

Structure-Property Relationships of Composite Films

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Synopsis

Coextruded multifilms of varying chemical composition and structure were studied by the dynamic mechanical technique. The films studied were two- and three-ply combinations of a polyimide (Kapton) and fluorinated ethylene-propylene copolymer (FEP) and four other two-ply polyethylene and modified polyethylene composites: low-density polyethylene (LDPE)-ionomer, rubber-modified high-density polyethylene (HDPE)-ionomer; ethylene-vinyl acetate (EVA) copolymer-LDPE, and EVA-modified HDPE-LDPE. The mechanical spectra of individual film components were also obtained at 110 Hz between -120° and 120°C (220°C for the Kapton-FEP system). Mechanical relaxations were examined to determine the degree of interaction between adjacent films and correlate them with tensile and ultimate properties of the composite.

INTRODUCTION

A new development in the plastic film technology has been the one-step manufacture of multilayer films by coextrusion.¹⁻³ These composite films have a combination of useful properties which in some cases can be predicted once the geometry of the composite and the individual component properties are known.² In other cases where the composite consists of a large number of thin films, interlayer interactions play a significant role, and the composite film properties cannot be simply predicted from additive contributions from the individual layers.^{4,5}

The aim of the present work was to study the dynamic mechanical properties of a few types of commercially useful composite films. It is well known that mechanical relaxations are sensitive to intermolecular interactions and/or the state of mixing of polymers.^{6,7} Therefore, it was intended to examine these and correlate them with such parameters as the chemical nature of the individual film layers, the variation of composition for the same type of structure, and the effect of film structure for the same overall composition. The results would also be used to explain the ultimate properties of these films reported in the literature or obtained in this laboratory.

EXPERIMENTAL

Material and Measurements

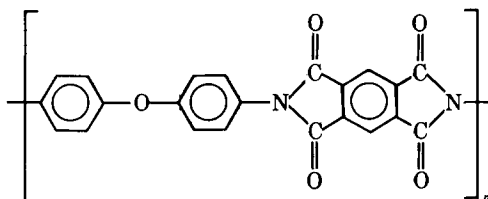
The composite films used are given in Table I. The choice of the particular systems was determined by the aims of this study. Of prime consideration was good adhesion between the individual layers of the composite. The importance of good adhesion cannot be overemphasized since poorly bonded layers can cause friction giving spurious mechanical relaxations. This led to the choice of the coextruded composite films listed.

TABLE I
Composition and Individual Layer Thickness of Composite Films Studied

Film no.	Composition, ^a mils	Kapton content		Supplier
		Wt-%	Vol-%	
1	F, 5.0	0	0	du Pont de Nemours
2	K, 1.0; F, 1.0	40	50	
3	K, 1.0; F, 0.5	57	67	
4	F, 0.5; K, 2.0; F, 0.5	57	67	
5	K, 2.0; F, 0.5	73	80	
6	K, 2.0	100	100	
Polyethylene-Based Composites				
7	ionomer, 1.4; LDPE, 2.5			U.S.I Film Products
8	rubber-modified HDPE, 4.4; ionomer, 2.6			
9	EVA-modified HDPE, 1.5; LDPE, 1.5			
10	EVA copolymer, 1.5; LDPE, 4.5			

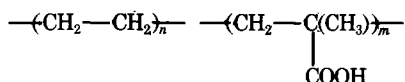
^a K = Kapton; F = FEP (see text); EVA = ethylene-vinyl acetate copolymer.

The effect of varying composition and structure was studied using a Kapton H*–FEP composite. Kapton (K) is the trade name (du Pont) for a polyimide, poly[N,N'-(*p,p'*-oxydiphenylene)pyromellitimide]:



and FEP (F) is a tetrafluoroethylene–hexafluoropropylene copolymer of the structure $\text{-(CF(CF}_3\text{)-CF}_2\text{)}_n\text{-(CF}_2\text{-CF}_2\text{)}_m\text{-}$. Comparison of the relaxation spectra with those reported by McCrum⁸ indicated that the hexafluoropropylene comonomer constitutes approximately 10 mole-% of the copolymer.

The other composite films examined (see Table I) were combinations of polyethylene with some of its modified forms. The ionomer in film 7 was an ethylene–methacrylic acid copolymer of the structure



partially ionized, with Na⁺ as a counterion. The HDPE in film 8 was modified with polyisobutylene. The ethylene–vinyl acetate copolymer in film 10 had less than 5% by weight of vinyl acetate comonomer.

Composite films were used as received. Except for the Kapton, FEP, and ionomer films, which were available as such, the other individual components were produced in film form by compression molding from pellets supplied by

* "Kapton H" is the commercial name of the film. The (k) was introduced as a short "code" for Kapton in the subsequent discussion.

the same manufacturer that produced the composite. Molding conditions were 180°C at 2000 psi for 3 min and cooling to 25°C within approximately 5 min. For the LDPE products, a lower temperature was used (150°C). It is assumed that the coextruded films were similarly air quenched. It is recognized that this might introduce some error (in some systems) in predicting the composites' properties from those of the pure components if the heat treatment was greatly different.

Dynamic mechanical measurements were carried out at 110 Hz with the Rheovibron Viscoelastometer Model DDV-IIC of Toyo-Baldwin Co., Ltd., Tokyo, Japan. Temperature range was -120° to +120°C for the PE composites and to 220°C for the Kapton-FEP films. A slow stream of precooled nitrogen prevented moisture from condensing on the sample. In calculating the quantity $|E^*|$, the small deformation of the instrument clamps was taken into account. Typical specimens dimensions were 2.50 cm \times 0.2 cm \times 0.01 cm.

Stress-strain properties were studied at 35°C by the incremental addition of loads at a constant rate (50 g/5 min) at the lower clamp of the test film strip suspended in a thermostated glass chamber. The extension was obtained by measuring the distance between two fiduciary lines on the film with a traveling microscope to an accuracy of 0.2 mm. Typical specimen dimensions were 2.50 cm \times 0.50 cm \times 0.01 cm.

RESULTS AND DISCUSSION

In Figures 1-3 the relaxation spectra of some composite films and their components are reported. Tensile and ultimate properties for the Kapton-FEP system used were obtained from the literature⁹ and are summarized in Figure 4. Table II lists typical tensile and ultimate properties of the PE composites supplied by the manufacturer. Properties of the pure components were obtained

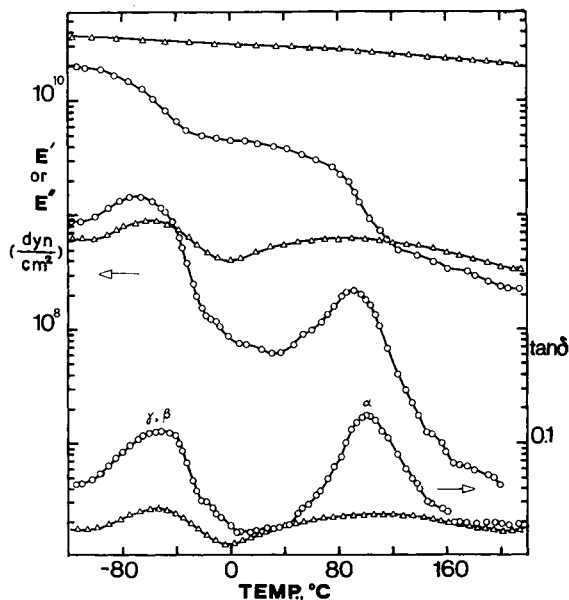


Fig. 1. Temperature dependence of storage modulus E' , loss modulus E'' , and loss tangent $\tan\delta$ of Kapton ($-\Delta-$) and FEP ($-O-$) at 110 Hz.

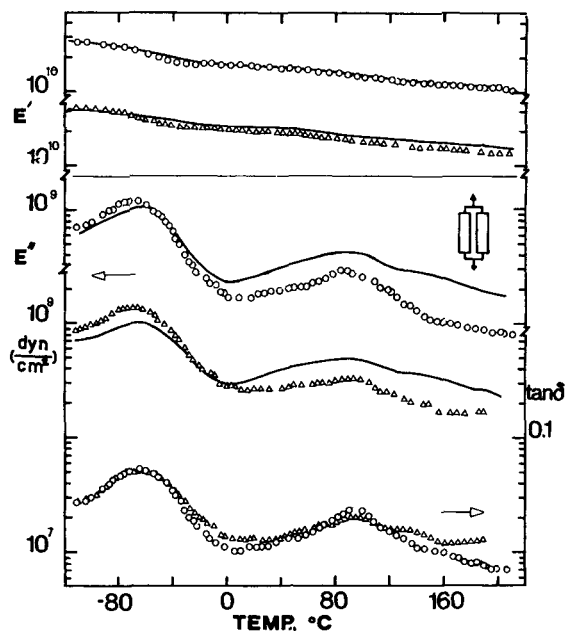


Fig. 2. Temperature dependence of storage modulus E' , loss modulus E'' , and loss tangent $\tan\delta$ of Kapton-FEP composite films at 110 Hz: (—○—) film 2; (—△—) film 3; (—) calculated values using parallel model.

wherever possible from literature sources.^{10,11} Lack of reliable pure component data made it necessary to measure their stress-strain properties as well as those of films 8 and 9. Because of differences in testing conditions it is not expected that the results would agree with those reported in Table II. Ours are used for comparative purposes only.

Kapton-FEP Composites

The dynamic mechanical spectra of the pure components (see Fig. 1) are in substantial agreement with the results of McCrum⁸ and Gillham.¹² Inspection of the relaxation spectra in Figure 2 does not reveal any significant mixing or interaction at the interface. As the amount of the FEP content decreases, the β peak decreases also. However, its position remains unaltered. In the same figure a comparison is made with observed and calculated values of the moduli E'_c and E''_c of the composites using the parallel model of connection valid for these systems (see insert, Fig. 2). Use was made of the pure component data and of the following expressions, which do not take into account any interaction between adjacent film layers:

$$E'_c = \frac{1}{t} \sum_i t_i E'_i \quad \text{and} \quad E''_c = \frac{1}{t} \sum_i t_i E''_i$$

where E'_i , E''_i , and t_i are the storage modulus, loss modulus, and thickness of the i th individual layer, respectively, and t is the total film thickness.

The agreement between observed and calculated values is good, especially for the storage modulus, again indicating no mixing at the interfaces. It should be noted that E'' is subject to a larger error than E' because it is an indirectly measured quantity.

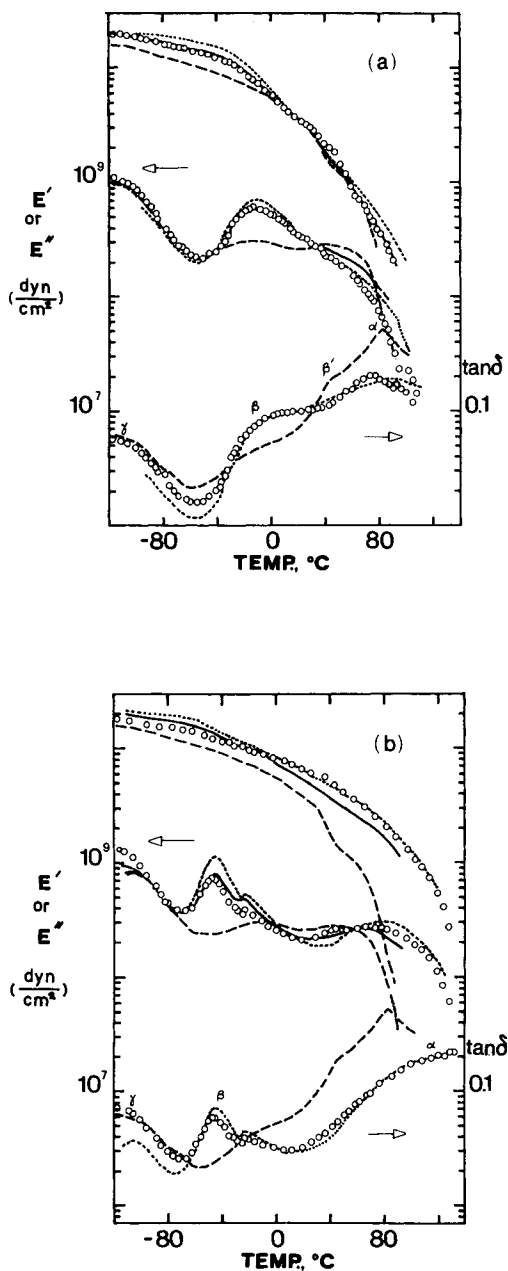


Fig. 3. Temperature dependence of storage modulus E' , loss modulus E'' , and loss tangent $\tan\delta$ of polyethylene-based composite films at 110 Hz: (a) (—○—) film 7, (---) LDPE, (-·-) ionomer; (b) (—○—) film 8, (---) rubber-modified HDPE, (-·-) ionomer. (—) Calculated values using parallel model (all Figures).

In Figure 4 it is seen that only the tensile modulus varies linearly with volume percent Kapton throughout the composition range. The storage modulus has the same value because of low damping. The ultimate properties attain their maximum value already at 80% by volume Kapton, giving a nonlinear composition dependence. In general, there is a reinforcement with respect to yield,

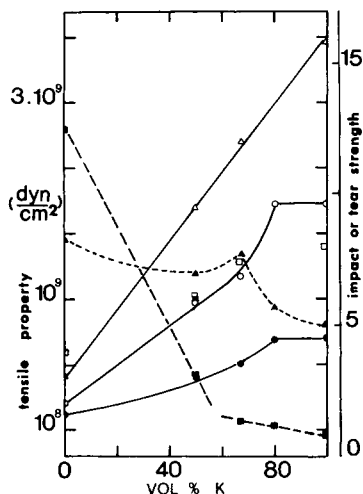


Fig. 4. Tensile and ultimate properties of Kapton-FEP composites: (—○—) ultimate tensile strength (dyn/cm²); (—●—) yield point at 3% (dyn/cm²); (—△—) tensile modulus (dyn/cm²) × 10⁻¹; (—▲—) loss modulus (β relaxation) (dyn/cm²); (—□—) impact strength (kg cm/mil); (—■—) tear strength, propagating Elmendorf (g/mil) × 10⁻¹.

TABLE II
Typical Mechanical Properties of Polyethylene-Based Composite and Pure Component Films^a

Film	Yield strength, kg/cm ²	Ultimate strength, kg/cm ²	Elongation, %	Tear strength propagating Elmendorf, g/mil	Area of β relaxation ^b
No. 7	110	237	400	20	0.0673
No. 8	165	177	420	60	0.0273
No. 9	118	226	470	80	0.1149
No. 10	112	209	450	55	0.0960
Ionomer ^c	136	350	250	~12	—
LDPE	82	122	~400	~100	—
EVA copolymer	99	163	~450	—	—

^a Machine direction at 25°C.

^b Quantity proportional to area, arbitrary units.

^c Surlyn 1601, du Pont.

ultimate strength, and impact strength. This is due to the higher elongation of the FEP component (300%) than the Kapton film (70%), leading to a higher ductile deformation of the latter beyond the 60% composition. However, beyond the 80% composition the decrease in tear strength is significant, limiting further reinforcement. A similar type of ductile reinforcement has been reported² for the pairs ionomer-nylon 66 and polystyrene-polyethylene.⁴

We note in Figure 4 that the loss modulus E'' associated with energy absorption is decreasing as the amount of Kapton increases. This explains why tear strength decreases in the same direction. Such correlation is well established for rubbers.¹³ Comparison of films 3 (two-ply) and 4 (three-ply), which have different structures but the same overall composition, did not reveal any significant difference in their properties.⁹ The simple additivity rule could satisfactorily predict the temperature variation of their dynamic mechanical properties E' and E'' .

Polyethylene-Based Composites

Ionomer-LDPE [Fig. 3(a)]

The relaxation behavior of the pure components has been adequately discussed.^{14,15} The main features of the relaxation spectrum of the composite film is a better resolution of the β peak, the disappearance of the β' peak, and a reduction of the α peak compared to that of the ionomer. The position of the α peak is also shifted to a lower temperature (76°C). Some mutual reinforcement (increase of E') is evident between 20° and 60°C while the disappearance of the β' peak indicates a reduction of hydrogen bonding. This is most probably a result of coextrusion and is further supported by IR examination of the composite film.

Comparison of the IR spectra of the pure components with that of the composite film indicates a new absorption band at 1740 cm^{-1} . This is attributed to the monomeric carbonyl stretching vibration.¹⁶ Correspondingly, the intensity of the 1700 cm^{-1} band attributed to dimerized carbonyl stretching vibration is decreased. More drastic changes associated with the internal viscosity are manifested by the reduction and shift to lower temperatures of the α relaxation. This shift can also be attributed to reduced hydrogen bonding. Combination of the more rigid ionomer with the flexible LDPE improves the ultimate strength more than what would be expected by simple linear additivity (see Table II). Mutual reinforcement takes place because of the ductile deformation of the ionomer film attached to LDPE with a higher capacity for elongation.

Rubber-Modified HDPE-Ionomer [Fig. 3(b)]

The main relaxations at -105°C (γ) and 120°C (α) are associated with the HDPE.¹⁴ The absorption at -45°C is due to the rubbery phase and the small peak at -24°C, to the high-frequency (or temperature) shoulder with respect to the main relaxation, predicted by Ferry and co-workers.¹⁷ The main features in the mechanical spectrum of the composite are those of the first component above. Again, the most significant change is associated with the α peak. Above room temperature there is considerable deviation of the E' values from those predicted by the simple parallel model. The connectivity of the layers is not simple because of the rubbery dispersed phase. A combination of a series and parallel model proposed by Takayanagi¹⁸ would be more appropriate. In Figure 5 it is seen that because of ductile mutual reinforcement the composite film has a higher ultimate strength than both pure components.

For films 9 and 10, the mechanical spectra could be predicted quite well using the parallel model. The relaxation spectrum of film 9 indicated some reduction in crystallinity which can be attributed to the coextrusion process. Stress-strain measurements indicated also a mutual reinforcement.

The tear strength of these composite films correlates well with the magnitude of the β relaxation. Tear strength increases with the area of the β (E'') relaxation (see Table II). An anomaly is observed in the case of the rubber-containing composite. This is probably due to the different reinforcing mechanism of the rubber-containing film and that of the rest of the films. In the latter case tear strength, like impact strength, may be related to movements in the main chain, while in film 8 the rubbery inclusion contributes additionally by arresting crack propagation at the rubber-plastic interface.

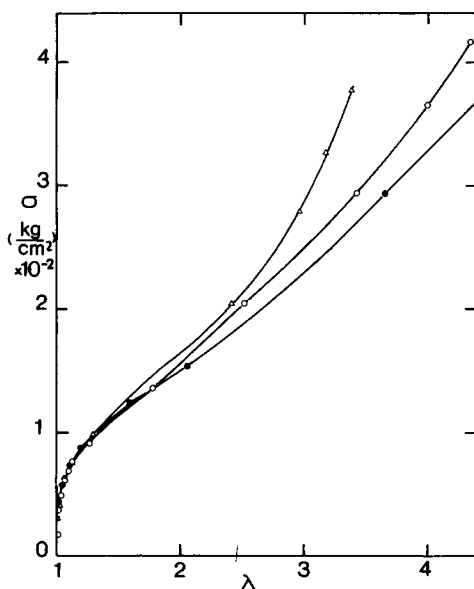


Fig. 5. True stress-strain properties of film 8 at 35°C: (—○—) composite; (—△—) ionomer; (—●—) rubber-modified HDPE.

CONCLUSIONS

The dynamic mechanical technique can indicate the degree of interaction in composite films when the adjacent layers are chemically related. Provided that the individual layers adhere strongly without mixing, the technique can also be used to examine chemically nonrelated film combinations. This is useful either for the purpose of correlating composite properties with those of the pure components or to obtain the relaxations of one of the components when the spectra of the other are quite "flat."

Ultimate properties can be related to low-temperature relaxations. Also, coextrusion ensures good interlayer adhesion in the composites studied and, as a rule, leads to mutual ductile reinforcement when rigid and flexible layers are combined.

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