Poly(Vinylidene Fluoride)/Poly(Methyl Methacrylate) Blend의 전이성질

文　卓　珍　·　金　衡　九

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(1987년 10월 13일 접수)

Transition Behavior of Poly(Vinylidene Fluoride)/ Poly(Methyl Methacrylate) Blends

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(Received October 13, 1987)

요 약 : 용액 casting 방법으로 PVDF와 PMMA의 blend를 15% DMF 용액으로 부터 만들었다. PVDF와 PMMA blend의 전이성질을 DSC를 이용하여 10℃/min의 승온속도로 −100℃에서 200℃의 온도구간에서 조사하였고, 동적 기계적성질을 1℃/min의 승온속도로 −120℃에서 150℃의 온도구간에서 조사하였다. 조성에 관계되는 유리전이온도가 단 하나 존재한다는 사실과 PVDF 성분의 녹는점 강하가 크게 일어난다는 사실로 PVDF와 PMMA가 상용성임을 알았다. 또한 표준 열역학적인 관점에서 PVDF의 녹는점 강하가 혼합열의 발열을 나타냄을 알았고 PVDF와 PMMA가 강력히 결합하였음을 알 수 있었다. PVDF가 많이 함유된 경우, PVDF의 결정화 때문에 모든 전이와 이완은 매우 복잡한 메카니즘에 의해 이루어지며 조성에 크게 의존함을 알았다. 각 blend의 절단 단면의 형태를 SEM으로 조사한 결과 상분리는 일어나지 않았음을 알았다.

Abstract : Blends of PVDF and PMMA were prepared by solution-casting method from a 15 weight percent DMF solution. The transitional behavior of PVDF / PMMA blends was examined by differential scanning calorimetry(DSC) over a temperature range from −100℃ to 200℃ at a heating rate of 10℃/min and by dynamic mechanical measurements from −120℃ to 150℃ at 1℃/min. PVDF / PMMA blends were judged to be miscible on the basis of the presence of single, composition dependent glass transitions and of the strong melting point depression of the PVDF component. The depression of the PVDF melting point in PVDF / PMMA system judged to be miscible was analyzed using standard thermodynamic arguments to show the exothermic heat of mixing. This exothermic heat of mixing indicated the presence of strong interaction between the binary pairs. All transitions and relaxations were affected by blend composition but in a complex manner owing to the crystallization of PVDF from blends rich in this component. Morphology of fracture surfaces of blends was studied by scanning electron microscopy(SEM) and no signs of phase separation was observed.

INTRODUCTION

In 1960s, miscible polymer blends were noted to be extremely rare and have a quite unexpected behavior.[1,2] However, in 1970s, a large number of miscible systems were revealed.[2]

Due to their technological importance, polymer blends have attracted considerable attention during the past decade. A complete miscibility in the segmental scale is not a necessary condition for a blend to have desirable physical properties.[2,3]

Polymer blends can be characterized by their phase behavior as being either miscible or immiscible. Immiscible blends show multiple amorphous phases. Each phase of a completely immiscible blends contains an essentially pure blend component whereas the phases of partially immiscible blends may contain some of each material in the blend. Finally, blends can also be found which are completely miscible and have only one amorphous phase.

The miscibility of polymer-polymer systems is the exception rather than th rule. For thermodynamic reason, i.e., slight volume contractions on mixing,[1] most polymer pairs are immiscible and their degree of miscibility is of underlying importance to the microphase structure and, consequently, to the mechanical properties of the blend.

Most theoretical and practical investigations on the properties of polymer blends have been concerned mainly with systems containing amorphous components. Recently, both for fundamental and practical reasons, blends with crystallizable components have received increasing attention. Below the melting temperatures, blends with crystallizable components are heterogeneous as upon cooling one or more of the components separates from the mixtures as a pure crystalline phase, even though in the melt the components are compatible. However, phenomena of miscibility in the remaining amorphous phases may still be possible.

Since there is no unanimity for the terminology of polymer mixtures, the terms compatibility and polymer-polymer miscibility are used here in the spirit of ref(2) and(3).

The most interesting aspects of these crystallizable systems concern the influence of composition, processing, and crystallization conditions on the overall morphology, on the rate of crystallization, on the crystallinity, and on the melting behavior. The two components in fact may influence each other giving rise to interesting effects such as depression of the melting temperatures and of the growth rate of spherulites and modifications of shape and structure of spherulite.

Several compatible polymers have been discovered, including semi-crystalline poly(vinylidene fluoride) (PVDF) and poly (methyl methacrylate)(PM-MA).[4-6]

It was believed that PVDF crystallized in the blend if its weight fraction exceeds 0.5. It was illustrated by Nishi and Wang[6] that the two polymers were miscible above the PVDF melting point of 170℃, but that the PVDF could crystallize when a blend was held at any temperature between the glass transition temperatures of the two components. An interesting feature of this miscible blend is that the PVDF component partially crystallizes from the mixture which imparts the same complexities to the transitional behavior of this blend that plagues most semi-crystalline polymers. The multiple transitions reported by McBrierty et al.,[8] illustrated the complexity of PVDF thermal behavior.

The most widely accepted and least unambiguous test for miscibility is the glass transitional behavior which categorizes particular blend systems as miscible or immiscible depending on whether a single T_g is observed or not. One expects a single, composition dependent T_g for a miscible blend that connects simply with the T_g of either component. Examples of this are well-known even for systems where one polymer crystallizes-the single T_g is indicative of a mixed amorphous phase in such cases. Therefore, even though the glass transition temperture of PVDF may be somewhat uncertain, the presence of a single T_g in the blend can be taken as a sign of miscibility.

However, this approach does not provide any quantitative thermodynamic information about the strength of the interaction between the com-

ponents, e.g., heat of mixing, in a miscible system. In 1975, it was shown by Nishi and Wang[6] that the classical theory of melting point depression in blends containing a crystallizable component might provide such information. From the melting point depression, calculation of interaction energy density, B, for this system ranging from 0 to -3.85 cal / (cm^3 of PMMA) were made.[6,9,10] In addition to the melting point depression measurements, the Flory-Huggins[11] interaction parameter, χ_{12}, from small angle X-ray data was calculated by Wendorff.[10] The two interaction parameters are related to $\chi_{12} = BV_{1u} / RT$ where V_{1u} is the molar volume of the PMMA, R is the gas constant, and T is absolute temperature. This findings resulted in an interaction parameter which was always negative, but varied with the composition of the blend. Depending on the technique utilized, χ_{12} ranged from -0.49 to -0.7 at 90 wt. percent PVDF and -0.04 to -0.12 at 10 wt. percent PVDF.

The relaxation mechanism of PVDF has been studied in detail by mechanical[5,12~14] and dielectric measurements.[12,15~20] PVDF polymer exhibited three transitions with peaks at 50°C (designated as α) ; -35°C (designated as β), and -80°C (designated as γ).

According to these studies, the α transition was assigned to molecular motion in the crystalline region including lamellar surface and to crystalline defects ; the β transition was assigned to micro-Brownian motion in the amorphous region ; the γ transition was assigned to local molecular motion in the amorphous region. The glass transition temperature of PVDF is around -40°C.[16,21] PMMA polymer exhibited two transitions[5,22,23] : α transition (the main T_g) and β transition(arising from the rotations of the ester side group).

It was found to be interesting both from a practical and a theoretical point of view to study the transition behavior of PVDF with PMMA blends.

In this study the detailed transitional behavior for binary blends and the individual components of the PVDF / PMMA system was studied by differential scanning clorimetry (DSC) and dynamic mechanical measurements plus scanning electron microscopic observation.

EXPERIMENTALS

Materials

A poly(vinylidene fluoride) (PVDF) resin, KYNAR 460, in pellet form was obtained from the Penwalt Corp. The poly(methyl methacrylate) (PMMA) was Plexiglass zk 20 supplied by the Rohm and Hass in pellet form.

Preparation of Samples

N,N-Dimethylformamide(DMF) was used as a solvent in the preparation of film-cast samples. Blends were prepared by solution casting. For solution casting, a total of 20g of PVDF / PMMA mixture in weight ratios of 100 / 0, 80 / 20, 60 / 40, 40 / 60, 20 / 80, and 0 / 100 was dissolved in 15 wt. percent DMF for at least 1 day at 40°C with stirring. Blends were cast on glass plates and all film samples were dried in air oven for 12 hours at 60°C.

Dried films were subjected to heating in a small-muffle furnace for 1 hour at a temperature about 190°C to remove the solution history and to reduce the roughness of surface.

It was interesting to note that certain blends of PVDF / PMMA adhered strongly to the glass plates on which their films were cast. PVDF and blends rich in this compoent were easily removed from the plates, while PMMA and blends containing less than 60 percent PVDF adhered strongly to the plates. Removal was facilitated in these cases, by immersion in SK disperser.

Film thickness was measured with a micrometer at several points of the film. The average film thickness was 0.08 mm ± 0.005 mm.

Testing

DSC

Thermal analysis were performed using a Dupont 1090 Thermal Analyzer with a Differential Scanning Calorimetry (DSC) 910 module under nitrogen gas purging. The samples weighed 10-13 mg.

Glass transitions, melting points, and heats of fusion were measured between $-100°C$ and $200°C$ at a heating rate of $10°C$ / min. The inflection point was taken as the T_g, and the apex temperature of the melting peak was defined as T_m.

Rheovibron

The direct-reading viscoelastometer(Rheovibron, Model DDV-II from Toyo Baldwin Co., Tokyo) utilizes the forced vibration technique and has been developed by Takayanagi.

The measurement chamber was kept moisture free by a stream of precooled nitrogen gas. Test specimens were 4.8 cm long, 0.4cm wide, about 0.008 cm thick. Beginning at $-130°C$, measurements were taken at $3-5°C$ intervals Specimens were held for about 15 min at each temperature to ensure thermal equilibration.

The experimental mechanical loss tangent, tan δ, were determined between $-130°C$ and $150°C$ at 110 Hz for PVDF / PMMA blends.

The imaginary component, E'', of the complex tensile modulus was calculated from the damping data and manual equation.

SEM

Fracture surfaces of various blends were studied by Scanning Electron Microscopy(SEM, JEOL JSM-35CF). Samples were fractured at liquid nitrogen temperatures.

RESULTS AND DISCUSSION

Thermal Analysis of Blends

Shown in Fig.1 are some characteristic thermograms of PVDF / PMMA blends after quenching from the melt in liquid nitrogen. As Noland et al.[4] observed, certain blends rich in PVDF have a melting endotherm characteristic of PVDF whereas blends rich in PMMA are totally amorphous.

Features of particular interest are the glass transition and the melting endotherm. Locations of transitions were marked by circles, triangles or squares in accordance with the key shown in Fig. 1.

It will be noted from this thermal history that blends containing 40 percent or less PVDF developed

no crystallinity : whereas, those containing 50 percent or more did. The corresponding point for the PVDF / PMMA system[24] was 30 percent.

In Fig. 2 the heat of fusion of each blend was plotted against blend composition. The value shown for pure PVDF yielded a percentage crystallinity under these conditions, of 46 percent when compared to the estimated value of 25 cal /g for 100 percent crystalling PVDF.[17,25] This is slightly less than 50 percent level normally observed for this polymer.

The dashed line in Fig. 2 connects the zero value for amorphous pure PMMA with the observed heat of fusion for pure PVDF. This is the peak
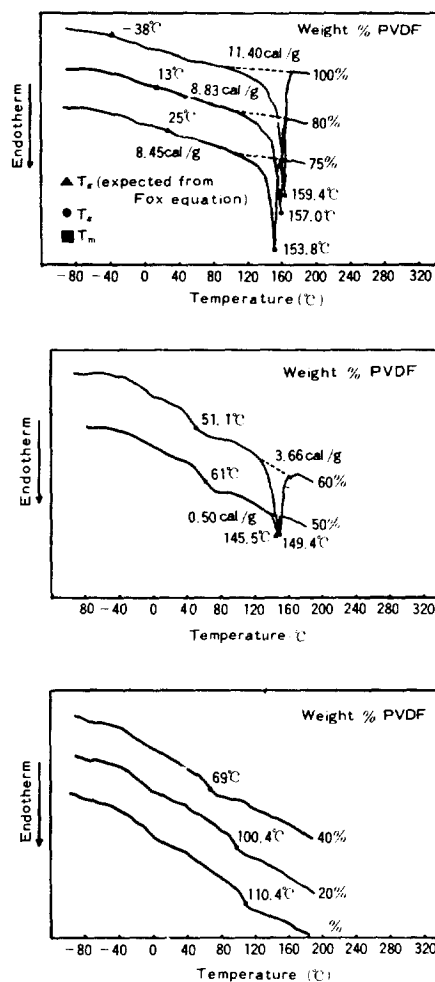

Fig. 1. Thermograms of PVDF / PMMA blends recorded by DSC at a heating rate of $10°C$/ min.

area expected if PMMA did not interfere with PVDF crystallization but merely diluted the sample mass. Obviously, blending did interfere with crystallization. Heat of fusion ($\triangle H_f$), crystallinity and melting temperature of PVDF / PMMA system are shown in Table 1.

The melting point of pure PVDF was 159.4℃ and the boiling point of DMF is in this range. So, it was thought that the heat of fusion in pure PVDF was affected by the heat of evaporation in DMF. However, PVDF homopolymer was stable up to 300℃ when heated in air at the rate of 5℃/min as the Thermogravimetric Analysis(TGA) thermogram in Fig. 3 indicated. Little amounts of DMF remained after experimental procedure.

The location of the T_g and T_m varied with blend composition as shown in Fig. 4. The melting point was depressed as PMMA was added to the PVDF.

For a blend of two miscible polymers one expects the T_g to progress smoothly from the T_g of one component to that of the other as composition is varied in much the same manner as observed in a copolymer system. The dashed line in the lower portion of Fig. 4 shows this expectation as estimated via the Fox equation.[26]

All the blends less than 80 percent PVDF, showed a single T_g by DSC, within the limits of detection which was quite strong for the wholly amorphous samples. The location of this transition
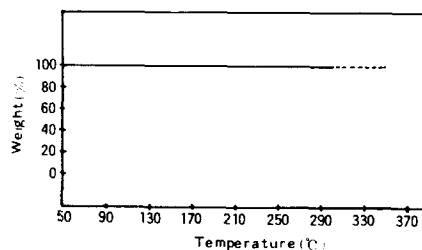

Fig. 2. Heat of fusion for PVDF / PMMA blends obtained from Fig. 1.

Table 1. Heat of Fusion($\triangle H_f$), Crystallinity, and Melting Temperature of PVDF / PMMA Blends.

Blend Composition PVDF / PMMA	$\triangle H_f$ (cal / g)	Melt. Temp. (℃)	Crystallinity (percent)
100 / 0	11.40	159.4	45.6
80 / 20	8.83	157.0	35.3
75 / 25	8.45	153.8	33.8
60 / 40	3.66	149.4	14.6
50 / 50	0.50	145.5	2.0
40 / 60	—	—	—
20 / 80	—	—	—
0 / 100	—	—	—

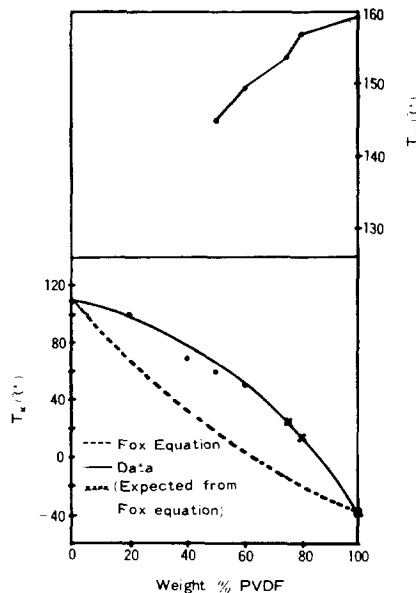Fig. 3. TGA curves of pure PVDF.

Fig. 4. Location of T_m and T_g from Fig. 1 as a function of blend composition.

as a function of blend composition was shown in the lower portion of Fig. 4. As crystallinity increases with the increasing PVDF content, the intensity of this transition diminished rapidly.

The T_g—composition curve in Fig. 4 illustrated positive deviation. It was known[27] that in general the so-called miscible polymer-polymer blends presented a T_g —composition curve which was concave. Very strong interactions are necessary to produce a straight line or a convex T_g—composition curve.

Owing to the large proportion of crystalline structure in PVDF and the rapid crystallization which occurs while heating rapid quenched amorphous samples(see Fig. 5), it was difficult experimentally to obtain a well-defined glass transition of 80, 100 percent PVDF. Noland et al.[4] encountered similar difficulty in measuring by thermal analysis or dilatometry the T_g of blends very rich in PVDF.

However, they stated their T_g data, which cover a composition range similar to that in Fig. 4, were consistent with extrapolation to $-40℃$ to $-60℃$ for pure PVDF.

Mandelkern et al.[28] reported a value "below $-40℃$" based upon an extrapolation of the T_g data for vinylidenefluoride-chlorotrifluoroethylene copolymers in accordance with the Fox equation,

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

Where W_1 and W_2 are the weight fractions, and T_{g_1} and T_{g_2} the glass transitions(absolute temperature) of components 1 and 2 respectively.

The location of the PVDF melting point for the various blends obtained from thermograms in Fig. 1 was illustrated in the upper part of Fig. 4. The melting point depression of the PVDF caused by PMMA was approximately $14℃$. In the next section, this depression will be analyzed more fully.

Analysis of T_m Depression

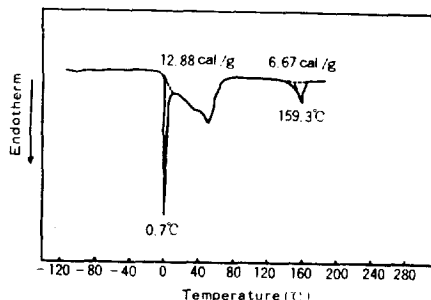Since PVDF crystallizes, the concept of melting point depression analysis is a potentially useful

Fig. 5. Thermograms of rapid quenched pure PVDF at a heating rate of $10℃$ / min.

scheme for quantifying the thermodynamic behavior of the system of interest here.

The T_m data in Fig. 4 for the PVDF / PMMA system can be explained along the lines suggested by Nishi et al.[6] and Imken et al.[24]

The classical theory of melting point depression by a miscible diluent can be developed into useful equations if a suitable model for the thermodynamics of mixing is employed. A simple but yet conceptually appropriate model for polymer—polymer mixtures is the Flory-Huggins treatment.[3,11]

In their approximation, the equilibrium melting point depression caused by a miscible diluent can be divided into additive parts stemming from entropic and enthalpic contributions, i.e.,

$$\triangle T_m = (\triangle T_m)_S + (\triangle T_m)_H \qquad (1)$$

However, the entropic contribution is independent of the degree of interaction between the components but does depend on their molecular weight.$(\varDelta T_m)_S$ was of the order of $1℃$ or less when both components had molecular weights larger than $10,000$.[29]

Most of the polymers of interest probably meet this condition, so the entropic contribution to $\triangle T_m$ may be assumed to be less than $1℃$.

Therefore, it is considered only enthalpic effect, $(\triangle T_m)_H$.

$$\frac{1}{T_m} - \frac{1}{T_m°} = -\frac{RV_{2U}}{\triangle H_{2U}V_{1U}}\left\{\frac{\ln V_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\right.$$
$$\left. \times (1-V_2) + \chi_{12}(1-V_2)^2\right] \qquad (2)$$

Where, with the subscript 1 identified with the amorphous polymer and 2 with the crystalline polymer, V is the volume fraction, V_U is the molor volume of the repeating units, m is the degree of polymerization.

Also χ_{12} is the polymer-polymer interaction parameter, R is the gas constant, and T is the absolute temperature.

Eq. (2) is obtained by equating the chemical potential of component 2 in the crystalline state to that of this component in the amorphous mixture at the melting point of the mixture, T_m, where T_m is the melting point of undiluted 2.

For the problem at hand, both m_1 and m_2 are very large compared with unity ; eq. (2) therefore reduces to

$$\frac{1}{T_m} - \frac{1}{T_m{}^0} = \frac{RV_2u}{\triangle H_2u \; V_1u} \; \chi_{12}(1-V_2)^2 \quad (3)$$

Eq. (3) therefore describes the melting point depression due to mixing of a crystalline polymer and amorphous polymer. It is assumed χ_{12} is of the following form by neglecting the effects of entropy[30] and V_2,[31]

$$\chi_{12} = BV_1u \; / \; RT \quad (4)$$

where B is the interacion energy density characteristic of the polymer pair. Substitution of eq.(4) into eq.(3) yields the following eq.(5).

$$\triangle T_m = T_m - T_m{}^0 = -T_m{}^0 (\frac{V_2u}{\triangle H_2u})BV_1{}^2 \quad (5)$$

Eq.(5) suggests plotting the melting point depression $\triangle T_m$, vs. $V_1{}^2$ as done in Fig. 6. The ratio ($\triangle H_2u \; / \; V_2u$) gives the latent heat of fusion of 100 percent crystalline component 2 per unit volume which for PVDF has a value of 44.0 cal / cm^3, $\triangle H_2u = 1.6$kcal / mole[17] $V_2u = 36.4$ cm^3 / mole.[6]

Published data ($V_1u = 84.9$cm^3 / mole, $\rho_1 = 1.20$g / cm^3, and $\rho_2 = 1.52$g / cm^3,[35] where ρ is the density) were used to convert the weight fractions into volume fractions at 155℃.

The data in Fig.6 formed a very nice straight line within the limits of experimental uncertainty ; however it did have a very small nonzero intercept
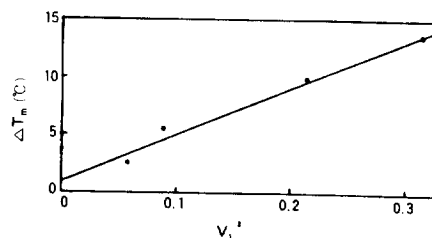

Fig. 6. Expetimental depression of the PVDF melting point caused by PMMA. Plot is the form suggested by Eq. 5 so that the slope is related to the parameter B.

(⟨1℃) which might result from a small entropic effect. The parameter B was computed as -3.57 cal / cm^3 from the slopes of the straight line drawn in Fig. 8 which compared very closely with the value of -3.18 obtained by Imken et al.[24] for the PVDF / PMMA system and with -2.98 by Nishi et al.[6]

By necessity, this value indicated an exothermic heat of mixing, arising from some strong specific interaction in PVDF / PMMA system, since in a system where entropic effects are very small, only negative heat of mixing can lead to miscibility or melting point depression.[24,29]

Dynamic Mechanical Properties of Blends

For miscible polymer blends, one expects a single T_g which depends on composition in such a way as to connect the T_g's of the two pure components.

However, there was very little to suggest what should happen to secondary amorphous peaks or those associated with motions in crystalline regions which would include PMMA β transition and PVDF α, and γ transition according to the interpretations noted in introduction section.

All evidence strongly suggested that PVDF and PMMA were miscible : All of the blends showed no suggestion of multiple peaks as might be expected for immiscible blends.

Thus one might expect the PVDF β peak to shift to higher temperatures as PMMA is added, and to connect with the T_g of PMMA. Further, one might expect the PVDF α peak to diminish in magnitude as PMMA is added and subsequently

to disappear when all crystallinity is lost, given that the α peak is associated with PVDF crystalline regions. However, the data for the blends did not conform to these expectations. From this, it was thought that the dynamic mechanical behavior of PVDF / PMMA system was very complex.

The dynamic mechanical properties, E'' and tan δ, of the blends of PVDF / PMMA and pure components were measured at 110 Hz by a Reovibron viscoelastometer.

The dynamic mechanical behavior of PVDF has been reported by numerous authors.[5,12~14] These measurements have involved polymers from a variety of sources with varying thermal and mechanical histories, : however, they showed that there were three relaxation processes which might be equated with the α, β, and γ dispersions observed dielectrically.

In Fig. 7, Rheovibron data was plotted against the temperature for pure PVDF. It showed peaks near 53℃ and -38℃ with a shoulder in the vicinity of -70℃. These have been associated with α, β, and γ respectively described earlier.

It has been suggested that the precise location of the α peak depends somewhat on previous thermal history.[12]

In Fig. 8, two relaxations, α and β for pure PMMA were found. The α peak was the main

T_g, and the data located it at 107℃ by E'' and at 143℃ by tan δ. This wide separation of the peaks is common for wholly amorphous polymers[33]. The β region is believed to arise from rotations of the ester side group,[22,23] and it appeared here as a shoulder in E'' and tan δ in the vicinity of 50℃.

For the 80 and 60 percent PVDF blends (Figs. 9 and 10) which are partially crystalline, there
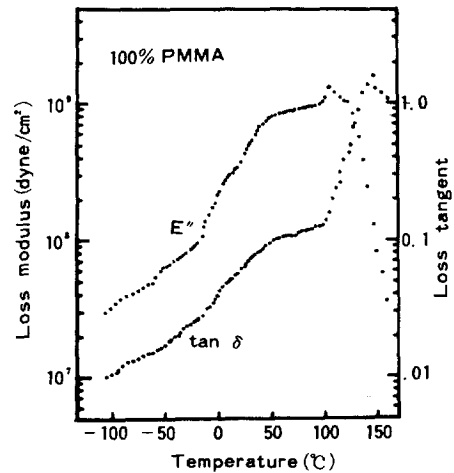
Fig. 8. Loss modulus (E'') and tanδ as a function of temperature for pure PMMA.
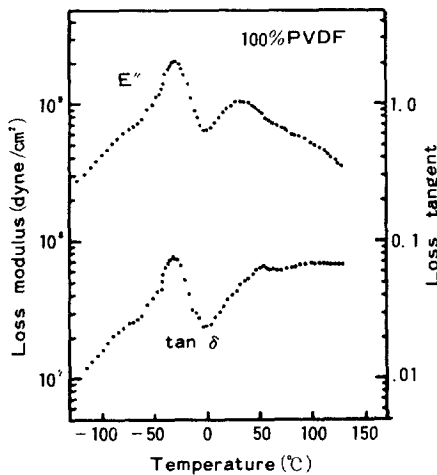
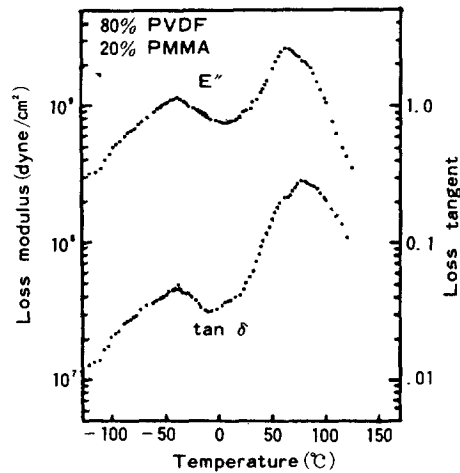Fig. 9. Loss modulus (E'') and tanδ as a function of temperature for the PVDF / PMMA=80 / 20 blend.

Fig. 7. Loss modulus (E'') and tanδ as a function of temperature for pure PVDF.

were two major peaks in either E″ and tan δ. As PMMA content increased, the higher temperature peak became larger and shifted toward higher temperature. It appeared to degenerate into the α peak of pure PVDF shown in Fig.7 when PMMA content decreased to zero. The lower temperature peak decreassed in magnitude and shifted toward lower temperatures as PMMA content increased. When all PMMA was eliminated, it appeared

to reduce to the PVDF β peak.

For the noncrystalline 40 and 20 percent PVDF blends(Figs. 11 and 12), there was one major peak. This peak was very large, and the magnitude of tan δ was almost the same for the two materials. Its location shifted to higher temperatures as PMMA content increased. It merged directly into the pure PMMA peak when all PVDF was eliminated.

Shoulders in Figs. 11 and 12 were not clearly apparent and was thought as the PMMA β dispersion. Another weak shoulders appeared at or below −60℃ for these two blends.

In Fig. 13 peak locations for the well-defined peaks in Figs. 7-12 as a function of blend composition were plotted. Smooth curves, although sigmoidal in shape, could be drawn through the upper transtions for the blends which connected with the major peak of pure PMMA and the α peak of pure PVDF.

Only the E″ peak was shown for the lower temperature transition since tan δ peaks located at substantially the same location. Only two points were shown for blends since these were the only ones that showed a distinct peak. They could be connected to the pure PVDF β peak by a simple curve.
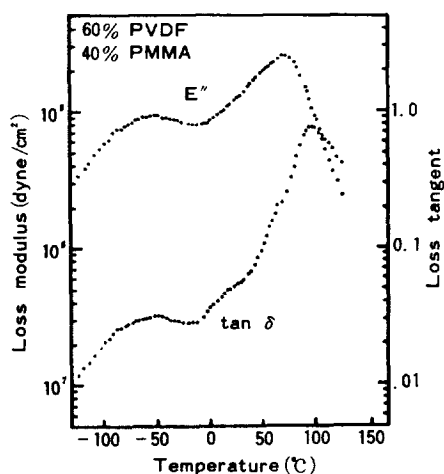

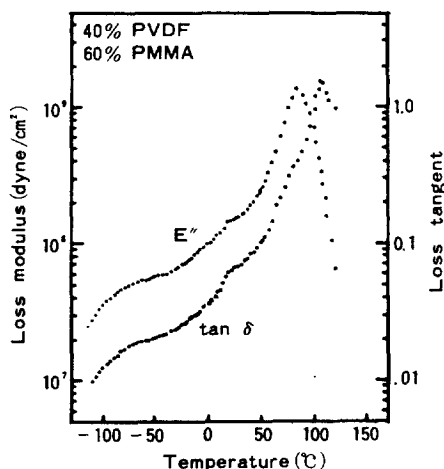Fig. 10. Loss modulus (E″) and tan δ as a function of temperature for the PVDF / PMMA= 60 / 40 blend.

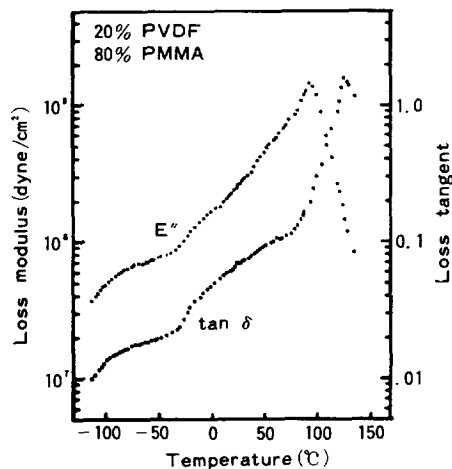Fig. 11. Loss modulus (E″) and tan δ as a function of temperature for the PVDF / PMMA= 40 / 60 blend.

Fig. 12. Loss modulus (E″) and tan δ as a function of temperature for the PVDF / PMMA= 20 / 80 blend.
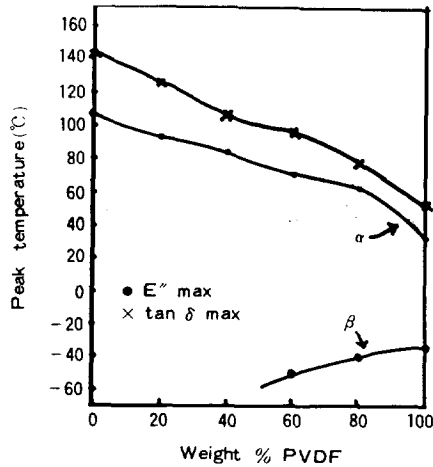
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Fig. 13. Temperature location of relaxation peaks for PVDF / PMMA blends from dynamic mechanical data.

Nakagawa and Ishida[17] described very extensive and thorough investigations of relaxations and molecular motions in PVDF. They concluded that the β region was the T_g for PVDF. : however, they did note a number of peculiarities by which the T_g behavior of PVDF differs from that of other polymers, and they suggested that $-38\,°C$ is only an apparent T_g.

Morphology of Fracture Surfaces of Blends

A microscopic investigation of the fracture surfaces of various blends was conducted.

Fig. 14 represents the scanning electron photomicrographs of fracture surfaces. In all photomicrographs, the scale was indicated in the lower left-hand side corner.

The fracture surface of pure PMMA, as shown in Fig. 14(a), appeared smooth, which was a typical
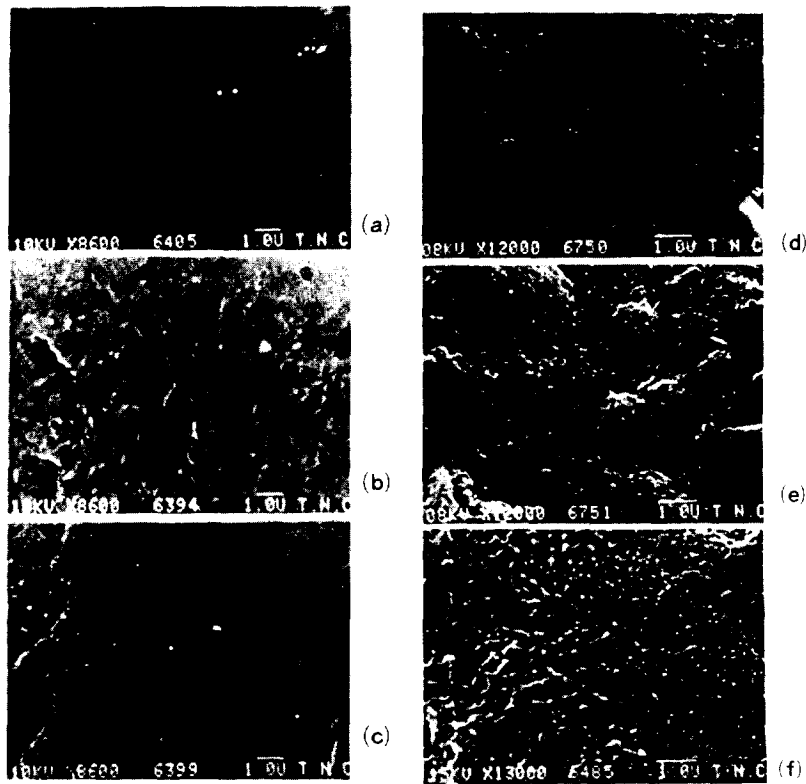

Fig. 14. Scanning electron micrographs of fractured surfaces at liquid nitrogen tempetature for PMMA / PVDF blends.
(a) pure PMMA, (b) PMMA / PVDF=80 / 20, (c) PMMA / PVDF=60 / 40, (d) PMMA / PVDF=40 /60, (e) PMMA / PVDF=20 / 80, (f) pure PVDF.

fracture characteristic of brittle materials. As the amount of PVDF in the blend was increased, the fracture surface became progressively rougher.

It is also instructive to note that, on all SEM photomicrographs, the fracture surface of each blend was characterized by a uniform pattern. The microscopic evidence clearly suggested that the blends were compatible.

If, for instance, a phase separation occured, one would expect to see two different fracture patterns on each phase : a smooth fracture pattern on one phase which is rich in PMMA and a rougher fracture pattern on the other phase which is rich in PVDF. Such fracture patterns, however, were not observed.

CONCLUSIONS

It was clear from this study and the earlier work of Noland et al. and Nishi et al. that PVDF and PMMA were compatible.

This conclusion was based on a variety of behavioral characteristics such as shifts in the location of various viscoelastic relaxations and thermal property changes indicative of molecular mixing of the components, and the consistency of the melting point depression with classical thermodynamic formulations. The latter gave a significant exothermic heat of mixing comparable to that deduced for PVDF/PMMA which explained thermodynamically the miscibility observed for these two systems.

All samples containing 50 percent or more PVDF were shown to be partially crystalline. The melting point of these blends was found to be decreased as the amount of PVDF was decreased, indicating PMMA molecules interfered with crystallization, thereby altering the morphology and causing the depression of melting temperature.

Crystallization of PVDF from blends rich in PVDF did not signal immscibility since the evidence indicated that all the PMMA and the remaining PVDF formed a homogeneous amorphous phase.

Scanning electron micrographs showed a uniform pattern on the fracture surface of each blend. No signs of phase separation were observed.

Considerable surface roughness was noted in PVDF-rich formulations.

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