

LETTERS TO THE EDITORS

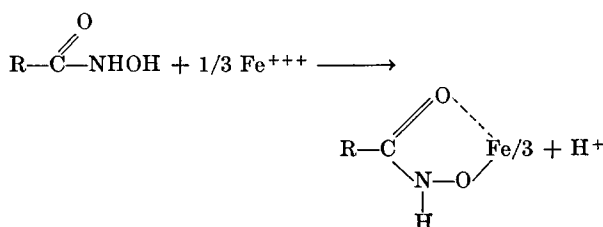
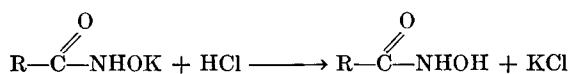
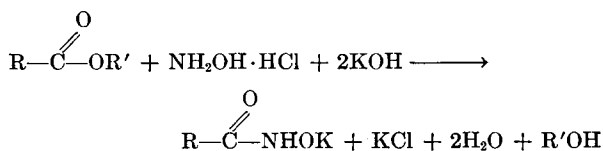
Colorimetric Differentiation of Polyester- and Polyether-Based Urethane Polymers

Urethane polymers, such as flexible and rigid foams, elastomers, various coatings, and adhesives, are formed by polyaddition polymerization of diisocyanates and polyhydroxyl compounds. In practically all commercial applications either polyesters or polyethers are used as hydroxyl terminated compounds. A quick, qualitative differentiation between urethane polymers based on polyesters and those based on polyethers is highly desirable because the successful application in special cases may depend on this knowledge and may save a large number of mechanical tests or a fairly complicated saponification followed by a more difficult determination of the hydrolysis products.

A general analytical method for the detection of polymers containing urethane groups was recently published.¹

Qualitative Color Test for Polyesters^{2,3}

The colorimetric test is based on the following reactions, where R and R' are di- or poly functional:



The hydroxamic acid from the polyester reacts with the ferric ion to form an inner complex salt which is water-soluble and of an intensive violet or purple color for most hydroxamic acids.

Reagents

- 2 N solution of KOH in methanol plus phenolphthalein to a dark pink color.
- Saturated solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in methanol.
- 1 N hydrochloric acid.
- 1-3% solution of FeCl_3 in water.

Procedure

Approximately 50 mg. of the polymer are cut into small pieces and reacted with a few drops of Reagent (a) and then a few drops of Reagent (b) are added. The resulting mixture must be alkaline as indicated by the phenolphthalein. Heat-

ing for 20-40 seconds to not more than 50°C. will increase the reactivity considerably but is only necessary for higher crosslinked polymers. After 30-60 seconds reaction time, the mixture is acidified with Reagent (c) and reacted with one drop of Reagent (d). In the presence of esters the characteristic violet color will appear immediately.

Discussion

This color test is only specific for polyesters if no other esters are present, as from solvent, plasticizers, or flow agents. Normally occurring functional groups in urethane polymers, such as urethane, urea, allophanate, biuret, amine, or isocyanate groups, do not interfere with the color test under the test conditions. Since ethers also will not react with hydroxylamine in this test, the polyester-based polymers can easily be differentiated from the polyether-based polymers.

Polyesters made from castor oil or dimerized fatty acids, sometimes used in urethane polymers, will give a brownish or brownish-violet color rather than the violet color. This brownish color, however, should not be confused with the yellow-brownish color resulting from the ferric chloride alone.

On some materials, such as flexible foam, the test may be carried out as a spot test directly on the foam by dropping a few drops of each of the four reagents in order. In this case the test may be made at room temperature and the color will develop immediately. The entire test requires about one minute to complete.

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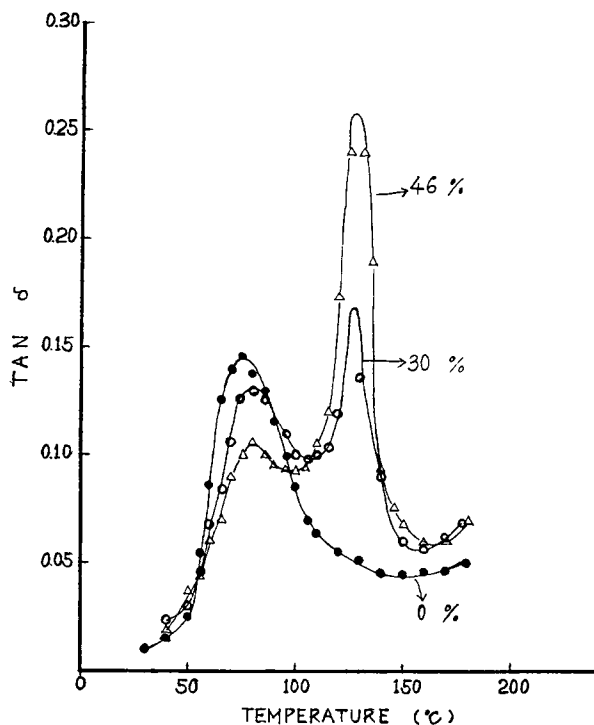
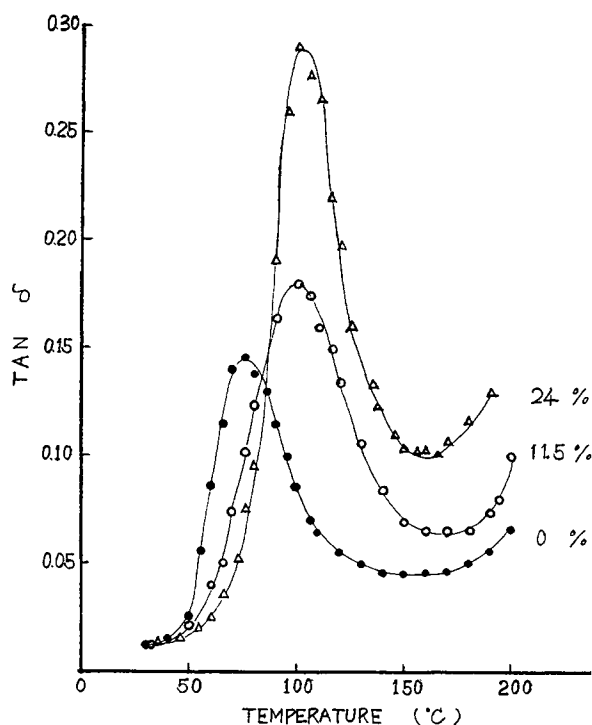
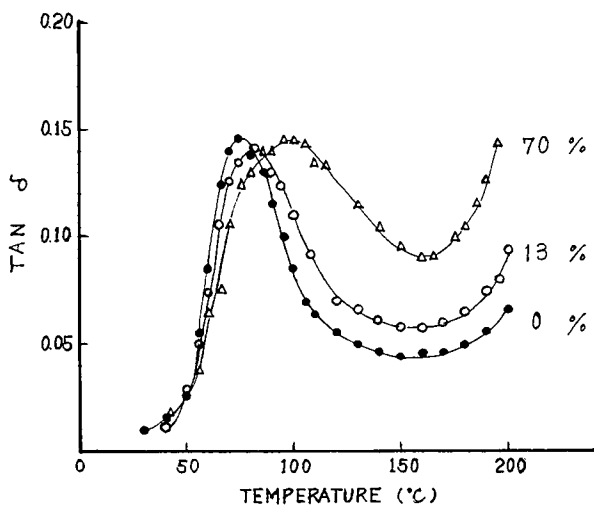
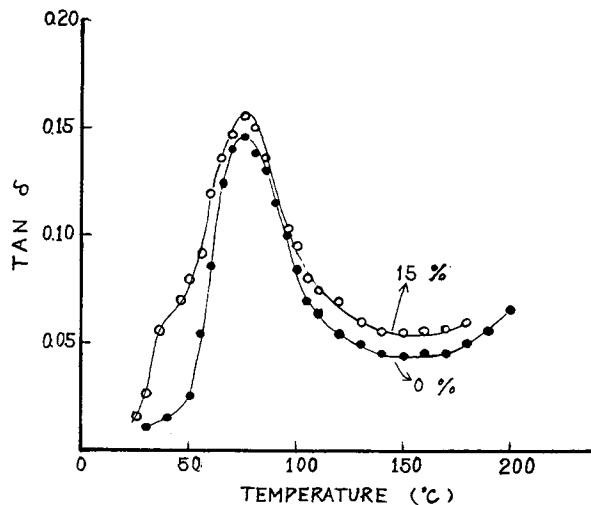
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Dynamic Mechanical Properties of Graft Copolymers of Nylon

Many works^{1,2} have been devoted to the measurement of the dynamic mechanical properties of polymers in the solid state as a function of temperature for the elucidation of internal structure and atomic movement. However, studies for graft copolymers have not as yet been published. Recently a method for the preparation of graft copolymers by irradiation of ionizing radiations has been presented.^{3,4}

Fig. 1. Tan δ vs. temperature for nylon grafted with MMA.Fig. 2. Tan δ vs. temperature for nylon grafted with AA.Fig. 3. Tan δ vs. temperature for nylon grafted with AN.Fig. 4. Tan δ vs. temperature for nylon grafted with VAc.

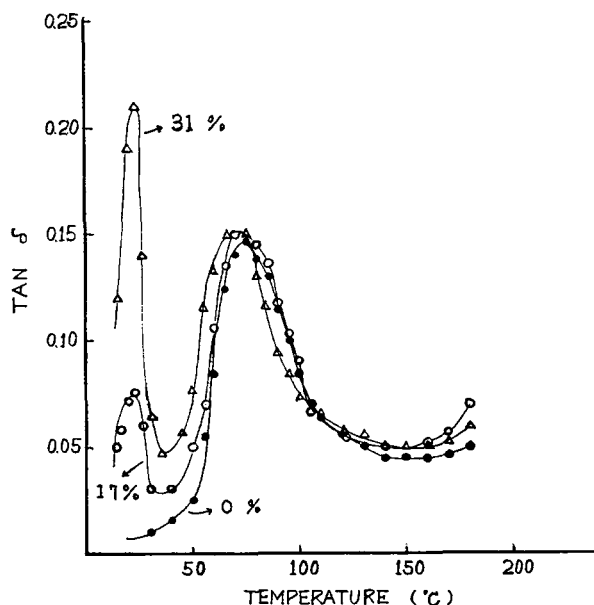
This work studies the temperature dependency of the torsional rigidity and tan δ (loss factor) for graft copolymers of nylon prepared by the irradiation method.

Undrawn 60 denier nylon 6 filament was used as a trunk polymer. Filamentous graft copolymers were obtained by irradiation of nylon filament with γ -rays from Co^{60} in the vapor phase of vinyl monomer mixed with water. Preliminary experiments showed that the addition of water increased the rate of graft polymerization remarkably. By this technique, an irradiation for 10 hours or less at a dose rate of 1×10^4 r/hr. at room temperature led to a doubling of the weight of the sample. The vinyl monomers which were grafted were methyl methacrylate (MMA), acrylic

acid (AA), acrylonitrile (AN), vinyl acetate (VAc), methyl acrylate (MA), and ethyl acrylate (EA).

In the present study the rigidity and tan δ for the grafted filaments were measured by the free vibration method. To determine the dependency of these properties on the moisture content, the samples were dried before measurement and set in a vacuum to carry out the measurements at various temperatures.

Figures 1 to 7 show the rigidity and tan δ for the prepared graft copolymers as functions of temperature. Numerical values (%) on the curves in the figures indicate the degree of grafting, which is defined as the ratio of the increased weight to the original weight.

Fig. 5. Tan δ vs. temperature for nylon grafted with MA.

There are two relaxation regions characterized by peaks in tan δ in the temperature range from -20 to 150°C . for each graft copolymer. All samples have one peak located at about 80°C . Nylon 6 also has a relaxation region at about 80°C . The temperature of the other relaxation peak is close to the relaxation peak of the corresponding vinyl homopolymer, as shown in Table I. Moreover, the height of this peak increases as the degree of grafting increases.

TABLE I

Monomer	Relaxation region other than 80°C . for graft copolymer ($^\circ\text{C}$.)	Relaxation region for vinyl homopolymer ¹ ($^\circ\text{C}$.)
MMA	125	120
AA	105	—
AN	100	100
VAc	38	33
MA	21	25
EA	-5	-5

It is generally believed that the relaxation peak reflects the onset of some chain mobility. For example, the origin of the 80°C . peak in nylon, which is proposed as the α' peak by Schmieider and Wolf,¹ and Deeley, Woodward, Sauer, and Kline,² is said to arise from segmental motion caused by the breaking of the hydrogen bonded intermolecular bridge in the amorphous region. It is therefore highly probable that the two peaks for graft copolymers are due to the onset of segmental motion of the trunk nylon polymer and the grafted vinyl polymer, respectively.

Another interesting result is that when the temperature of the relaxation peak of the vinyl homopolymer is higher than that of nylon (i.e., 80°C .), the height of relaxation peak at 80°C . decreases. However, on the other hand, when the temperature of the peak of the vinyl homopolymer is lower

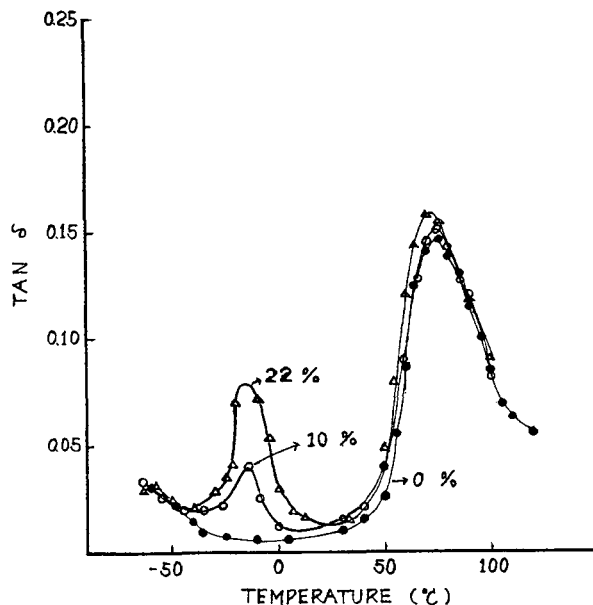
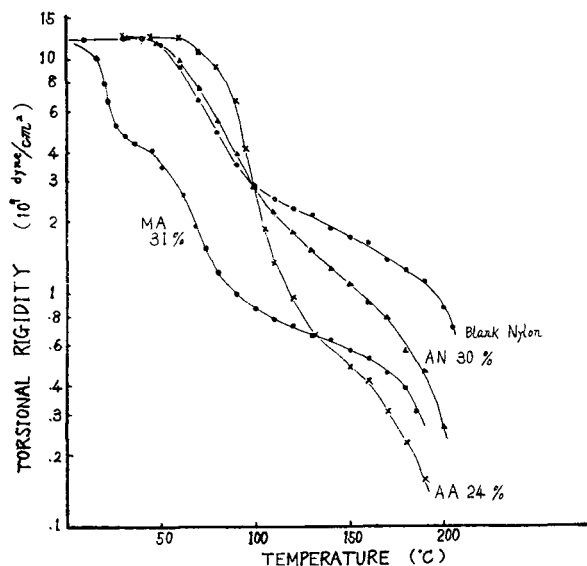
Fig. 6. Tan δ vs. temperature for nylon grafted with EA.

Fig. 7. Torsional rigidity vs. temperature for several graft copolymers of nylon.

than 80°C ., the shape of the peak remains unaltered from that of the ungrafted nylon.

This fact may be explained as follows: In the former case the grafted vinyl polymer has not relaxed and is in the frozen state at 80°C . Accordingly, at this temperature the grafted vinyl polymer may fix, to some extent, the motion of nylon molecules at branching points, so the height of the peak at 80°C . is lowered. However, in the latter case, the vinyl polymer has already relaxed at 80°C .; in other words the segments of this polymer can move freely at this temperature. Therefore this grafted vinyl polymer does not affect the segmental motion of the trunk nylon molecules, so the shape of the 80°C . peak is not altered.

Similar results were obtained for the graft copolymers of polyethylene.

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The Graft Polymerization of Methyl Methacrylate to Natural Rubber

At the recent International High Polymer Conference (Nottingham, July 21-24, 1958) the problem of isolating ungrafted polymethyl methacrylate from a mixture with grafted polymethyl methacrylate-natural rubber and free natural rubber attracted some comment. Cooper, Vaughan, Miller, and Fielden¹ obtained free homopolymer by extracting the reaction product, either in the form of a cast film or as the coagulated and dried mixture, with hot acetone for a minimum period of 24 hr. Turner and Angier² and Kobryner and Bandaret³ pre-extracted ungelled natural rubber with cold gasoline and then isolated free homopolymer by extracting with hot acetone for three to five days. An accurate estimate of the proportions of ungrafted polymer is of great significance in determining the reaction kinetics of the γ -radiation-initiated graft copolymerization. It was decided therefore to compare several techniques for the isolation of uncombined homopolymer. Five graft polymer mixes containing 50 parts of polymethyl methacrylate per 100 parts of natural rubber were examined. Sample A was a tertiary butyl hydroperoxide-polyamine-initiated system whereas the others were prepared using γ -radiation initiation under conditions which gave fairly high homopolymer contents. The results for percentage free homopolymer from extraction with hot acetone data are given in Table I.

It can be seen that extraction for less than 48 hr. gives low results and that 24 hr. extraction removes only about 80% of the free polymer. The amount is dependent, as would be expected, on the size of the sample, and using 0.5 g. quantities of cast film 94% of the free polymer is removed after 24 hr. extraction. It follows, therefore, that the results for proportions of grafted polymer quoted in the earlier paper¹ are too high, but, since the total amounts of free homopolymer (10-20%) were small, the values are not seriously affected.

One or two experiments were also carried out where the latex was not coagulated. Benzene was added with shaking

to the graft polymer latex and then free rubber and graft copolymer precipitated by pouring into excess acetone. Suspended graft copolymer was removed by centrifuging the solution. The amount of polymethyl methacrylate isolated in this way was generally considerably higher (ca. 20%) than in corresponding extraction experiments. However, the purity of the free polymethyl methacrylate isolated, as judged by oxygen content, was low (ca. 98%) and it clearly contained some rubber. If this were present as short chains attached to polymethyl methacrylate, the estimate of free homopolymer by this technique would give much higher values.

TABLE I

Sample	Treatment	Sample size, g.	Extraction time, hr.	% homopolymer
A	Acetone extraction of solid rubber	2	16	54.0
			32	59.7
			72	59.7
B	Acetone extraction of cast film	2	20	38.0
			44	47.0
			68	48.4
			84	48.4
B	Acetone extraction of coagulated polymer	2	24	41.7
			48	46.5
			64	46.9
C	Acetone extraction of cast film	2	24	23.3
			48	26.8
		0.5	24	26.6
			48	28.3
			72	28.6
D	Acetone extraction of cast film	0.5	24	24.4
			72	31.7
E	Acetone extraction of cast film	2	24	31.1
			72	37.7

It is concluded that all soluble homopolymer is extracted by hot acetone in 48-72 hr., the time being dependent on the size of the sample. The methods, however, particularly the precipitation separation, require further examination since the solubility characteristics of graft copolymers rich in one component are not completely known.

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