

Hydrolytic Degradation of Polymeric Insulation Materials as Measured by Infrared Absorption Spectroscopy

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Synopsis

The hydrolytic degradation of certain polymeric insulation materials can be monitored by an infrared band-ratio spectroscopic method. These polymers, used in the precision electronic components of the aerospace industry, were a polyester (Mylar), a polyvinyl fluoride (Tedlar), and a polyimide (H-film). The polymer films were synthetically aged under selected conditions of temperature, moisture, and time. As infrared bands appeared, assignments of the functional group bands of the degradation products were made. The band-ratio data gave a quantitative indication of the extent of degradation. The polyimide film showed the greatest resistance to hydrolysis, followed by the polyvinyl fluoride, and lastly, the polyester.

Acceptable insulating materials used in the precision components of the aerospace industry must demonstrate a high resistance to hydrolytic degradation. Infrared absorption spectroscopy is one of the methods in use in this laboratory for investigating the potential insulating materials which are aged under controlled conditions of temperature and humidity. The infrared data enable one to select insulators that should not hydrolyze in a sealed electrical unit and should thus improve reliability and quality.

Three types of insulating film, supplied by the Du Pont Company, were tested for degradation in a hermetic application. These films were a polyester (Mylar), a poly(vinyl fluoride) (Tedlar), and a polyimide (H-film) (all commercial films supplied by Du Pont). As a result of the investigation, the insulating film found most suitable in resisting hydrolysis was H-film. Tedlar was less effective though still acceptable. The severe degradation of Mylar obviated its use in these electrical units.

It is known that Tedlar has superior film life at elevated temperatures and is more resistant to alkaline hydrolytic attack than is Mylar.¹ H-film, a recent development, is also known to have superior thermal properties relative to that of Mylar.² The thermal stability index,³ which is a measure of the difference in specific gravity of samples as a function of time and temperature, is often not a true environmental testing condition for the polymer. The infrared spectroscopic technique affords a means of mon-

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itoring the chemical changes under more realistic testing conditions of detecting degradation of films which appear acceptable.

Experimental

Samples of film, each 2 mils thick, were inserted into Pyrex test tubes. Measured amounts of distilled water were added. The test tubes were heat-sealed and aged at 160°C. for periods ranging up to 300 hr. The films were then removed from the test tubes and stored over anhydrous CaSO_4 in a desiccator until examined by infrared absorption spectroscopy. If the film had not crumbled, it was examined directly by the infrared spectrometer. If the film had degraded severely into a powder, it was examined as a KBr pellet. The Perkin-Elmer Model 421 infrared spectrophotometer was used for all measurements. All absorbance data are relative to baselines drawn tangent to appropriate minima.

Results and Discussion

Infrared spectroscopy has been used for following the degradation of polymers.⁴ For this study, we chose the band ratio method to follow degradation. As the degradation of Mylar proceeded, there were two general changes in the spectrum, one associated with changes in intensity of the regular Mylar spectrum and one associated with the appearance of new bands as (acidic) degradation products form (Table I).

TABLE I
Infrared Detection of Polyester Degradation

Conditions	Water added to Mylar, cc.	Appearance after test	Absorbance Ratios			
			965 cm. ⁻¹ 840 cm. ⁻¹	2655 cm. ⁻¹ 865 cm. ⁻¹	2540 cm. ⁻¹ 865 cm. ⁻¹	774 cm. ⁻¹ 865 cm. ⁻¹
Control, no heat, no H ₂ O	0	Film	1.15	0.00	0.05	0.00
160°C., 1 hr.	0.1	Film	1.01	0.00	0.05	0.00
	0.2	Film	0.97	0.00	0.06	0.00
	0.4	Film	0.96	0.00	0.04	0.00
	1.0	Film	0.81	0.00	0.05	0.00
160°C., 96 hr.	0.1	Brittle	1.12	0.07	0.14	0.00
	0.2	Powder	1.07	0.00	0.06	0.00
	0.4	Powder	0.90	0.00	0.07	0.00
160°C., 300 hr.	0.1	Powder	0.64	0.00	0.00	0.21
	0.2	Powder	0.00	1.12	1.54	1.87
	0.4	Powder	0.00	1.25	1.77	2.18
	1.0	Powder	0.00	1.34	1.98	2.64

The absorbance ratio changes at 965 cm.⁻¹/840 cm.⁻¹ reflected skeletal vibration changes as the polyester was hydrolyzed. The absorbance ratio changes at 2655 cm.⁻¹/865 cm.⁻¹, 2540 cm.⁻¹/865 cm.⁻¹, and 774 cm.⁻¹/865 cm.⁻¹ reflected the appearance of new or ingrowth bands, namely

TABLE II
Infrared Detection of Poly(vinyl Fluoride) Degradation

Conditions	Water added to Tedlar, cc.	Appearance after test	Absorbance ratios	
			3530 cm. ⁻¹	3430 cm. ⁻¹
			1960 cm. ⁻¹	788 cm. ⁻¹
Control, no heat, no H ₂ O	0	Film	0.00	0.00
160°C., 96 hr.	0.2	Film	0.55	0.89
	0.4	Film	0.55	0.92
	1.0	Film	0.64	0.98
160°C., 300 hr.	0.1	Film	0.66	1.08
	1.0	Brittle	1.17	1.63

carboxylic acid OH at 2655 and 2540 cm.⁻¹ and a skeletal vibration at 774 cm.⁻¹.

Tedlar, the poly(vinyl fluoride), showed greater resistance to hydrolysis than the polyester film. As degradation of the Tedlar began, ingrowth bands appeared at 3430 and 3530 cm.⁻¹ (alcoholic OH), 2540 cm.⁻¹ (acidic OH), 1690 cm.⁻¹ (aldehydic or ketonic C=O), 960 cm.⁻¹ (—CH=CH—, olefinic *trans*), and at 1575, 1498, 1462, and 788 cm.⁻¹. The latter four bands were unassigned. A quantitative indication of the degradation of Tedlar is shown in Table II.

The ratio at 3430 cm.⁻¹/788 cm.⁻¹ clearly showed the progression of degradation of Tedlar. Although other frequencies showed a change, the quantitative work was limited to bands of absorbance less than 0.6 in this study.

H-film, the polyimide, showed a significant resistance of hydrolysis. Only one spectral change was grossly evident, namely, the hydroxyl at 3620 cm.⁻¹ which broadened and increased in intensity as the test proceeded. The infrared changes in the spectrum of H-film, as a function of temperature and moisture, were mainly due to absorbance intensity differ-

TABLE III
Infrared Detection of Polyimide Degradation

Conditions	Water added to H-film, cc.	Appearance after test	Absorbance ratios			
			3550 cm. ⁻¹	3620 cm. ⁻¹	3620 cm. ⁻¹	3620 cm. ⁻¹
			744 cm. ⁻¹	768 cm. ⁻¹	744 cm. ⁻¹	629 cm. ⁻¹
Control, no heat, no H ₂ O	0	Film	0.70	0.76	0.96	0.50
160°C., 96 hr.	0.1	Film	0.93	0.96	1.10	0.61
	0.2	Film	1.11	1.25	1.41	0.69
	0.3	Film	2.22	1.59	2.32	0.86
160°C., 300 hr.	0.2	Film	1.28	1.24	1.43	0.70
	0.4	Film	2.81	1.98	2.88	0.99

ences and not ingrowth of bands. This is shown in Table III. These changes reflected intensity differences at 768 and 744 cm.^{-1} (aromatic CH deformation), at 629 cm.^{-1} (a secondary amide skeletal band), and at 3550 cm.^{-1} (an amide NH stretch).

The polyester showed evidence of physical degradation (embrittlement) after 96 hr. at 160°C. in the presence of 0.1 cc. H_2O . In the presence of the same amount of water, the poly(vinyl fluoride) was still a continuous film after 300 hr. at 160°C. During the entire test, the polyimide only showed slight discoloration but never any evidence of embrittlement at the most severe conditions. The H-film or polyimide became the insulation material of choice.

References

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Résumé

On peut déterminer la dégradation hydrolytique de certains polymères aptes à servir de matériaux d'isolation par spectroscopie infra-rouge en utilisant un rapport de bandes. Ces polymères employés dans des appareils électroniques de précision de l'industrie aérospatiale sont les suivants: un polyester (Mylar), un fluorure de polyvinyle (Tedlar) et une polyimide (H-film). Les films de plastique sont vieillis artificiellement sous diverses conditions de température, d'humidité et de temps. On attribue l'apparition de bandes d'absorption nouvelles à des produits de dégradation, le rapport des bandes donnant une indication quantitative du degré de dégradation. De tous les films étudiés, c'est le film de polyimide qui montre la plus grande résistance à l'hydrolyse, viennent ensuite le fluorure de polyvinyle et le polyester.

Zusammenfassung

Der hydrolytische Abbau gewisser polymerer Isolierungsmaterialien kann mittels einer infrarotspektroskopischen Methode zur Bestimmung des Bandenverhältnisses verfolgt werden. Die untersuchten Polymeren, die in den elektronischen Präzisionskomponenten der Raumfahrtindustrie verwendet werden, waren ein Polyester (Mylar), ein Polyvinylfluorid (Tedlar) und ein Polyimid (H-Film). Die Polymeren wurden künstlich unter ausgewählten Temperatur-, Feuchtigkeits-, und Zeitbedingungen gealtert. In dem Masse, als zugewachsene Banden auftraten, wurde eine Zuordnung der Banden von funktionellen Gruppen der Abbauprodukte vorgenommen. Die Daten für das Bandenverhältnis lieferten ein quantitatives Mass für den Abbau. Die Polyimidfilme zeigten die grösste Hydrolysenbeständigkeit, dann folgte das Polyvinylfluorid und schliesslich der Polyester.

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