

Poly(vinylidene fluoride) / Poly(methyl methacrylate) Blend의 유전특성

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(1987년 10월 13일 접수)

Dielectric Properties of Poly(vinylidene fluoride) Poly(methyl methacrylate) Blends

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(Received October 13, 1987)

요 약 : 본 실험에서는 PVDF / PMMA blend의 유전성질을, 온도범위는 20~190℃의 온도 범위, 500 Hz~1 MHz의 주파수 범위에서 측정하였다. PVDF가 많이 포함되어 있는 영역에서는, 주파수가 감소할 수록 유전손실곡선이 점점 증가하고, 반대로 PVDF가 적게 포함되어 있는 영역에서는, 주파수가 감소할 수록 유전손실곡선이 감소하였다. 여기에서 PVDF50 / PMMA50의 조성에서는 α 이완과 β 이완의 2가지 영향이 같이 작용함을 관찰하였으며, 각 조성전이온도에서 ΔH_a 를 Arrhenius 수식을 이용하여 조사하였다. 결정성영역과 비정형 영역에 밀접한 관계가 있는 전이 영역은 전이 시간분포와 Cole-Cole 수식에 맞추어 조사하였으며, 동시에 유리 전이 온도는 PVDF가 많이 섞일 수록 점점 떨어지는 것을 관찰하였다. 이러한 결과에서 부터 PVDF / PMMA blend가 순수한 PMMA에서 PVDF50 / PMMA50의 영역 사이에서 미세영역균질성(mico-scale homogenities) 임을 알았다.

Abstract : Dielectric measurements were carried out for PVDF / PMMA blends over the frequency ranges of 500Hz~1MHz at temperatures between 20℃ and 190℃. In the PVDF rich portion P F, the magnitude of the dielectric loss curves was observed to be increasing regularly as the frequency decreased, but in the PVDF low portion it decreased as the frequency decreased. The relaxation peak of a mixture containing PVDF 50 / PMMA 50 suggested both the α relaxation and the β relaxation. The ΔH_a for the blends at transition temperature was observed according to the Arrhenius equation. The transition regions associated with a crystalline phase and an amorphous phase were found to fit the skewed arc function with a distribution of relaxation times. The depression of the glass transition temperature in order of increasing PVDF concentration was observed. These results lead to the conclusion that PVDF / PMMA blends exhibit micro-scale homogenities over the range of pure PMMA to PVDF 50 / PMMA 50.

INTRODUCTION

During the past few years there have been a large number of publications on the temperature dependence of dielectric properties of polymers.^{1~8} Dielectric relaxation processes have been interpreted in terms of motional modes of polar groups in long chain molecules.

PVDF (poly(vinylidene - fluoride)) is chosen because it is a partially crystalline polymer, and because it is known to be miscible with PMMA (poly(methyl-methacrylate)) in wide range. PMMA is chosen because it is an amorphous polymer, but it is known to be miscible with PVDF in wide range.^{9~15}

The earlier study did not give an information on any microscale phase separation between the components of the blends. Dielectric relaxation measurements are more sensitive to the presence of any micro-scale phase separation: They can also give additional information about the interactions of PVDF-PMMA blends and their relaxation processes.

The details of the dielectric relaxation of PVDF-PMMA blends are studied here and the normalized curves of the real and imaginary components of the dielectric constant are drawn. The parameters describing the dispersion curves of the blends will be discussed.

EXPERIMENTAL PROCEDURE

The PVDF(Kynar 460) used in this work was obtained in pellet form the Pennwalt Corporation. The PMMA is a commercial product of Plexiglass designated as ZK 20 in pellet form.

Five blends containing 0, 25, 50, 75, 100%, respectively by wt% of PVDF were prepared. In forming films, the mixture of the two polymers were prepared from solution of DMF by casting onto a glass plate and dried in an oven at 80°C for a day. It was followed by subsequent heating at 200°C for 30 min. to reduce the defects of the polymer surface. The thickness of films obtained was 0.05~0.09 mm. In order to eliminate any pos-

sibility of an air gap between the sample and electrode, aluminum electrode 1 cm in diameter were deposited directly on both sides of the film. The deposited electrodes should be sufficiently thick to conduct electricity. To attach the copper wire to the deposited electrode, silver paste was used before drying the sample in an oven. Dielectric measurement was carried out in the frequency ranges from 500 Hz to 1 MHz and in the temperature ranges from 20°C to 190°C.

Measurement of the dielectric constant and loss was made using the model 4192A Low Frequency Impedance Analyzer manufactured by Hewlett Packard Co. Ltd.. The results obtained at 1MHz were corrected taking into consideration the inductance of the sample cell and copper wire.

The melting temperature and glass transition temperature were measured with a Dupont 1090 Thermal Analyzer.

RESULTS AND DISCUSSION

The temperature dependence of dielectric loss and the dielectric constant of PVDF are shown respectively in Fig. 1 and Fig. 2. A well-defined maximum is not observed in Fig. 1 because of the ionic conductance. The dielectric loss of pure PVDF at a given frequency increased rapidly beyond the relaxation peak. (The α relaxation began at 80~90°C(500Hz) as indicated by workers.)

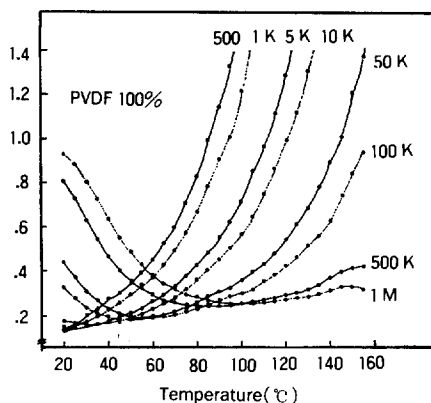


Fig. 1. Temperature dependence of the dielectric loss of PVDF at various frequencies.

Some factors such as the method of sampling and the selection of samples can be crucial.⁸

In Fig. 2, the dielectric constant from 500Hz to 5KHz increased with increasing temperature because of the ionic effects. However, the dielectric

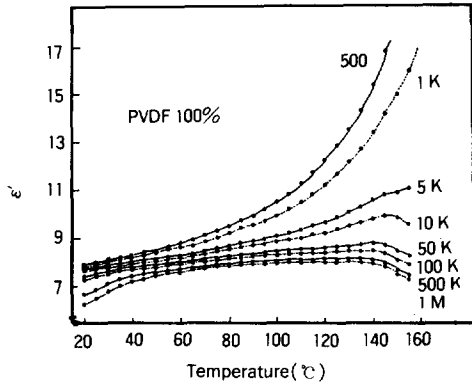


Fig. 2. Temperature dependence of the dielectric constant of PVDF at various frequencies.

constant for the higher frequencies went through a maximum and then decreased with increasing temperature. In this case, Uchidoi's⁸ results were interpreted as evidence for a phase change to a less ordered structure, while Furukawa and co-workers supported the view that the dielectric constant decreased because of a ferroelectric to paraelectric phase transition.

Unfortunately, we could not find out any relaxation in Fig. 2 because of the ionic effects and the temperature range, so that we quote S. Yano's results³ to explain our results discussed later.

In Fig. 3 reported by S. Yano,³ three relaxations, α , β , and γ , were observed near 80, -20, -80°C at 1KHz, respectively. The α relaxation is related to the molecular motions in crystalline regions, and the relaxation mechanism is explained as a property of the interior of the crystal and as a surface effect. In the folded-chain crystal, two

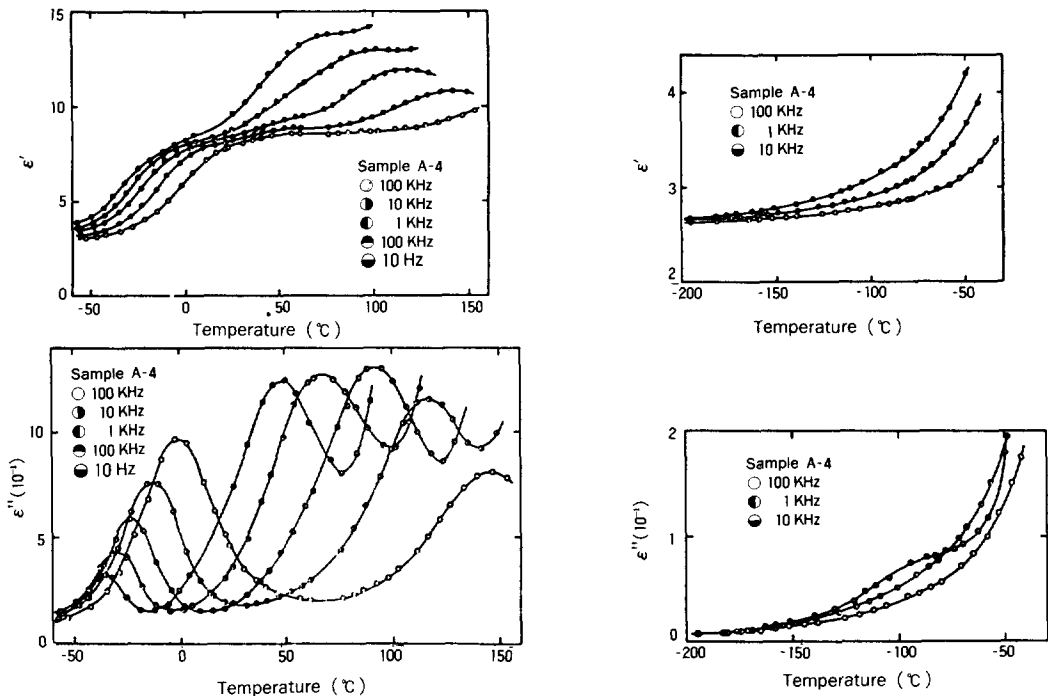


Fig. 3. Temperature dependence of the dielectric constant and the dielectric loss of PVDF at various frequencies (Reproduced from S. Yano, *J. Polym. Sci. Part A-2*, 8, 1057(1970)).

basic motion of chain formed loops at the crystalline surface. The chain rotation and twisting with a small lengthwise translation in the interior of the crystal was another explanation for the α relaxation. The β relaxation has been³⁻⁷ considered to be related to micro-Brownian motion of amorphous chain segments based on the following dielectric behavior, the magnitude of dielectric relaxation increased with decreasing the degree of crystallinity in homopolymer, regardless of the crystalline structure. T_{\max} related to the β relaxation was independent of the degree of crystallinity and crystalline structure. The γ relaxation has been to be related to a local motion of the frozen

main chain in amorphous regions. The γ relaxation was observed as a shoulder of the relaxation and was appeared as a peak separated from the peak. The magnitude of the γ relaxation, like the β relaxation, was inversely proportional to the degree of crystallinity.

The temperature dependence of the dielectric loss and dielectric constant of PVDF75 / PMMA25 are shown respectively in Fig. 4 and Fig. 5. Even if the relaxation peaks in Fig. 5 are observed, it was necessary to know what kinds of relaxation they represent, which will be discussed later.

The compatibility of PVDF / PMMA blends has been studied by several workers⁹⁻¹⁵ by measuring the glass transition behavior using the thermal analysis, the dilatometry, and the Rheovibron viscoelastometer, over a wide range of the composition. An explicit detection of the glass transition temperature beyond rich portion of PVDF was not possible in the paper previously mentioned. The glass transition temperature of PVDF 75 / - PMMA 25 was deduced to be located at near room temperature from data obtained by H. G. Kim¹⁶ et al. and ours.

In Fig. 4, the glass transition temperature related to the β relaxation was not appeared, since the dielectric loss due to the α relaxation is apparent. The shape of loss peaks for PVDF75 / PMMA25 is the same as that of loss peaks for pure PVDF and it is proper to say that the loss peak is related to the α relaxation. With increasing frequencies the loss curves shift to a higher temperature, and the magnitude of the dielectric loss decreases.

At the same time, the dielectric constant curves in Fig. 5 also shift to a higher temperature with increasing frequencies, and the ionic conductance at 110~120°C (500Hz, 1KHz) is observed. From 5KHz to 1MHz the dielectric curves are shown to be decreased with increasing temperature near the melting temperature of pure PVDF.

The temperature dependence of dielectric loss and the dielectric constant of PVDF50 / PMMA50 are shown respectively in Fig. 6 and Fig. 7. A well-defined maximum in Fig. 6 is observed and is related to the α and the β relaxation. We deduced

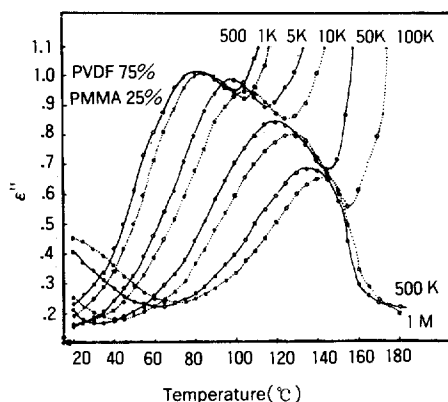


Fig. 4. Temperature dependence of the dielectric loss of PVDF 75 / PMMA 25 at various frequencies

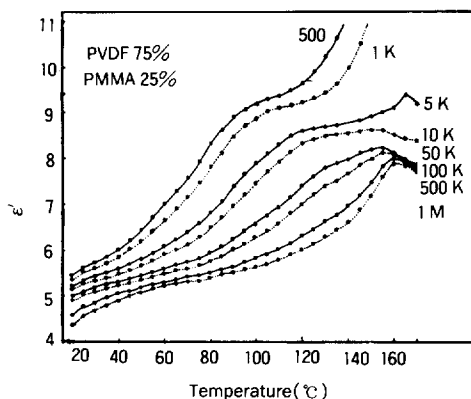


Fig. 5. Temperature dependence of the dielectric constant of PVDF 75 / PMMA 25 at various frequencies.

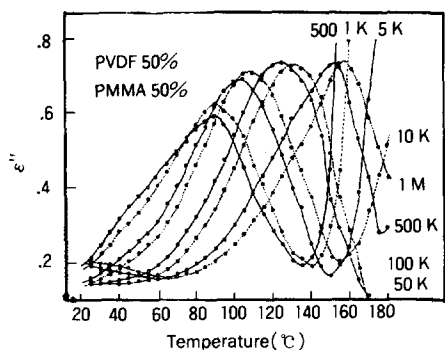


Fig. 6. Temperature dependence of the dielectric loss of PVDF 50 / PMMA 50 at various frequencies.

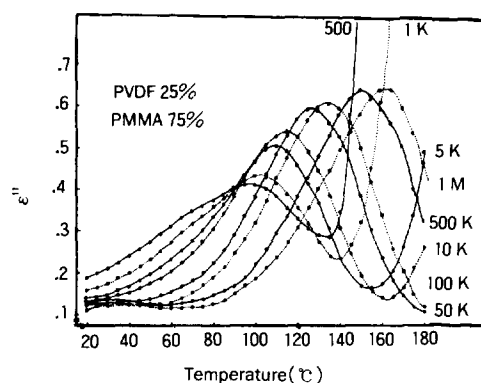


Fig. 8. Temperature dependence of the dielectric loss of PVDF 25 / PMMA 75 at various frequencies.

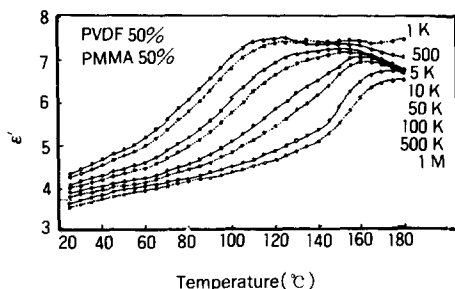


Fig. 7. Temperature dependence of the dielectric constant of PVDF 50 / PMMA 50 at various frequencies.

it from the following results. The degree of crystallinity for PVDF 50 / PMMA 50 is measured as 2% and the glass transition temperature as about 60°C, which are listed in Table 1. Assuming a complete miscibility of PVDF 50 / PMMA 50, the crystallinity and the glass transition temperature affect the dielectric loss curve.

With increasing frequencies in Fig. 6, the dielectric loss curves shift to a higher temperature and the magnitude of the dielectric loss peaks are found to be similar to each other because of the reasons mentioned above.

The temperature dependence of the dielectric loss curves for PVDF 25 / PMMA 75 is shown in Fig. 8. With increasing frequencies, the dielectric loss curves shift to a higher temperature and the magnitude of the dielectric peaks increase. The shape of the loss curves shown in Fig. 8 is different from that of the loss curves shown

Table 1. Glass Transition Temperature and Degree of Crystallinity of PVDF / PMMA Blends.

Composition PVDF / PMMA	Crystallinity (%)	T _g (°C)
100 / 0	45.6	-40
75 / 25	33.8	25
50 / 50	2	60
25 / 75		104
0 / 100		110

previously. There are following reasons : The degree of crystallinity for PVDF 25 / PMMA 75 is 0% as listed in Table 1. The loss peaks in Fig. 8 are only related to the glass transition temperature, where it is called the β relaxation. The β relaxation was closely related to the glass transition temperature, which is discussed previously. The loss peaks at given frequency in Fig. 8 shift to a higher temperature than that of PVDF 50 / PMMA 50. That is, the glass transition temperature shifts to a higher temperature. The glass transition temperature measured by DSC is listed as 104°C in Table 1. This result is coincident with the dielectric loss curve at 1KHz.

It is found that the ionic conductance occur in the dielectric constant and the dielectric loss curves for PVDF 25 / PMMA 75. The dielectric loss curves, like Fig. 6, at low frequency in Fig. 8 rapidly increase near the melting temperature of pure PVDF.

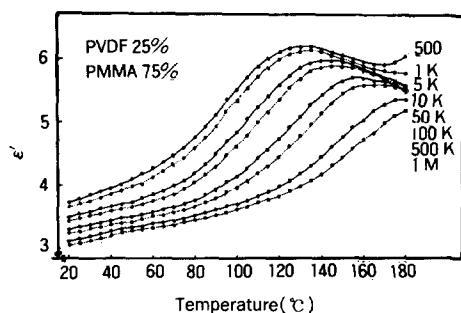


Fig. 9. Temperature dependence of the dielectric constant of PVDF 25 / PMMA 75 at various frequencies.

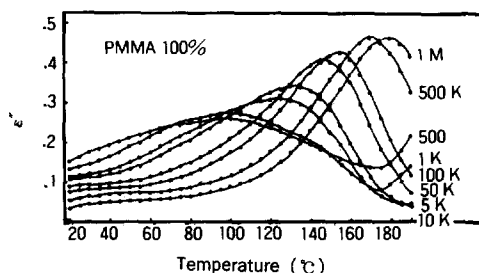


Fig. 10. Temperature dependence of the dielectric loss of PMMA at various frequencies.

In Fig. 9 the dielectric constant curves also shift to a higher temperature with increasing frequencies. The temperature dependence of the dielectric loss and the dielectric constant of pure PMMA are shown respectively in Fig. 10 and Fig. 11. In Fig. 10, the only β relaxation is observed. J. Paul et al.,¹⁵ however, reported that two transitions are shown to be measured by Rheovibron viscoelastometer. The α relaxation related to the glass transition was located near 150°C by the loss modulus curve. This wide separation of peak was common for wholly amorphous polymer. The β region was believed to arise from rotations of the side group, ester, and it was appeared here as the shoulder in the loss modulus and $\tan \delta$ in the vicinity of 50°C.

The dielectric loss peaks in Fig. 10 are closely related to the α transition. (The α transition in pure PMMA is the same as the β transition previously mentioned.) The loss peak at 1 KHz

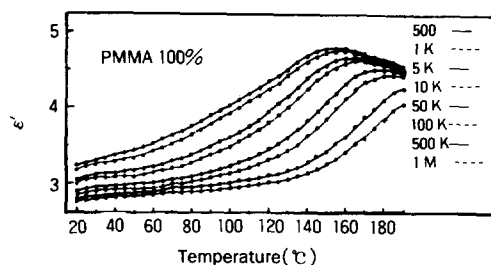


Fig. 11. Temperature dependence of the dielectric constant of PMMA at various frequencies.

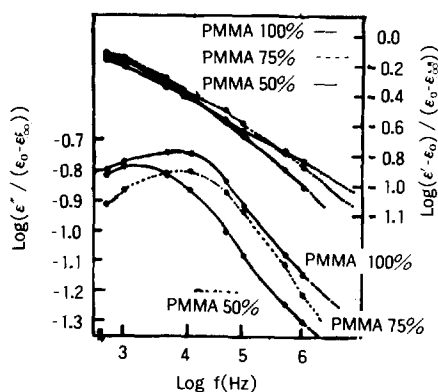


Fig. 12. Comparison of the dielectric constant and loss normalized curves of PVDF / PMMA blends at their transition temperatures.

is located near 108°C. This result agrees to the data obtained by DSC in Table 1. The dielectric loss curves shift to higher temperature with increasing frequencies. Similar data are obtained for PVDF 50 / PMMA 50 and PVDF 25 / PMMA 75.

The dielectric constant and dielectric loss values have been normalized in the form of $(\epsilon' - \epsilon_0) / (\epsilon_0 - \epsilon_\infty)$ and $\epsilon'' / (\epsilon_0 - \epsilon_\infty)$ function. A comparison of the dielectric constant and loss normalized curves of PVDF / PMMA blends is shown in Fig. 12 at transition temperature. It is seen that the position and shape of the dielectric constant normalized curves change with blend composition. At low frequencies, the blend normalized curves are slightly closer to that of PMMA and at high frequencies decrease in the order of increasing the content of PMMA. It is also seen in Fig. 12 that the position of the dielectric loss peaks

shifts to a lower frequency but the magnitude of the dielectric loss curves for PVDF50 / PMMA 50 is higher than that of the dielectric loss curve for PVDF 25 / PMMA 75. It is due to the crystallinity contained its blend.

The apparent activation energy, ΔH_a , of the transition can be calculated from the Arrhenius equation :

$$f = f_0 \exp(-\Delta H / RT) \quad (1)$$

where f is the measuring frequency, f_0 is the frequency when T approaches infinity, and T is the temperature corresponding to the maximum of ϵ'' curve. The data obtained for PVDF / PMMA blends are plotted in Fig. 13 using¹⁰ Eq. (1) . Straight lines are obtained.

ΔH_a is calculated from their slopes and listed in Table 2. A regular decrease from pure PMMA

Table 2. The Activation Energy and the Parameter of Skewed are Plot of PVDF/PMMA Blends.

Composition PVDF / PMMA (Kcal / mole)	ΔH	α	β
75 / 25	17.2		
50 / 50	13.9	0.22	0.871
25 / 75	14.2	0.307	0.962
0 / 100	15.5	0.33	0.99

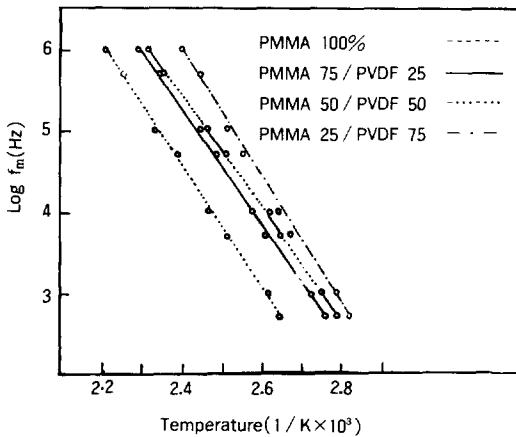


Fig. 13. Arrhenius plot of the dielectric loss peaks of PVDF / PMMA blends.

to PVDF 50 / PMMA 50 is observed. This decrease is mainly due to the decrease of T_g of the blends contained the higher concentration of PVDF.

Increase in ΔH_a for PVDF 75 / PMMA 25 is due to the α transition related to the crystalline region.

In the Table 2, the α is larger for pure PMMA than that for PVDF / PMMA blends. This is due to the low dipole moment of PMMA repeats unit as compared with that of PVDF. The α and β of the blends decrease slightly with increasing PVDF concentration.

The skewed arc function plot is shown in Fig. 14. It is found that the data are well fitted to the relaxation function.

$$\epsilon(\omega) = \epsilon(\infty) + [\epsilon(0) - \epsilon(\infty)] / \{[1 + (i\omega\tau)^\alpha]^\beta\}$$

where ω is the angular frequency ($\omega = 2\pi f$), $\epsilon(\infty)$ is the instantaneous value, $\epsilon(0)$ is the equilibrium value, τ is the relaxation time, and both α and β are a parameter expressing a distribution of relaxation time. This result contrasts with those found by Wetton et al. These workers found that

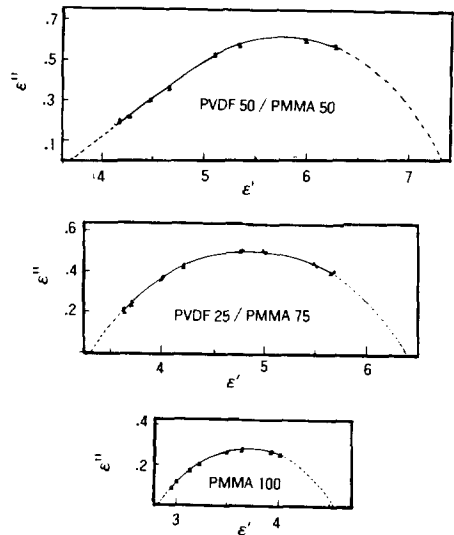


Fig. 14. Skewed representation of the dielectric properties of PVDF / PMMA blend : The experimental values(\circ), The complex dielectric constant calculated(\triangle).

the single T_g by calorimeter, dynamic mechanical, and dielectric measurements was shown. The effect of α was interpreted primarily as arising from a wide range of local concentrations which are present in the miscible blends: in other words it was interpreted as arising from a micro-scale phase separation. Since PVDF / PMMA blends do not exhibit any effect of this sort, it is suggested here that they are homogeneous over the range from pure PMMA to PVDF 50 / PMMA 50 at micro-scale level.

CONCLUSIONS

The dielectric loss peak for pure PVDF was not observed because of the ionic conductance.

The magnitude of the dielectric loss peak for PVDF 75 / PMMA 25 increased with decreasing frequency.

The dielectric losses at maximum peaks for PVDF 50 / PMMA 50 have nearly the same intensity, which is due to the α transition and the β transition.

Shown in PVDF 25 / PMMA 75 and pure PMMA, the dielectric loss increased regularly with increasing frequency as a function of the composition of the blends. At a given frequency, the position of the dielectric loss peak shifted toward a higher temperature with increasing PMMA concentration.

The regular drop of the glass transition temperature from pure PMMA to PVDF 50 / PMMA 50 and the in skewed arc function lead to the conclusion that PVDF / PMMA blends exhibit micro-scale homogeneities over the range of pure PMMA to PVDF 50 / PMMA 50.

Acknowledgement: The financial support for this work from the New Materials Research, Ministry of Education is gratefully acknowledged.

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