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1. REPORT NUMBER # 17	NT'S CATALOG NUMBER
4. TITLE (and Subtitle) Effect of Water Content on the Piezoelectric Properties of Nylon 11 and Nylon 7	OF REPORT & PERIOD COVERED Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) B.A. Newman, K.G. Kim and J.I. Scheinbeim	8. CONTRACT OR GRANT NUMBER(s) N00014-88-K-0122
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rutgers, The State University of New Jersey College of Engineering, P.O. Box 909 Piscataway, NJ 08855-0909	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. Joanne Milliken Office of Naval Research Arlington, VA 22217	12. REPORT DATE May 1991
	13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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91-01965

18. SUPPLEMENTARY NOTES

Published, J. Mat. Sci.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Studies of the piezoelectric properties of odd numbered nylons such as Nylon 11 and Nylon 7 are important, not only in their own right, but because they provide a way to examine the generality of concepts put forward to explain the piezoelectric and pyroelectric properties of poly(vinylidene fluoride) films. Over the past several years, a series of studies of Nylon 11 and Nylon 7 have been carried out. In a recent study appropriate sample preparation and poling techniques were described, which gave rise to mechanically unoriented but polarized films of Nylon 11 with values of the piezoelectric strain coefficient, d_{31}, as high as 7.1 pc/N.

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-88-K-0122

Technical Report No. 17

EFFECT OF WATER CONTENT ON THE PIEZOELECTRIC PROPERTIES OF NYLON 11 AND NYLON 7

by

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Prepared for Publication in

J. Mat. Sci.

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May 1991

Introduction

Studies of the piezoelectric properties of odd numbered nylons such as nylon 11 and nylon 7 are important, not only in their own right, but because they provide a way to examine the generality of concepts put forward to explain the piezoelectric and pyroelectric properties of poly(vinylidene fluoride) films. Over the past several years, a series of studies (1-6) of nylon 11 and nylon 7 have been carried out. In a recent study (4) appropriate sample preparation and poling techniques were described, which gave rise to mechanically unoriented but polarized films of nylon 11 with values of the piezoelectric strain coefficient, d_{31}, as high as 7.1 pc/N.

It is now understood that bulk polarization in poly(vinylidene fluoride) results from oriented dipoles in the crystalline regions, which may be caused by a ferroelectric switching process, phase transformations occurring during the poling process, or as a result of biased crystallization under high electric fields. The results of some of the studies on nylon 11 and nylon 7 are not easily understood using these concepts.

The possible crystal structures of nylon 11 and nylon 7 are not well determined at the present time, owing to the paucity of x-ray reflections from these materials. The crystal structure proposed by Kinoshita (7) Slichter and others (α-form) (8), on the basis of x-ray studies carried out on oriented fibers, or solvent cast films, is non-centrosymmetric and highly polar. However, a recent study (3) has shown that the x-ray diffraction patterns obtained from melt-crystallized pressed films, (although very similar to that expected from the α-form), cannot be completely explained on the basis of the α-form structure. The structure of these films will be referred to as α'-form and will be the subject of a subsequent publication. From observations of x-ray diffraction patterns from solvent cast films (using trichloroacetic acid), Sasaki (9) reported a γ-phase. At elevated temperatures the melt-crystallized films (3) show a transition to a pseudohexagonal structure (δ -form). X-ray diffraction patterns from melt-pressed and quenched films are similar to patterns from the δ-form, but show considerable disorder.

Melt pressed films of nylon 11, well crystallized into the α'-form, do not show appreciable bulk polarization following poling. However, values of the piezoelectric strain constant, d_{31}, of poled quenched films of nylon 11 can be as high as 3.0 - 4.0 pc/N, depending on poling conditions (7). Films (10) obtained by quenching and subsequent annealing at 120°C, show that some crystallization into the α'-form occurs on annealing which yields lower values of d_{31} after poling.

On the other hand, studies of the temperature dependence of d_{31} have shown a large increase in d_{31} above the glass transition temperature. This behavior is also observed for poly(vinylidene fluoride), also a semicrystalline polymer, whereas for the case of an amorphous polymer such as poly(vinyl chloride), the opposite behavior is usually observed; the bulk polarization and d_{31} decrease rapidly to zero above the glass transition temperature.

While studying nylon 11 (and also nylon 7), small apparently inconsistent increases and decreases in the value of d_{31} were observed from day to day. Upon more careful examination, these changes were traced to daily changes in relative humidity which led to different degrees of water absorption. It is well known that water absorption in nylons can have major effects on mechanical and electrical properties. For this reason, it was decided to investigate the effect of water absorption on the piezoelectric response of nylon 11 and nylon 7 films.

Experimental

The nylon 11 polymer was obtained from Rilsan Corporation (Glen Rock, NJ). It was synthesized by a polycondensation reaction of 11-aminoundecanoic acid and contained no additives. The polymer was used without further treatment.

The nylon 7 polymer used in this experiment was synthesized by the method of C.F. Horn et. al. (11). Ethyl-7-aminoheptanoate, a monomer for nylon 7, was first synthesized and then a two step polycondensation process was used. First, the low molecular weight precursor was prepared and then the final high molecular weight polyamide was synthesized by condensation polymerization. A semicrystalline white solid was obtained which was pulverized into a fine powder using a Spex Freezer Mill. Water and acetone extractions of the fine powder yielded ~1.5% extractable material which appeared to be of an oligomeric nature.

A hydraulic press was used to prepare thin films. Well crystallized films were prepared by melting nylon 7 or nylon 11 and pressing between aluminum foil in the hot press. The samples were allowed to cool slowly overnight. In order to produce quenched films, melt-pressed polymer-aluminum foil layers were plunged quickly into an ice-water bath. The aluminum foil was subsequently removed by dissolution using a 20% NaOH solution. The films were then washed and dried in a dessicator for a prolonged period.

Reflection and transmission scans of the nylon 7 and nylon 11 films were obtained using a Phillips wide angle diffractometer and CuK_α radiation. Flat film forward reflection photographs were also taken. Both nylon 11 and nylon 7 films which were slowly cooled, crystallized into the α'-form, characterized chiefly by two strong reflections with d-spacings at 4.44 Å and 3.73 Å.

A thin layer of aluminum was evaporated on both sides of the films to serve as electrodes for poling and electrical measurements. All films were poled under high vacuum ($\sim 10^{-6}$ Torr) at 75^{o}C for 30 minutes, with a poling field of 500×10^{3} V/cm. The films were cooled to room temperature under field.

The films were soaked in distilled de-ionized water for 13 hours at room temperature (23^{o} C), and then inserted in the specimen chamber of the Toyo Seiki Piezotron®. High purity (dry) nitrogen gas was allowed to flow through the specimen chambers so that the films slowly dried out. The piezoelectric strain and stress constants, d_{31} and e_{31}, the elastic modulus, c, and the dielectric constant, ε, were measured at 3Hz as the film dried out over a period of 12 hours.

The dielectric constant provided a measure of water content. However, to put this measure on an absolute basis, a separate experiment was carried out. The film weight was measured as the film dried out in the presence of a flow of high purity nitrogen gas in a precision balance. Simultaneously, the dielectric constant was measured. Finally, the weight of a dry sample was found by drying the film for five days at 100^{o}C in a vacuum oven. This experiment enabled the water content (as a weight percentage) to be determined directly from measurements of the dielectric constant.

Results and Discussion

Figures 1 and 2 show the variation of piezoelectric strain constant, d_{31}, and piezoelectric stress constant, e_{31}, with time as the films dried out. For all four types of film; nylon 11, slow crystallized (α'-form) and quenched, and nylon 7, slow crystallized (α'-form) and quenched, the magnitude of both d_{31} and e_{31} decreased with time as the films dried, the greatest decrease occurring during the first 100 minutes. Figures 3 and 4 show the variation of elastic modulus, C, and dielectric constant, ε, with time, as the films dried. As expected, for all four types of film, the modulus increased and the dielectric constant decreased with time.

Figures 5 and 6 show the variation of piezoelectric strain constant, d_{31}, and piezoelectric stress constant, e_{31}, directly with the water content. Both d_{31} and e_{31} decrease with decreasing water content. The water content of the nylon 7 melt-quenched films was higher (~4.7%) than for any of the other films (3.5 - 3.8%). Under the drying conditions used, the nylon 11 α'-form films dried out more than any of the other films. It was anticipated that with identical melting and drying conditions, the water content would depend on the amide-group density and the crystallization conditions, and this was observed. The films were not dried out by raising the temperature, since this is also known to change the piezoelectric response (10).

For the same degree of water content (over the range of water content measured) the highest value for d_{31} was given by the quenched nylon 11 films, while the lowest value was found for the well-crystallized (α'-form) nylon 11 films. The difference was more than an order of magnitude. Intermediate values were measured for the nylon 7 films: in this case, the d_{31} values for the well-crystallized α'-form films being higher than for the quenched films. The magnitude of the variation in d_{31} and e_{31} with water content was much greater for the nylon 7 films than for the nylon 11 films. A similar variation of e_{31} with water content was observed for all four films.

Figures 7 and 8 show the variation in elastic modulus and dielectric constant with water content for all four types of film. As anticipated, the elastic modulus decreased with decreasing water content and was higher for the nylon 7 films. The dielectric constant increased with increasing water content and in general was higher (at a given water content) for the nylon 7 films. The variation in both elastic modulus and dielectric constant was greater for the nylon 7 films.

In the discussion of these results, it should first be noted that the behavior of the poled nylon 7 films does not parallel the behavior of the poled nylon 11 films. In understanding the piezoelectric response (d_{31} and e_{31}) of poled polymer films, the elastic properties and dielectric constant are important as well as the bulk polarization achieved in the poling process.

The mechanical and dielectric properties of nylon films are dominated by two principal relaxations. The α-relaxation (usually taken as the glass transition) occurs in the range 55 - 65°C for nylon 11 and 45 - 55°C for nylon 7. The γ-relaxation occurs in the range -110 to -100°C for nylon 11 and -120 to -110°C for nylon 7. The α-relaxation appears to involve segmental motion in the amorphous regions, although some reports suggest that motion of segments in rotationally disordered crystalline regions contribute. The α-relaxation appears to be due principally to cooperative motions of CH_2-units between amide groups. A third smaller relaxation in the range -50°C to -10°C appears to be associated with the presence of water. The relaxation transition temperatures are affected by the presence of water, the effect being greatest for the relaxation. To some extent, the water acts as a plasticizer and with a high enough water content, the α-relaxation can be shifted below ambient temperature.

If we assume that the only effect of absorbed water is to shift the α-transition temperature, then the variation of modulus and dielectric constant with water content should be similar to the variation of these properties with temperature. The modulus should decrease substantially and the dielectric constant increase substantially at a certain critical water content (the glass-transition water content). This transitional behavior is shown completely only for the α'-form nylon 11 films in Figure 7 and Figure 8. Apparently, the range of water content obtained in this experiment for the nylon 7 films (2.2% to 3.8% for the slow crystallized films and 3% to 4.5% for the quenched films) was insufficient to show the complete transitional behavior. For the films with the highest water content, the modulus is still decreasing sharply and the dielectric constant still increasing sharply, with increasing water content. For the nylon 7 films, the "glass transition water content" appears to be much higher than for the nylon 11 films. Below the glass transition, the higher modulus of the nylon 7 films can be attributed to the higher hydrogen bond density. Above the glass transition, the higher dielectric constant for the nylon 7 films can also be anticipated in view of the higher dipole density and higher water content. The elastic modulus of α'-form nylon 7 and quenched nylon 7 appears to be essentially the same at the same level of water-content where this comparison can be made, and, as expected, the elastic modulus decreases with increasing water content. For the same level of water content, the α'-form films show a significantly higher dielectric constant. In fact, the data of Figure 8 would suggest that a higher water content is required to decrease the Tg to ambient temperature for the case of the quenched nylon 7 films than for the α'-form films. However, these results should be interpreted with caution, since the details of the interaction between water content and polymer structure, and the effect on dielectric constant are not clear at this point.

The variation in piezoelectric strain constant, d_{31}, and the piezoelectric stress constant, e_{31}, with water constant (Figures 5 and 6) can be interpreted as the same kind of transitional behavior as the modulus and dielectric constant. Clearly, d_{31} will be strongly dependent on the elastic modulus. The transitional behavior of modulus, dielectric constant, and Poisson's ratio, with water content should be reflected by a transitional behavior in d_{31} and e_{31} and this is observed.

A comparison of the piezoelectric response of quenched and slowly crystallized nylon 7 films does not show the same order of magnitude difference in behavior as that observed for nylon 7. A detailed study of both nylon 7 and nylon 11 is being carried out to further elucidate these questions.

Conclusions

This study has demonstrated for the first time that the piezoelectric response of a polymer can be sensitive to water content. Investigations of the effects of water content on the piezoelectric, dielectric, and dynamic mechanical response of nylon 7 and nylon 11 have shown that:

1. The piezoelectric response of poled films is sensitive to water content.
2. The sensitivity is significantly higher for nylon 7 than nylon 11 because of the higher density of amide groups in nylon 7.
3. Water has a plasticizing effect on the relaxational behavior of these nylons, shifting relaxations to lower temperatures with increasing water content. This shift in relaxation temperature results in a decreasing modulus and increasing dielectric constant.
4. The changes in dielectric and mechanical behavior caused by the shift in transition temperature gives rise to an increased piezoelectric response with increasing water content.

Acknowledgement

This work was supported by the Office of Naval Research and the Center for Advanced Food Technology of Rutgers University.

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Figure Captions

Fig. 1 d_{31} vs. drying time for nylon 11 and nylon 7 samples.

Fig. 2 e_{31} vs. drying time for nylon 11 and nylon 7 samples.

Fig. 3 Modulus vs. drying time for nylon 11 and nylon 7 samples.

Fig. 4 Dielectric constant vs. drying time for nylon 11 and nylon 7 samples.

Fig. 5 Effects of water content on the piezoelectric strain constants of nylon 11 and nylon 7 samples.

Fig. 6 Effects of water content on the piezoelectric stress constants of nylon 11 and nylon 7 samples.

Fig. 7 Effects of water content on the moduli of nylon 11 and nylon 7 samples.

Fig. 8 Effects of water content on the dielectric constant of nylon 11 and nylon 7 samples.

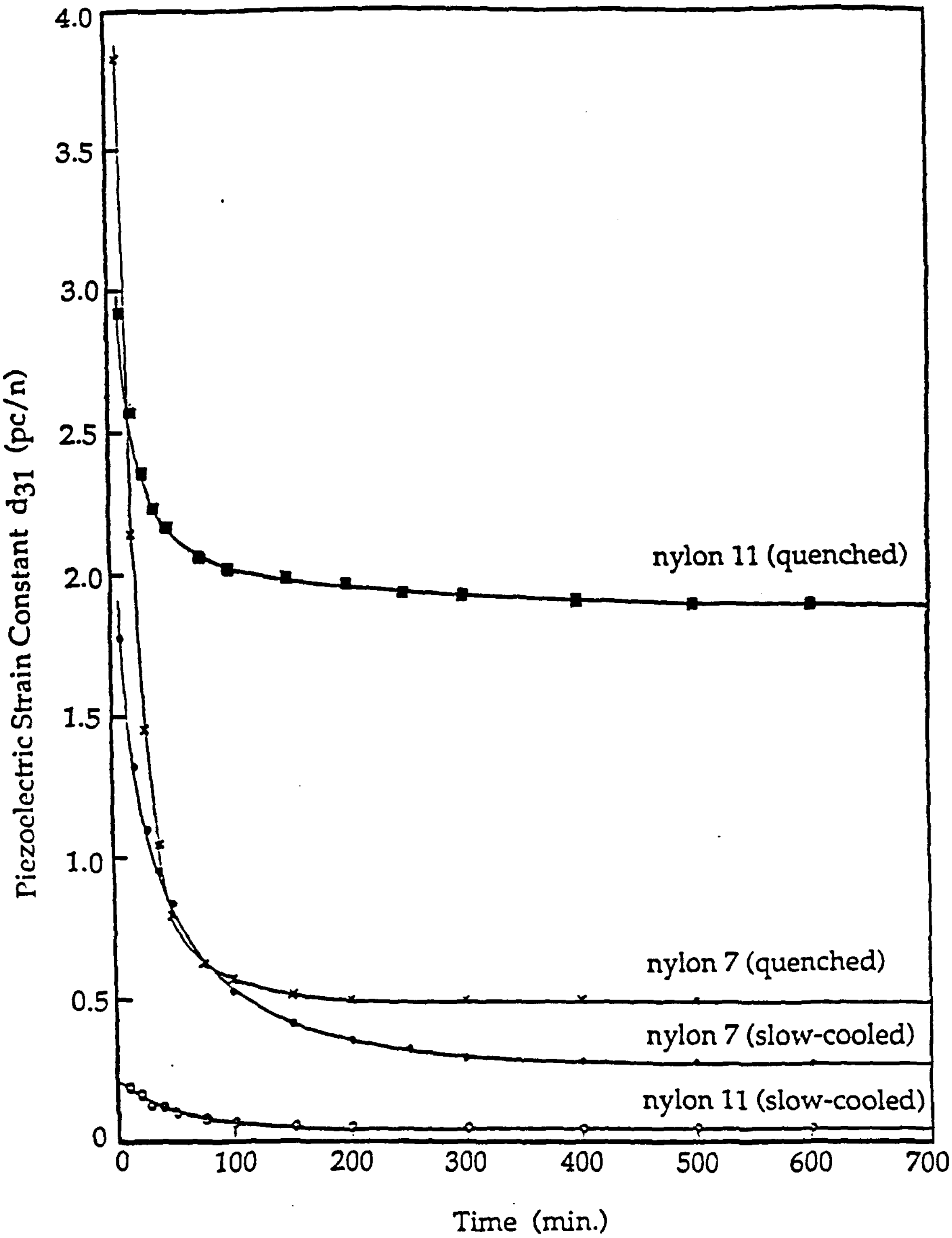

Fig.1. d_{31} vs. drying time for nylon 11 and nylon 7 samples.

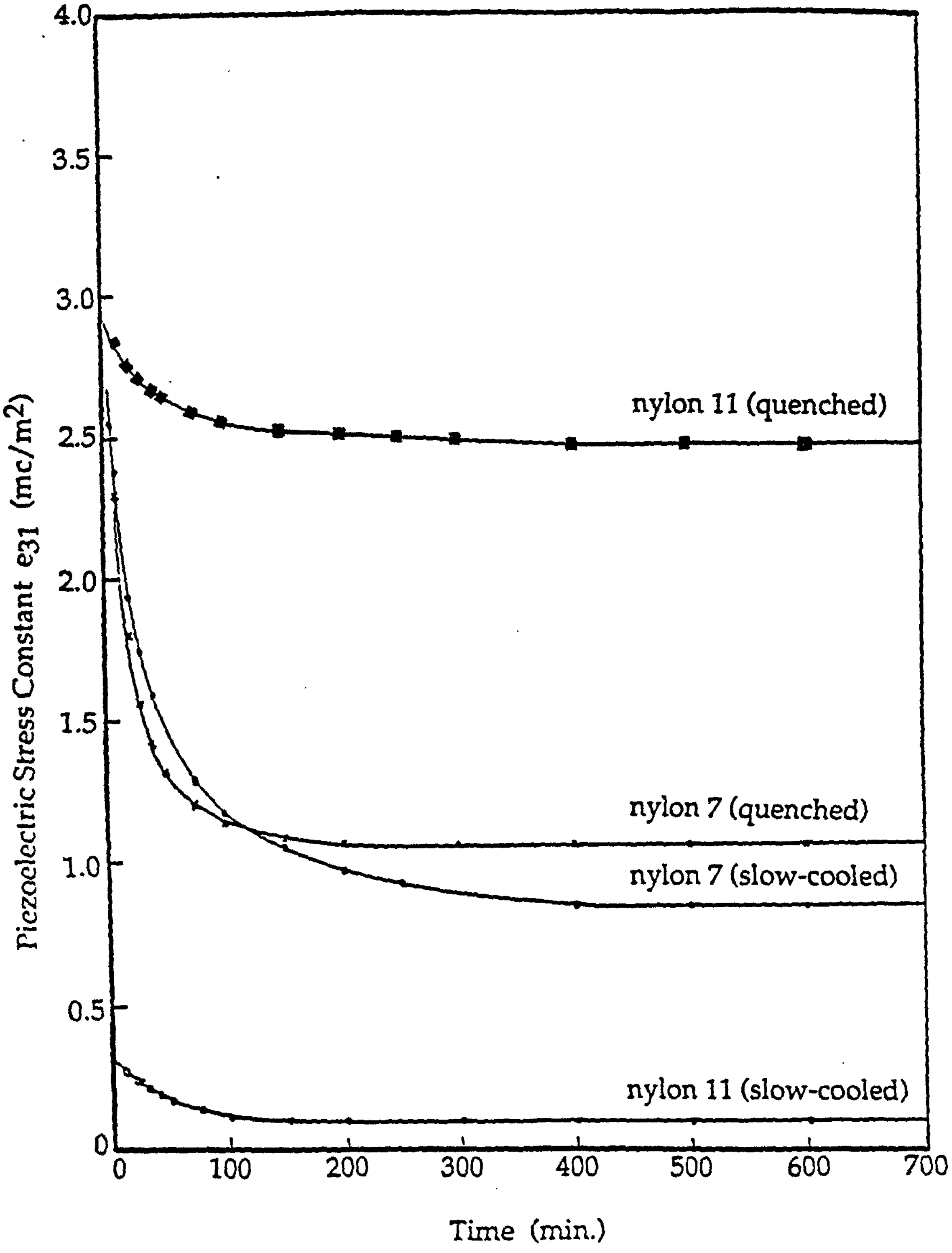

Fig.2. e_{31} vs. drying time for nylon 11 and nylon 7 samples.

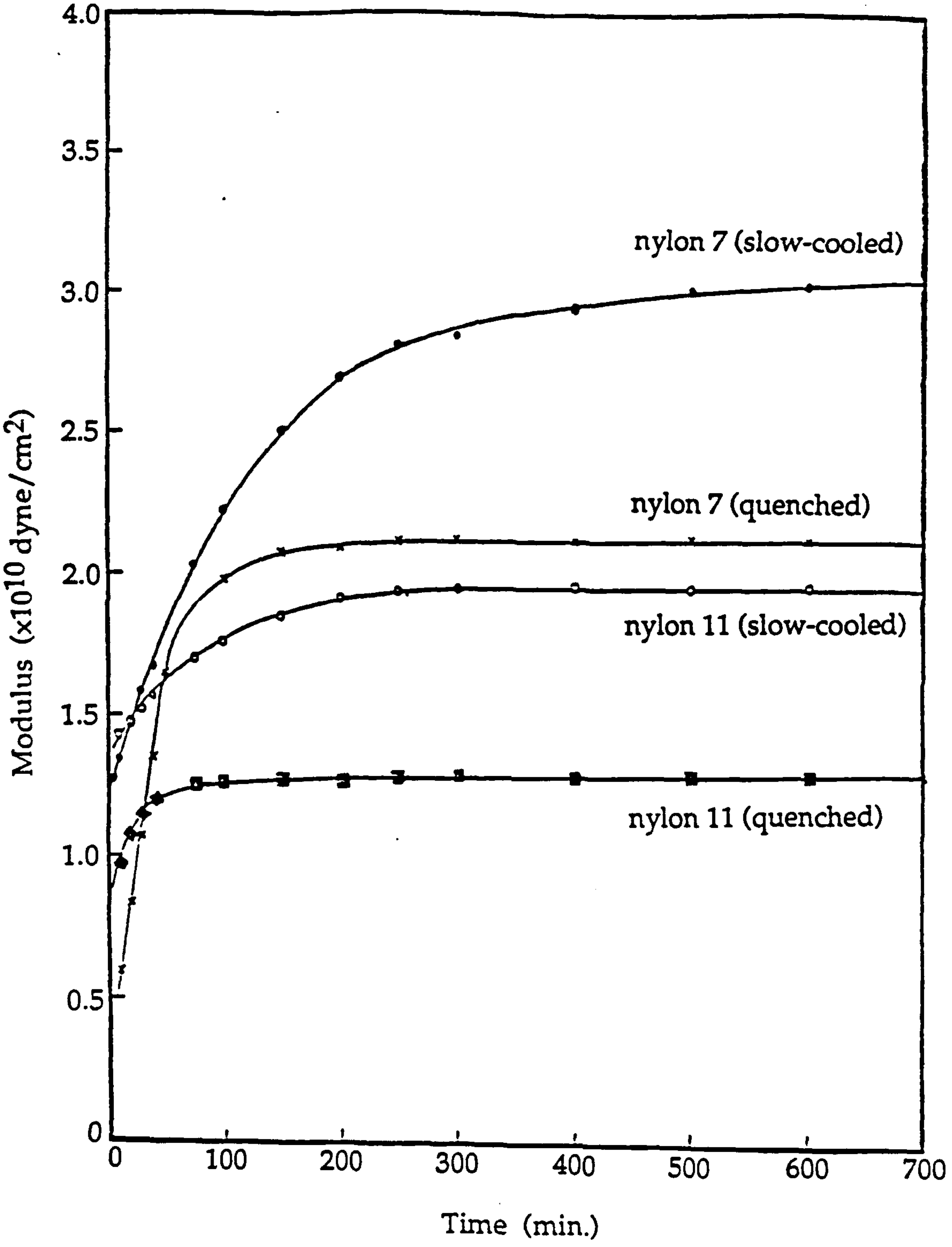

Fig.3. Modulus vs. drying time for nylon 11 and nylon 7 samples.

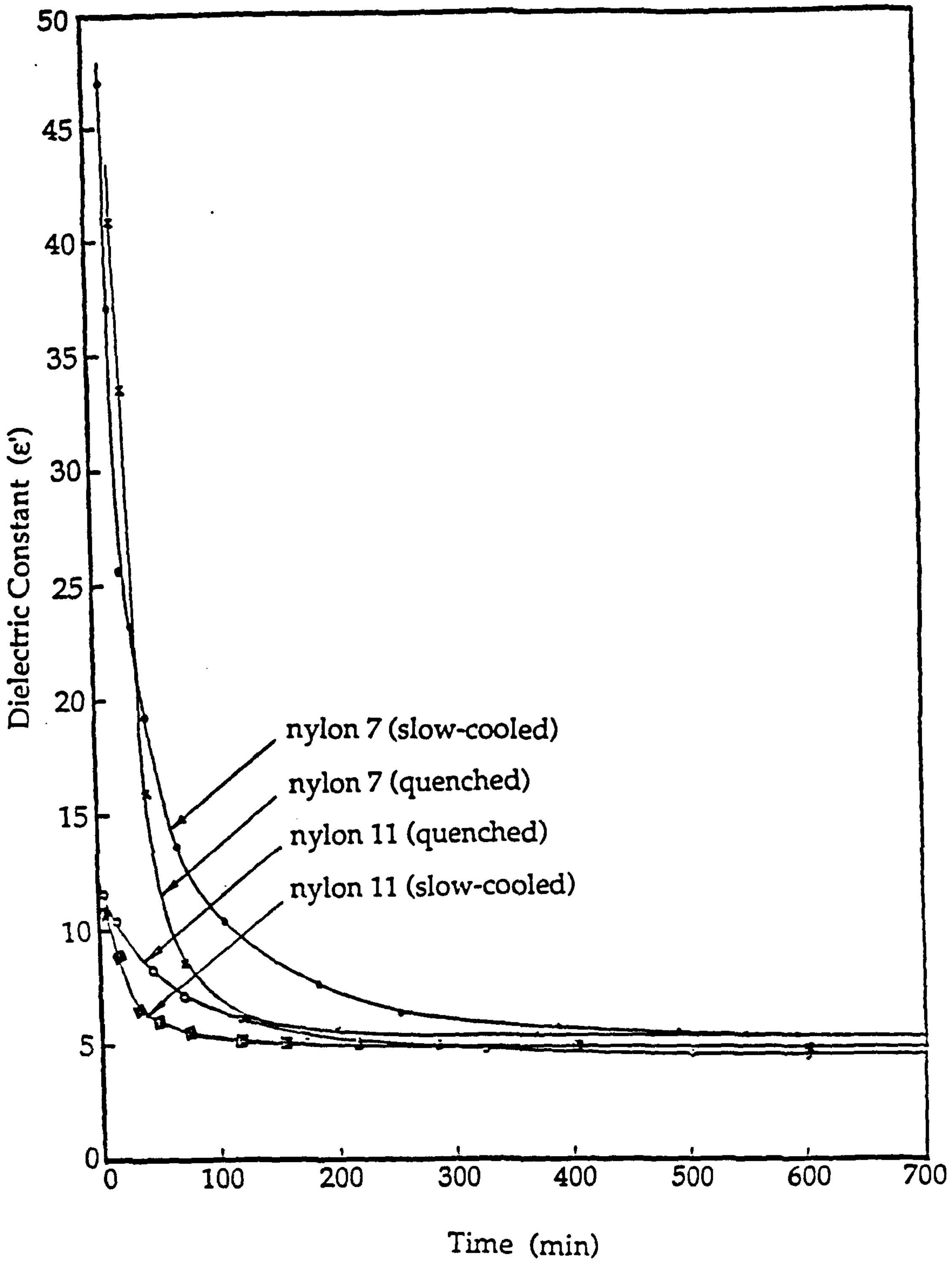

Fig.4. Dielectric constant vs. drying time for nylon 11 and nylon 7 samples.

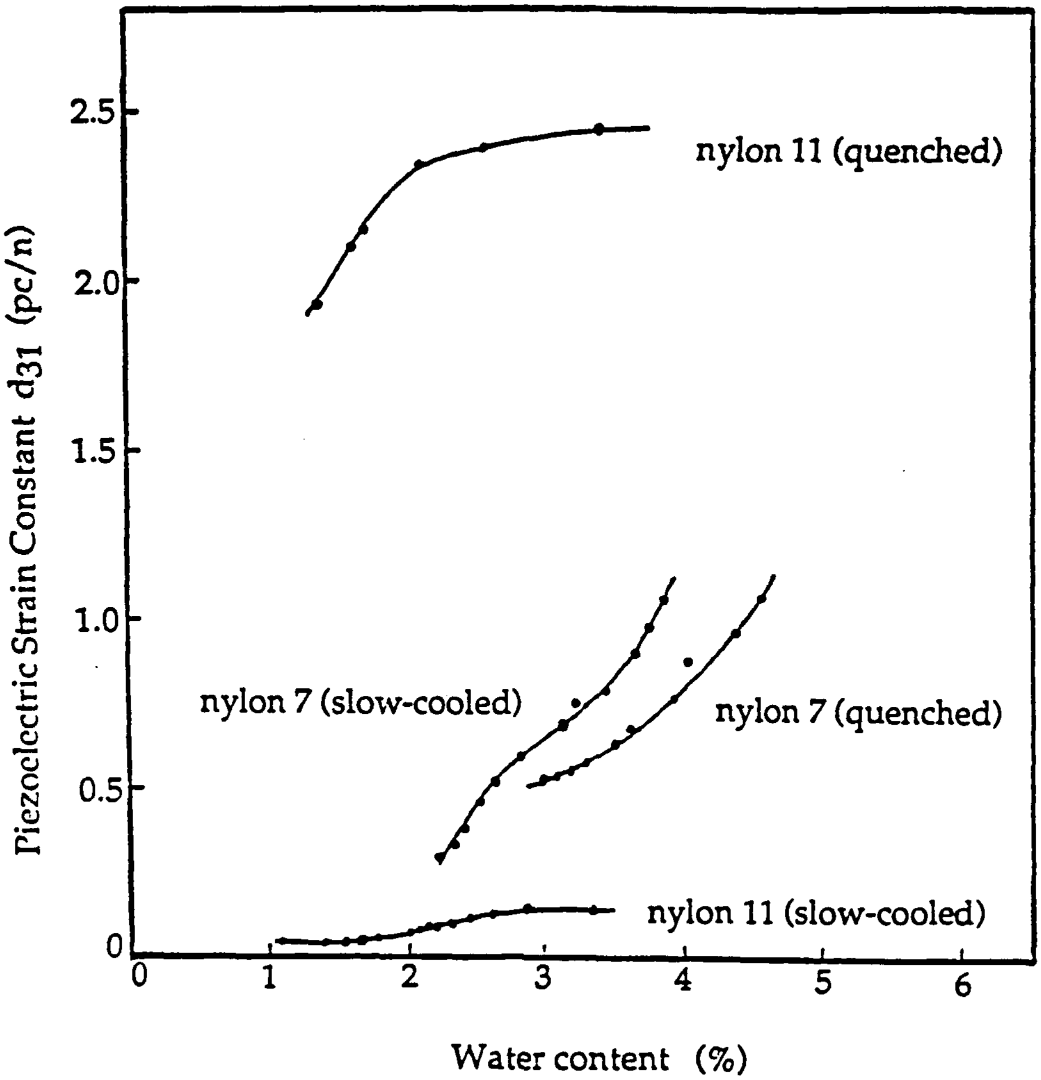

Fig.5. Effects of water content on the piezoelectric strain constants of nylon 11 and nylon 7 samples.

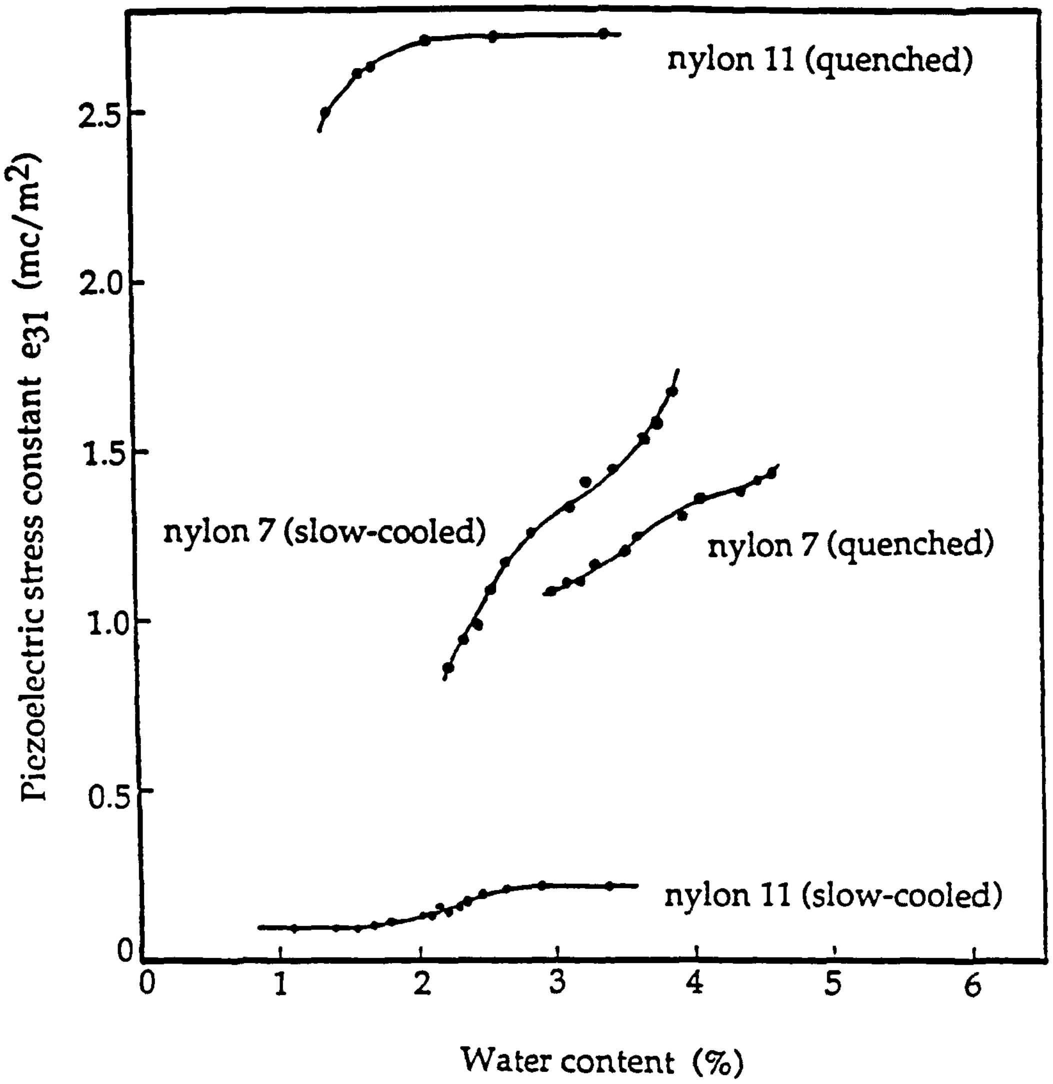

Fig.6. Effects of water content on the piezoelectric stress constants of nylon 11 and nylon 7 samples.

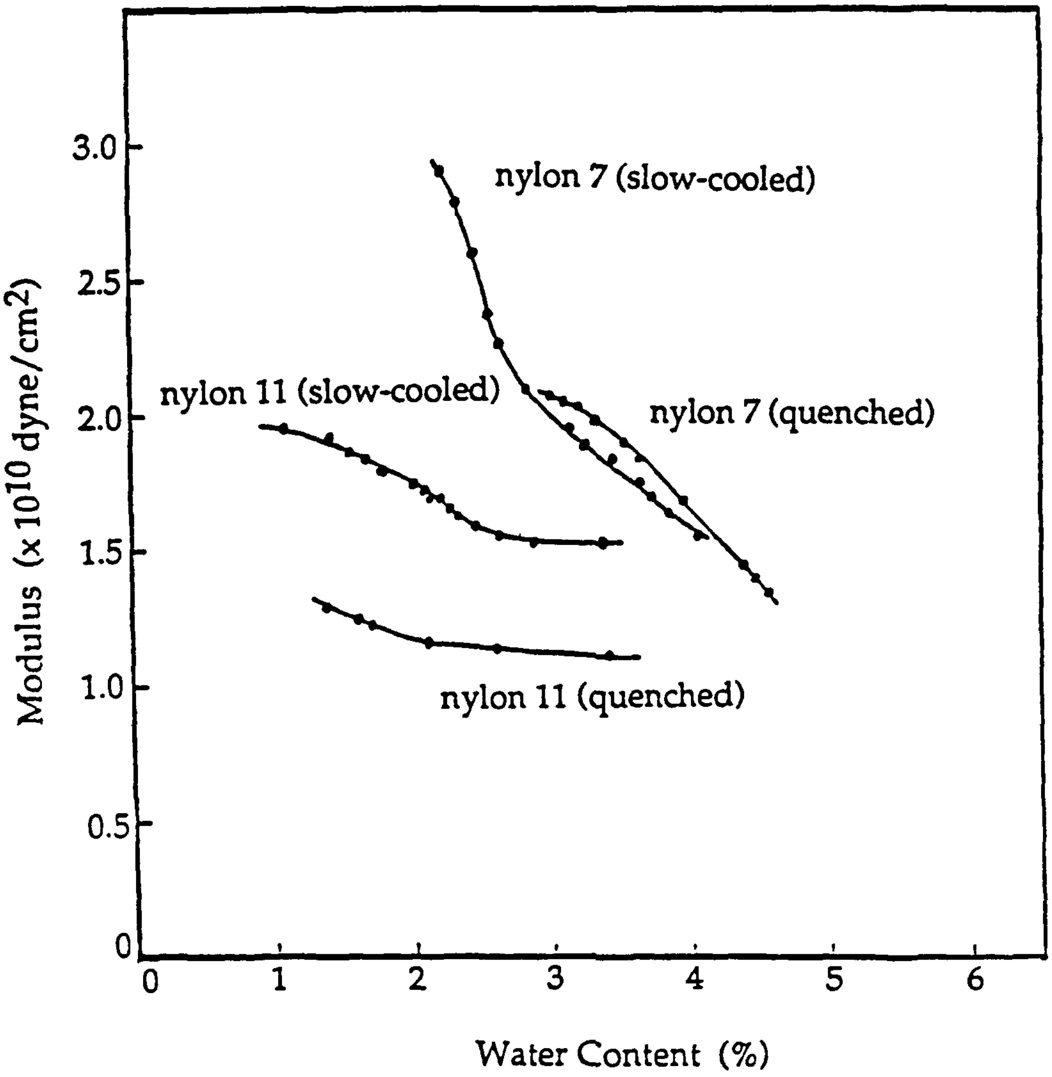

Fig.7. Effects of Water Content on the moduli of nylon 11 and nylon 7 samples.

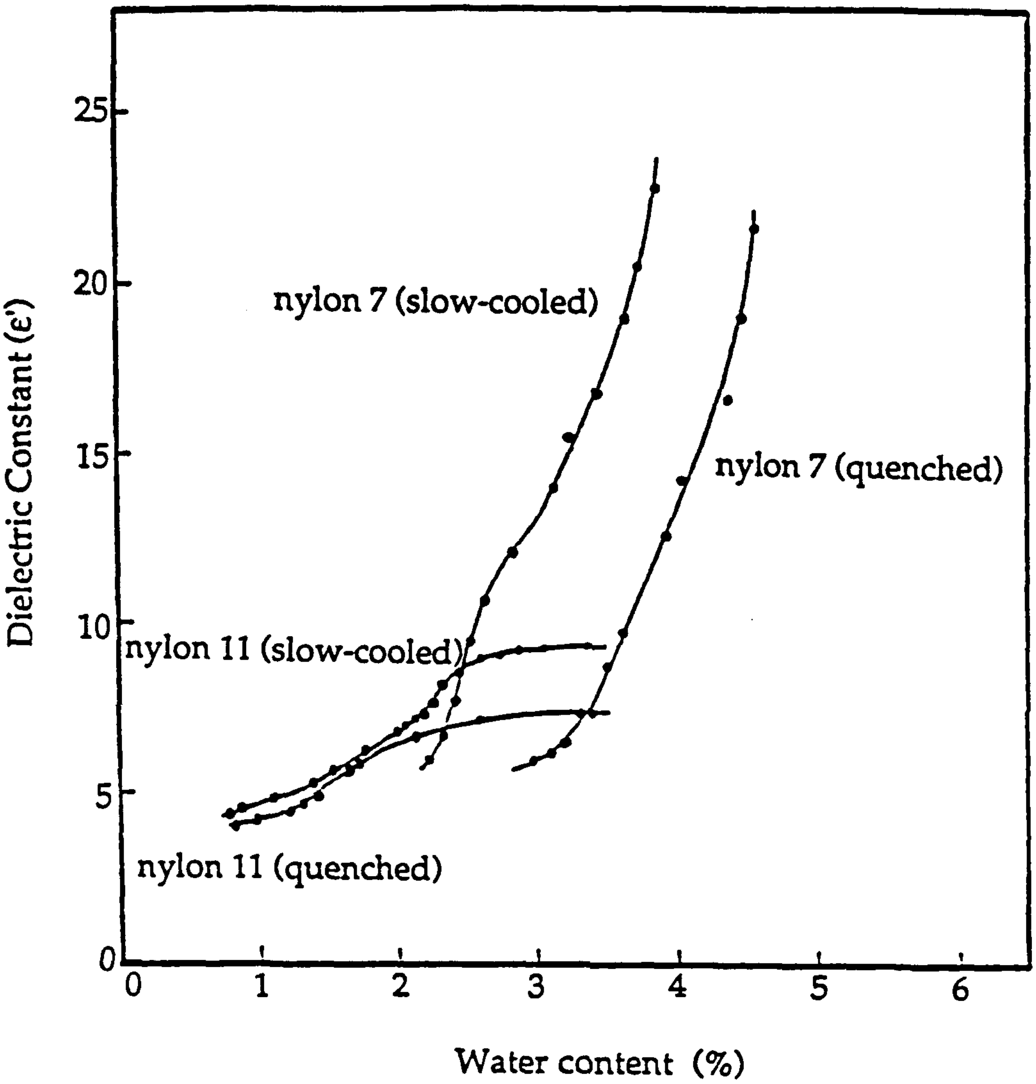

Fig.8. Effects of water content on the dielectric constant of nylon 11 and nylon 7 samples.