample stops and sample begins to cool down. At achievement of a sample temperature of room meanings the applied voltage is stopped and TSR spectrum is obtained. The appropriate spectrum is shown on Fig. 1, curve 3. The TSR spectrum also contains two peaks, first of which is observed at T = (95 – 100)°C, and the second at T = 125°C. Appropriate charge density is: $\sigma_p= 2{,}0\cdot10^{-7}$ C/cm^2

Comparison of obtained results shows that all TSR spectrums irrespective of a kind of electrical effect contain two peaks and the appropriate peaks are fixed approximately in the same temperature intervals. This fact unequivocally testifies on a determining role of chemical structure and structural peculiarities of researched materials in charge storage process.

3. Results

Analyze of results have shown that the value of total charge storaged in the researched materials treated by flame and corona discharges by an order of magnitude less than at polarization in a direct electrical field. In development of these researches we spent the series of experience on revealing the effect of polarization temperature to the charge introduction into material. The PVDF films were polarized in a direct electrical field at temperatures: (25, 50, 70, 100, 130)°C during the time of 1 hour. The appropriate TSR spectrums are shown on Fig. 2.

As it is visible from Fig. 2, in increasing of polarization temperature the TSR curves maximums are shifted to the higher temperature area, but thus the total charge values obtained from TSR spectrum are practically equal. The results obtained at higher electrization temperatures are apparently concerned with formation of more perfect and, hence, more stable structural units-grains.

Values of the stored charge density in PVDF and (80% PVDF + 20% Silicagel) samples made at various pressure and then subjected to effect of the negative polarity corona discharge are equal:

$\sigma_1 = 1{,}6\cdot10^{-8}$ C/cm^2 – at pressure of 5 Atm;
$\sigma_2 = 2{,}3\cdot10^{-8}$ C/cm^2 – at pressure of 50 Atm;
$\sigma_3 = 3{,}9\cdot10^{-8}$ C/cm^2 – at pressure of 100 Atm;
$\sigma_4 = 4{,}3\cdot10^{-8}$ C/cm^2 – at pressure of 150 Atm;
80% PVDF + 20% Silicagel
$\sigma_1 = 1{,}6\cdot10^{-7}$ C/cm^2 – at pressure of 5 Atm;
$\sigma_2 = 1{,}4\cdot10^{-7}$ C/cm^2 – at pressure of 50 Atm:
$\sigma_3 = 1{,}8\cdot10^{-7}$ C/cm^2 – at pressure of 100 Atm;
$\sigma_4 = 1{,}6\cdot10^{-7}$ C/cm^2 – at pressure of 150 Atm.

These results showed that presence of Silicagel as a filler appreciable increases the stored charge in polymer compounds. It is necessary to note that presence of fine-pored Silicagel in the PVDF samples structure gives the stabilizing effect on charge formation in materials, that causes the charge value to be unchanged in increasing of external pressure applied to the melted samples.

Research of charging condition formation in the samples at various molding and crystallization temperatures of initial materials was carried out. It is obtained that in increasing of initial materials molding and crystallization temperatures the maximums of peaks on TSR spectra are shifted to the higher temperatures area and the values of total saved charge essentially decreases. However in case of (PVDF+ Silicagel) composites these changes appear not so essential as in case of PVDF-samples.

According to the linear model of amorphous-crystal polymers it is necessary to consider that in samples subjected to electrical effect the electrical charges are trapped by both amorphous and crystal areas of a material. More less value of stored charge in the samples molded and crystallized at higher temperatures is concerned with increasing of a material crystalline degree, and, hence, with defects reduction and formation of the more perfect crystal structural units in a material. The trapping of electrical charges in such materials carried by centers located in the amorphous areas, which have insignificant sizes, is the reason of stored charge reduction.

The stability of stored charge values in PVDF+Silicagel composites at increasing of molding and crystallization temperatures is concerned, obviously, with insignificantness of structural changes in a material.

The shifting of a current maximum to the higher temperatures area on TSR spectrum is concerned with a charge releasing from deeper trap levels and with more perfect structure.

Researches of a charging condition of PVDF samples no oriented as well previously oriented and then subjected to the thermal shrinkage at a free state showed that stored charge in the samples of both types are practically equals in value. It is a consequence of returning of oriented films to the initial no oriented structure due to thermal shrinkage.

4. Conclusions

1. New physical representations about the mechanism of electrical charging of dielectric film materials subjected to strong electrical fields and discharges effects are advanced. It is revealed that value of charge stored in the polymer materials is in many respects determined by the over molecular structure of these materials.
2. The obtained correlation between the over molecular structures and properties of polymer dielectrics represents an opportunity to operate the charge formation process in materials.
3. The key role of amorphous areas in materials on the charging condition formation is determined.
4. As a result of spent researches the new compound material for the polymer dielectrics preparing is offered. Material includes the polymer PVDF and fine-pored Silicagel and has the high charge density and stability.

REFERENCES

1. *Анищенко Л.М., Кузнецов С.Б., Яковлев В.А.* Физика и химия обработки материалов. 1984. № 5. С. 85 – 89.
2. *Гейл Ф.Х.* Полимерные монокристаллы. М., 1968.
3. *Вайнштейн Б.К.* Дифракция рентгеновых лучей на цепных молекулах. М., 1963.
4. *Ильченко Н.С., Кириленко В.М.* Электрофизическая аппаратура и электрическая изоляция, М., 1970.
5. Электреты. / Под ред. Г.Сесслера. М., 1983.

Поступила 17.02.03

Summary

Wide using of polymer dielectrics in various branches of modem engineering stimulates the researches of changing these materials properties under the various conditions. Especially it concerned with materials subjected to various external effects. In submitted paper the results of research of charging condition formation in some polymer dielectrics and compound materials under the effect of strong electrical fields and various kinds of electrical discharges in air environment are presented. Correlation between the materials charging processes and their structure and technological preparing conditions are considered. New physical representations about the charging process mechanism in solid dielectric materials, subjected to effects of the strong electrical fields and discharges are extended. Formation the electrical charge of anomaly high density up to (10^{-7}-10^{-8}) C/cm^2 in researched materials and revealing it charge only at heating a material is found out. Opportunities of control the process of charge injection in a material are analyzed.

Э.Н. Ахмедов

ЭЛЕКТРОРАЗРЯДНАЯ МОДИФИКАЦИЯ ПОЛИЭТИЛЕНА

Институт физики Академии наук Азербайджана,
пр. Г. Джавида, 33, г. Баку, 370143, Азербайджан

Осуществлен процесс электроразрядного синтеза привитого сополимера линейного полиэтилена низкой плотности с нитрилом акриловой кислоты без применения каких-либо катализаторов. Полученный сополимер не содержит нежелательного побочного продукта реакции – гомополимера прививаемого мономера.

Одним из перспективных направлений модификации полимеров является метод прививки сополимеров, который позволяет получать продукты, сочетающие в себе свойства различных по своей природе полимерных материалов. Для достижения желаемого сочетания физико-механических, электрических и эксплуатационных свойств продукта важным является выбор прививаемого мономера. Значительный интерес представляют мономеры акрилового ряда, позволяющие существенно улучшать характеристики полимеров: механическую прочность, адгезию к металлам, стойкость к действию агрессивных сред и т.д. В процессе синтеза привитых сополимеров в присутствии специфических катализаторов практически всегда образуются определенные количества гомополимера прививаемого мономера, отрицательно влияющего на все характеристики привитого полимера [1]. Процесс удаления из состава гомополимера значительно усложняет и удорожает технологию процесса. Это обстоятельство создает серьезное препятствие расширению производства привитых сополимеров и областей их использования.

Поэтому поиск методов получения привитых сополимеров, не содержащих гомополимера прививаемого мономера, а также исключения или ограничения применения катализаторов в процессе реакции, является актуальной научной и практической задачей.

© Ахмедов Э.Н., Электронная обработка материалов, 2003, № 4, С. 60–63.