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Characterization of an impact-modified nylon 66

M. T. HAHN, R. W. HERTZBERG, J. A. MANSON
Materials Research Center, Coxe Laboratory No. 32, Lehigh University, Bethlehem, PA 18015, USA

The structure and chemical compositions of an impact-modified nylon 66 are investigated using transmission electron microscopy (TEM), infrared spectroscopy, optical microscopy, differential scanning calorimetry (DSC), and dynamic mechanical spectroscopy. The morphology is found to contain spherical domains of a partially-crosslinked EPDM rubbery phase which are embedded within an N66 matrix. These spherical domains are 0.2 to 0.8 μm in diameter and comprise approximately 20 vol % of the blend; the N66 matrix in the toughened polymer contains spherulites which are 1 μm in diameter whereas the neat N66 solid contains 10 μm diameter spherulites. The crystalline fraction in N66 is found to be relatively independent of rubber content. The dynamic modulus is found to be more strongly affected by the addition of the rubbery phase than by changes in the morphology of the nylon.

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1. Introduction

There is a growing need to determine the response of polymeric materials to both static and cyclic stresses. Regarding the latter, it is recognized that semicrystalline and rubber-modified polymers generally show good resistance to fatigue crack propagation (FCP) [1]. Thus it is not surprising that an impact-modified grade of nylon has been found to be one of the most fatigue resistant polymers tested to date [2]. In this earlier study, the FCP resistance of impact-modified nylon was measured but no attempt was made to characterize the associated structure of this material. The present investigation was undertaken to study the structure of this polymer. Additional fatigue data were generated and are described elsewhere [3, 4].

2. Experimental procedures

2.1. Material composition

Injection-moulded plaques of the materials used in this study, 12.7 cm × 7.5 cm × 0.89 cm, were obtained in the dry as-moulded condition and stored in a desiccator prior to use. The compositions of the plaques included neat nylon 66 (Zytel 101), impact-modified nylon 66 (Hi-N66) (trade name Zytel ST801), and blends of Hi-N66 and nylon 66 containing 25, 50 and 75% Hi-N66. Hi-N66 consists of an unspecified polymer(s) added to neat nylon for increased toughness [5]. The number-average molecular weight, $\bar{M}_n$, of the nylon matrix was 17 000 according to the manufacturer and 17 800 as determined by intrinsic viscosity measurements of the Zytel 101 [6, 7]. No attempt was made to measure $\bar{M}_n$ in the nylon blends since it was not known whether separation of the nylon from the modifying phase would affect its molecular weight.

Since moisture has a profound effect on the mechanical properties of nylon, specimens were fatigue tested with moisture contents ranging from the dry as-moulded condition (< 0.2 wt %) to the fully-saturated state (8.5 wt %). To examine the effect of the method of water equilibration on the fatigue behaviour of the nylon, specimens were equilibrated either at elevated temperature or at room temperature. To equilibrate at elevated temperature, plaques of nylon were immersed in boiling water or in various boiling salt solutions, thereby achieving the range of relative humidities and equilibrium water contents shown in Table I [8, 9]. Equilibration procedures are discussed elsewhere [7]. For equilibration at room temperature,

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TABLE I Moisture equilibration of nylon 66

% Relative humidity	wt % H_2O in nylon	
0	0.2	Dry as-moulded
50	2.6	Immersed in boiling saturated potassium acetate solution for 100 h
66	4.0	Immersed in boiling saturated sodium phosphate solution for 100 h
100	8.5	Immersed in boiling water for 138 h

the plaques were stored in jars above water or saturated salt solutions at room temperature (24 ± 2° C) for approximately two years.

The moisture contents given in Tables I and II represent weight per cent water in the nylon 66 phase only since the impact-modifying phase does not absorb a measurable amount of water. As such, the amount of water imbibed by a plaque under a given set of conditions can be used to infer the amount of impact modifier added. After equilibration, all specimens were stored at the appropriate relative humidities until testing.

2.2. Spectroscopy and calorimetry

The storage modulus, E', and the loss compliance, D'', were measured by R. W. Lang and S. M. Webler using a computer-automated Rheovibron (model DDV-III C manufactured by IMASS Corp.). Tests were conducted on specimens 2 mm x 4 mm x 40 mm in size, in the temperature range from $-150°$ C to $+150°$ C. The heating rate was approximately 1° C $\min^{-1}$.

The crystallinity of the neat nylon and nylon blends was measured by J. Michel with a differential scanning calorimeter (DSC) manufactured by Perkin-Elmer (Model DCS-1B). Samples approximately 3 mm in diameter and 1 mm thick were cut from the centres of the plaques (thus minimizing edge effects). A heating rate of 20° C $\min^{-1}$ was employed with crystallinity being calculated using the size of the endothermic peak near 545 K. Two to three scans were made on each sample after allowing the disc to cool below 400 K between scans.

Infrared spectroscopy was used to identify the modifying phase of the Hi-N66 polymer blend. Samples were prepared from the plaques of Hi-N66 using two different methods. In one procedure, the nylon was dissolved from the polymer blend using formic acid. Since neat nylon 66 dissolves completely in formic acid and leaves a clear liquid, the milky liquid formed when the Hi-N66 was placed in formic acid presumably represents a suspension of the modifying phase in a solution of formic acid and the dissolved nylon. The suspension was vacuum-filtered with a 1.0 μm polycarbonate Millipore filter and washed with formic acid. The residue from the filtration was found to be partially soluble in tetrahydrofuran (THF).

TABLE II Results of DSC measurements on nylon blends

Material	T_{in}(K)	T_{max}(K)	T_{out}(K)	% Crystallinity
100% Hi-N66*	518	548	574	36.2
100% Hi-N66†	504	542	556	31.3
100% Hi-N66‡	505	545	560	31.7
Average % Crystallinity				33.1
75% Hi-N66*	504	542	555	29.2
75% Hi-N66†	504	542	555	33.3
Average % Crystallinity				31.2
50% Hi-N66*	505	540	550	33.3
50% Hi-N66†	505	540	555	32.6
50% Hi-N66†	500	543	555	33.6
Average % Crystallinity				32.8
25% Hi-N66*	504	542	551	32.2
25% Hi-N66*	507	547	565	32.3
25% Hi-N66§	505	547	560	28.5
Average % Crystallinity				30.7
Zytel 101				30

Thermal treatment: *As-received
†Cooled to 400 K in N_2
‡Cooled to 310 K in N_2
§Cooled to 350 K in N_2.

This THF-soluble portion was dipped onto a sodium chloride plate and the solvent evaporated to form a thin film on the plate. In the second sample-preparation method, the Hi-N66 itself was placed directly in THF and the soluble portion dipped onto a plate to form a film. Since nylon 66 does not dissolve in THF, the two methods should give similar results.

Preliminary IR results suggested that the modifying phase was ethylene-propylene-diene monomer rubber (EPDM); therefore, for comparison, a sample was prepared from EPDM supplied by Exxon Chemical Co., having a composition of 47.4% ethylene, 47.4% propylene and 5.2% norbornadiene. Like the modifying phase, the EPDM also did not dissolve completely in the THF, which indicates some crosslinking in both. The THF-soluble portion was dripped onto a sodium chloride plate to form a film.

Infrared spectra (per cent transmission against wave number) of the several samples were obtained with the assistance of Professor C. S. Kraihanzel, using a Perkin-Elmer Infrared Spectroscope. Scan time was 10 min. Results of consecutive tests were reproducible, thereby indicating that the solvent had been completely evaporated.

2.3. Microscopy

At the beginning of this work, it was not known whether the modifying phase in Hi-N66 had unsaturated carbon–carbon double bonds. However, the osmium tetroxide (OsO_4) staining technique, developed by Kato [10, 11] worked well. The reaction of OsO_4 with unsaturated carbon–carbon bonds creates atomic number contrast when viewed in the transmission electron microscope (TEM); that is, areas with unsaturated double bonds fix osmium and hence reveal a darkened image. Small pieces of the nylon blends, nominally 3 mm x 3 mm x 10 mm, were placed in a small glass jar with 0.2 g of OsO_4 for one week. The OsO_4 vaporized and thus stained the samples. Neat nylon did not stain during this treatment, indicating that all of the staining took place in the modifying phase. An ultramicrotome was used to cut slices of approximately 0.1 to 0.2 μm from the stained pieces. The staining made the polymers more brittle and easy to slice. These sections were prepared in three orientations in order to determine whether the microstructure of the material was isotropic. The slices were placed on copper grids and examined in a Philips EM300 TEM at accelerating voltages of 40 to 60 eV and magnifications from 11 000 to 80 000 times.

The spherulitic structure of the nylon was examined in transmitted light using thin sections. Two sectioning procedures were used with equal success. In the first method, 0.1 to 1.0 μm thick slices were cut using an ultramicrotome and then placed on a glass slide. In the second procedure, pieces of nylon were thinned by mechanical grinding through 600 grit silicon carbide paper, followed by polishing on wheels with slurries of 1.0 μm and 0.3 μm alumina powder. Samples were polished on one side and then attached to an aluminium specimen stub with double-stick cellophane tape. The other side of the sample was then ground and polished in similar fashion to the desired thickness.

3. Results and discussion

3.1. Characterization of modifying phase

As mentioned previously, the modifying phase in Hi-N66 contained double bonds which permitted TEM examination of samples stained with osmium tetroxide. TEM micrographs of 25, 50, 75 and 100% Hi-N66 are shown in Figs. 1 to 3. The modifying phase, which appears dark in these micrographs, is in the form of 0.2 to 0.8 μm diameter spheres. Though the average spacing of these particles is also 0.2 to 0.8 μm, their distribution is not completely random. The modifying phase tended to agglomerate, particularly in the leaner blends, as shown in Fig. 1. The area fraction of the dark-stained phase is about 0.2 in the 100% Hi-N66 material, in good agreement with the estimate of the fraction of the modifying phase from measurements of water adsorption. [Based

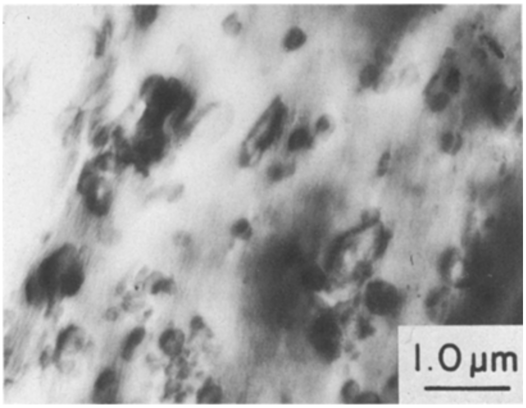

Figure 1 TEM micrographs of 50% Hi-N66, osmium tetroxide strain. Note clumping of the modifying phase.

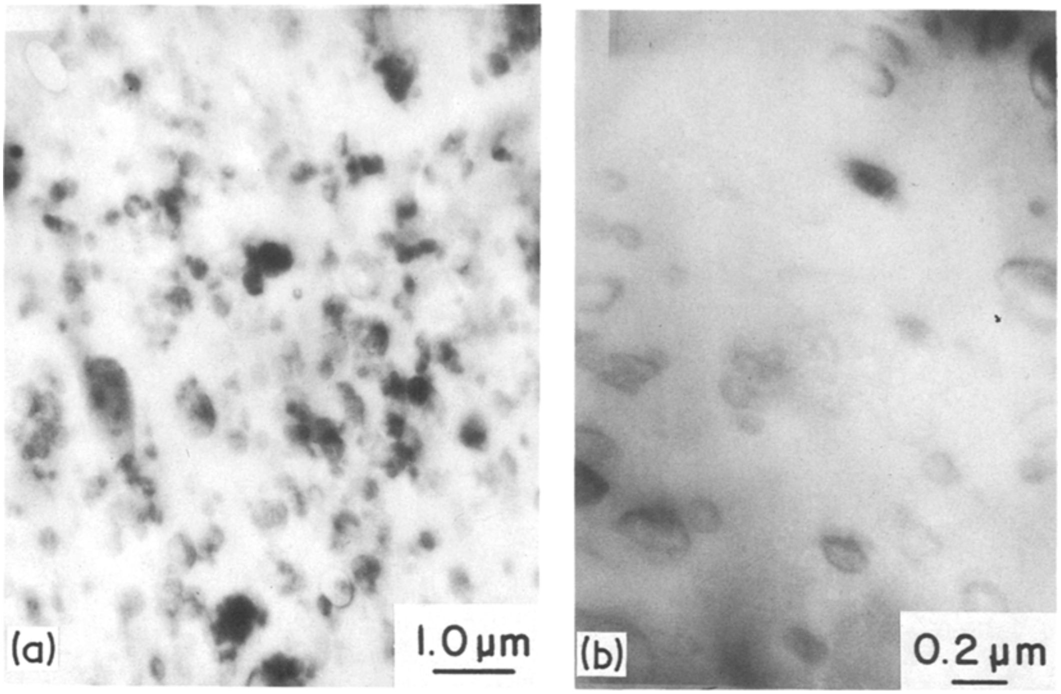

Figure 2 TEM micrographs of 75% Hi-N66, osmium tetroxide strain. The projection of the modifying phase onto the photograph is circular in both the (a) transverse and (b) short transverse directions.

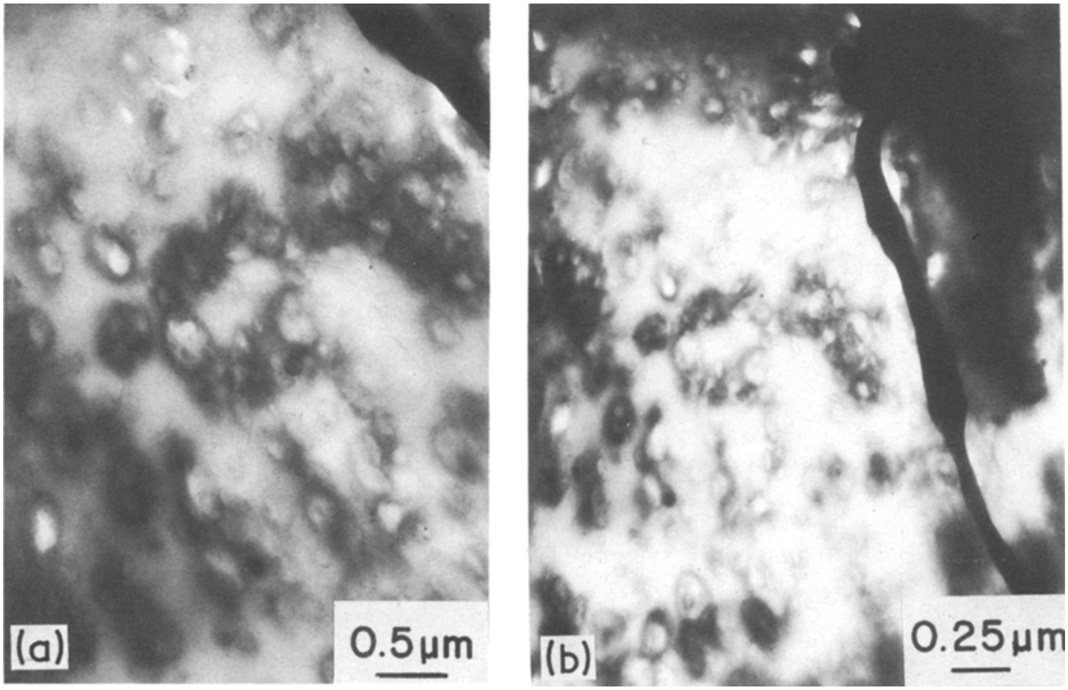

Figure 3 TEM micrographs of 100% Hi-N66, osmium tetroxide strain. Core-shell structure of the modifying phase is apparent both (a) before and (b) after restaining.

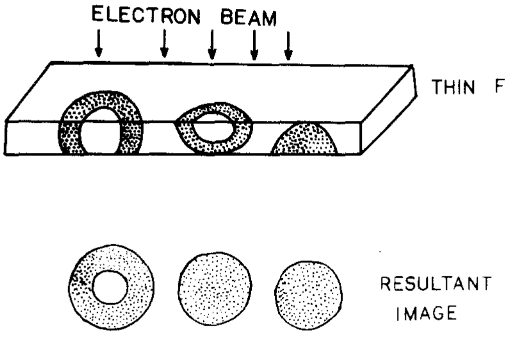

Figure 4 Schema showing interaction of electron beam with three modifying phase particles. The core-shell morphology would be observed in (a) but not in (b) or (c).

on the assumption that the modifying phase does not absorb water, the water content of Hi-N66 at saturation, 6.7% [9], indicates that the blend contains approximately 21% modifying phase (with proportionately less in the other blends)]. To check for possible shape anisotropy of the modifying phase, slices of 75% Hi-N66 were cut from planes parallel to the short transverse (S) and transverse (T) directions, respectively. The circular appearance of the particles seen in both sections (Fig. 2) reveal that the modifying phase assumes a spherical shape.

Often the modifying phase appeared to have a core-shell structure with a darker-coloured shell which surrounded a lighter core. At first, it was thought that the interior of the rubber particles might be incompletely stained. However, the core-shell morphology persisted after thin sections were re-exposed to OsO_4 vapour for an additional seven days. Since the light cores are not completely electron-transparent, it is safe to conclude that they are not holes caused by the tearing-out of the centres of rubber particles during ultramicrotoming. The most probable explanation of the observed core-shell morphology is that the modifying phase consists of an unsaturated (stainable) shell grafted onto a saturated (unstainable) core, in order to achieve good bonding with the nylon matrix. Indeed, examples of such practice are cited in the patent literature for Hi-N66 [5]. Since the thickness of the microtomed slices, 0.1 to 0.15 μm, is slightly less than the diameter of many of the particles, evidence for the core-shell morphology along with "apparent" solid core-shaped particles would be expected (Fig. 4).

Infrared spectra of the modifying phase and of EPDM (ethylene-propylene-diene monomer rubber) are shown in Figs. 4 to 7. Comparison of the measured spectra of the modifying phase with the measured spectrum of EPDM and with spectra from the literature (together with information from dynamic mechanical tests and from transmission electron microscopy) provide strong evidence for the presence of EPDM. Note that the spectra of the modifying phase (Figs. 5 and 6) lack the peak at 3250 cm^{-1} which is seen in the IR spectrum of nylon. The absence of this peak, corresponding to the –NH (amide) group, indicates

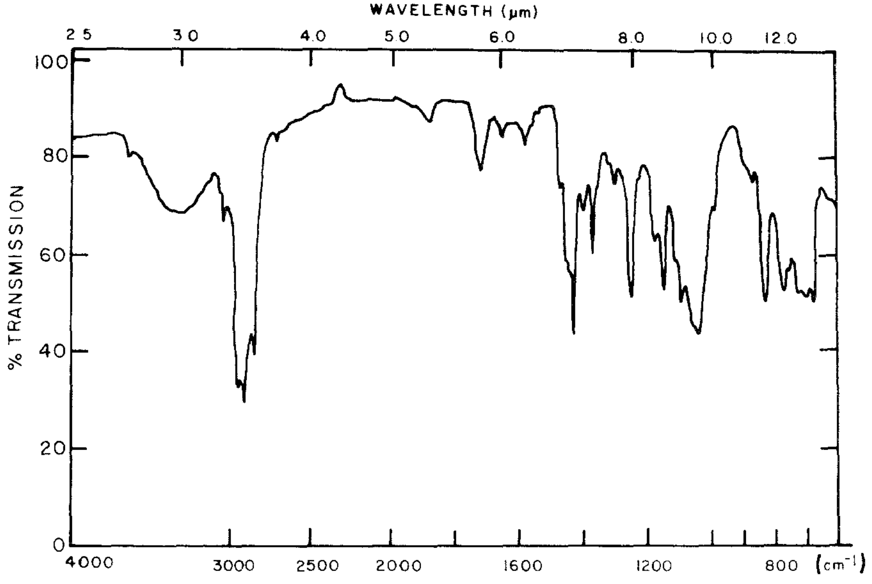

Figure 5 Infrared spectrum of modifying phase (THF-soluble portion of residue after dissolving nylon with formic acid).

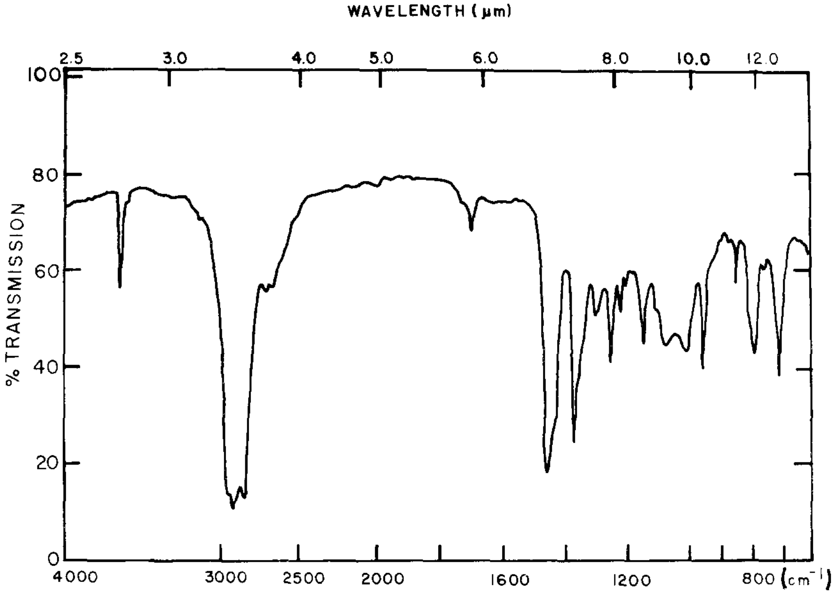

Figure 6 Infrared spectrum of modifying phase (THF-soluble portion of Hi-N66).

that the nylon was completely removed from the residue used for the IR spectra determination of the modifying phase. (Recall that both the modifying phase and the EPDM were only partially soluble in THF.

The most prominent bands in the spectra are caused by the $-CH_2-$ and $-CH_3$ groups. These bands are shown clearly in both Figs. 5 and 6. The bands at 2960 and 1375 cm^{-1} are due to $-CH_3$; the bands at 2920, 2850, 1460 and 1255 cm^{-1} are due to $-CH_2-$. Except for the peak at 1255 cm^{-1}, all of these peaks are present in the EPDM spectrum as well. The absence of other significant peaks indicates that the modifying phase is composed predominantly of $-CH_3$ and $-CH_2-$ groups, as in EPDM. Tertiary carbons $=CH-$, would also be expected but are not seen because they do not have strong IR absorption bands. Other polymers besides EPDM (for example, polypropylene, polyethylene and polyisobutylene)

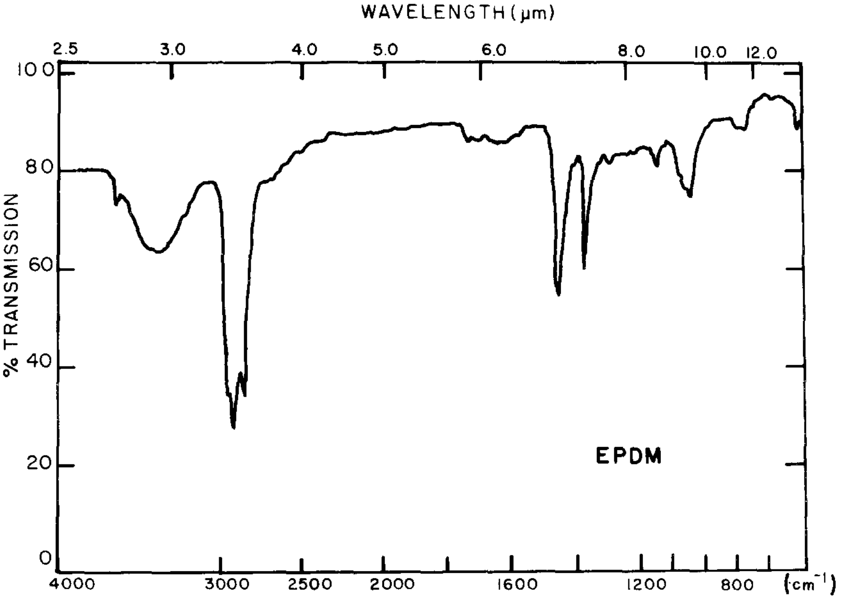

Figure 7 Infrared spectrum of EPDM.

also are composed of the $-CH_3$ and $-CH_2-$ groups, but they may be ruled out for various reasons. Though polypropylene (PP) and polyethylene (PE) have spectra similar to the modifying phase, both PP and PE are insoluble in THF. Comparing the spectra of PE and PP with that of the modifying phase, the relative heights of the peaks from the methyl and the $-CH_2-$ groups for the modifying phase were found to be intermediate between PP and PE. This suggests that in the modifying phase the concentration of methyl groups is intermediate between that of PP and PE, as would be expected of EPDM. Polyisobutylene may also be ruled out since, in its IR spectrum, the $-CH_3$ absorption bands which occur near 1375 and 960 cm^{-1}, are split because of the two methyl groups on the same carbon atom.

The modifying phase may also contain carbon–carbon and carbon–oxygen double bonds, as suggested by the bands seen at 1710 and 1640 cm^{-1}, respectively. This evidence is not strong, but it may be correct since it is in agreement with the observation that the modifying phase is stainable with OsO_4. Carbon–carbon double bonds would be found in EPDM, for example. The patent literature also cites acid groups in some of the possible formulations for the modifying phase [5].

In summary, the IR spectra offer strong proof that the modifying phase is EPDM. Furthermore, the glass transition temperature, T_g, of EPDM, $-60°$ C [12], is near the T_g of the modifying phase as observed in the dynamic mechanical studies ($-50°$ C) (see below). Both the IR spectra and the stainability of the material suggest that some double bonds are present.

3.2. Characterization of nylon 66 phase

The crystallinity of the nylon phase in the nylon blends was measured by differential scanning calorimetry (DSC) after making allowance for the amount of modifying phase present in the blend. Results of individual runs and average values of crystallinity are shown in Table II. It can be seen that the crystallinity of the nylon blends is approximately 31% and is not strongly affected by the amount of modifying phase.

The rubber particles in Hi-66 might be expected to influence the spherulite size, since the rubber particles could act as nucleation sites for crystal growth. This is especially likely since the rubbery phase may have a chemical affinity for nylon in order to achieve good bonding. Microscopic observations of thin sections of nylon using transmitted polarized light revealed that the spherulite size is, indeed, smaller in the modified nylon blends than in the neat nylon. Fig. 8 shows the microstructure in unmodified nylon 66 and reveals spherulites which are 10 to 20 μm in diamater. A spherulitic structure was also observed in the Hi-N66 blends, though the diameter of these regions was only 1 to 2 μm. As such, it was difficult to reveal the spherulitic structure with conventional metallographic procedures (Fig. 9). The size of the crystalline regions in the Hi-N66 blends was similar, regardless of the amount of rubbery phase present; this suggests that increasing the amount of "nucleating agent" had no effect on the spherulite size beyond that seen in the 25% Hi-N66. Thus, the nylon phase in any of the modified nylon blends has the same spherulite size which is approximately an order of magnitude smaller than spherulites found in the neat nylon. At the same time, the per cent crystallinity in both the blends and the neat polymer were comparable (recall Table I).

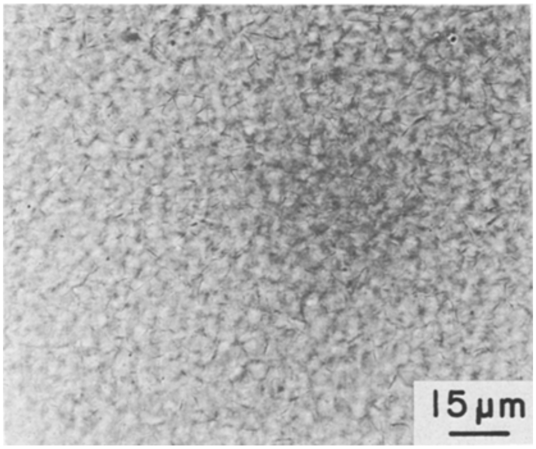

Figure 8 Transmitted light micrograph of nylon 66.

3.3. Viscoelastic properties of Hi-N66 blends

Fig. 10 shows the effect of water on the dynamic modulus of unmodified nylon. The storage modulus, E', and the loss compliance, D'', are shown for nylon with water contents of 0.2, 2.2, 4.0 and 8.5%. These viscoelastic data span the range of water contents used in the FCP tests. The effect of water is found to be similar to findings of previous investigators [13, 14]. That is, the addition of water shifts the glass transition

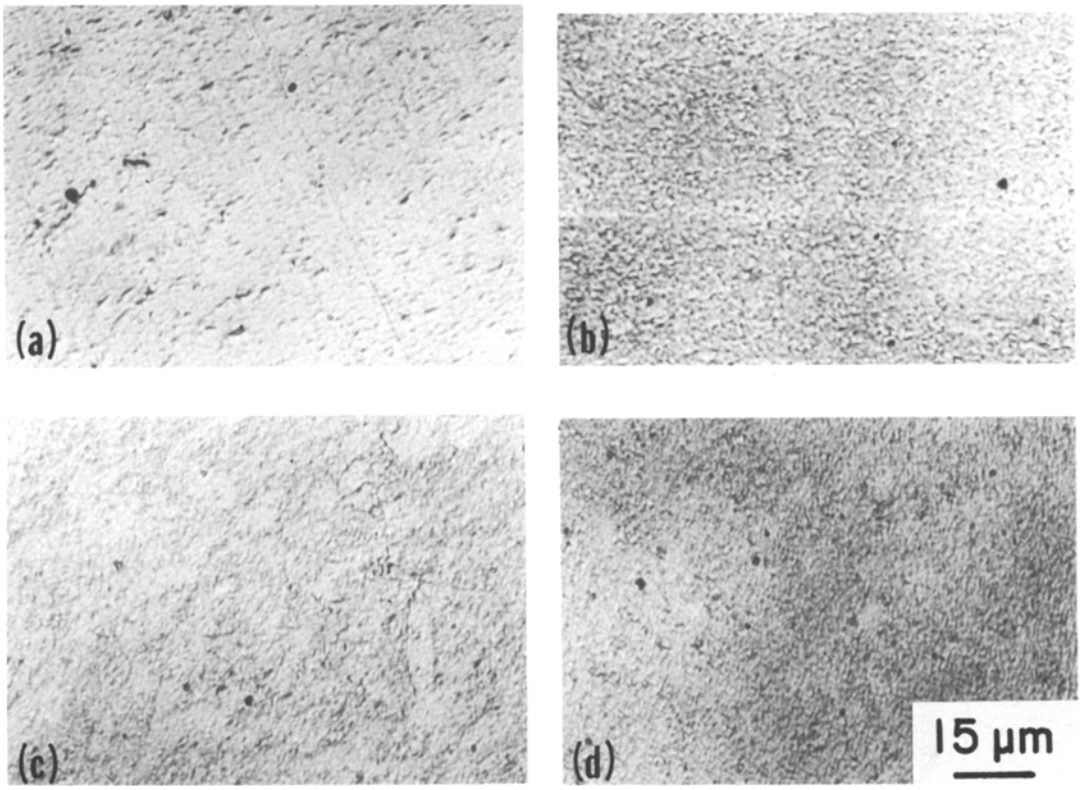

Figure 9 Transmitted light micrographs of (a) 25%, (b) 50%, (c) 75% and (d) 100% Hi-N66.

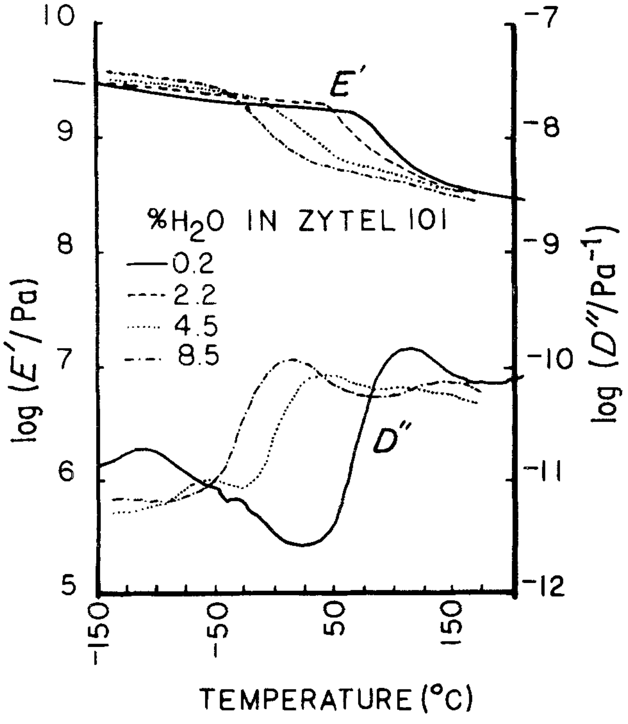

Figure 10 Dynamic spectra of Zytel 101 with 0.2, 2.2, 4.0 and 8.5% water (equilibrated at elevated temperature).

to lower temperatures, raises the modulus at temperatures below the glass transition, and lowers the rubbery modulus. The height of the alpha peak in D'' is also slightly higher in the water-equilibrated nylons. The shifting of the alpha peak to lower temperatures is important, since the initial rate of hysteretic heating is directly proportional to the value of D'' at the test temperature.

Dynamic modulus data for the modified nylons in the dry as-moulded condition are shown in Fig. 11. The addition of the rubbery phase lowers E' throughout the entire temperature range, with the decrease in modulus being slightly greater at higher temperatures. However, the temperature at which the glass transition occurs is not significantly altered by the presence of the rubbery phase. Note that the decrease in modulus is not directly proportional to the amount of rubbery phase. For example, there is little difference in modulus between Zytel 101 and 25% Hi-N66. This could be a result of a balance between a lower modulus expected from the addition of a rubbery second phase and a higher modulus due to the smaller spherulite size in the nylon blends [13]. Since the addition of more rubbery phase in 25% and 50% Hi-N66 is not accompanied by a further decrease in the spherulite size of the nylon matrix, the modulus would be expected to decrease to a greater degree. The difference in modulus between 75% and 100% Hi-N66 is slight; the explanation for this behaviour is not clear at the moment.

In the 75% and 100% Hi-N66 a small drop in E' is observed at $-50°$ C. This is accompanied by a peak in D'' seen in the 25% and 50% Hi-N66 blends as well, but not in Zytel 101. This peak represents the glass transition of the modifying phase. The fact that the temperature of this separate glass transition is unaffected by the amount of modifying phase present in the blend, is evidence of phase incompatibility. A compatible system would have a single glass transition whose temperature would be a function of the composition of the polymer blend [15]. Similarly, the magnitude and temperature of the alpha peaks in the blends are not greatly affected by the amount of modifying phase. The primary effect of the modifying phase is to raise the room-temperature value of D''. This signals the presence of a greater initial rate of heating in the blends containing higher fractions of the rubbery phase.

The effect of water on the dynamic modulus of the blends is shown in Fig. 12 which shows data for Zytel 101, 50% Hi-N66 and 100% Hi-N66 in

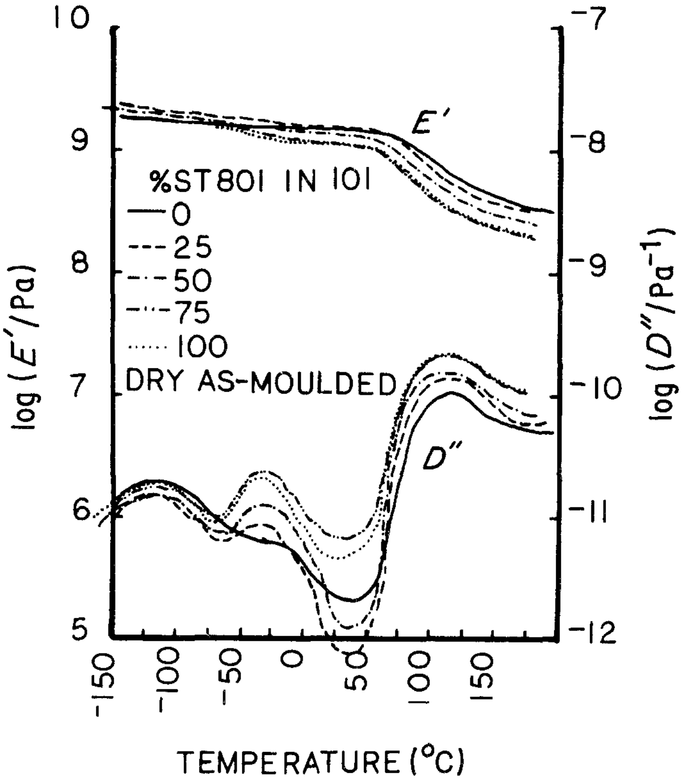

Figure 11 Dynamic spectra of dry as-moulded Zytel 101 and 25, 50, 75 and 100% Hi-N66.

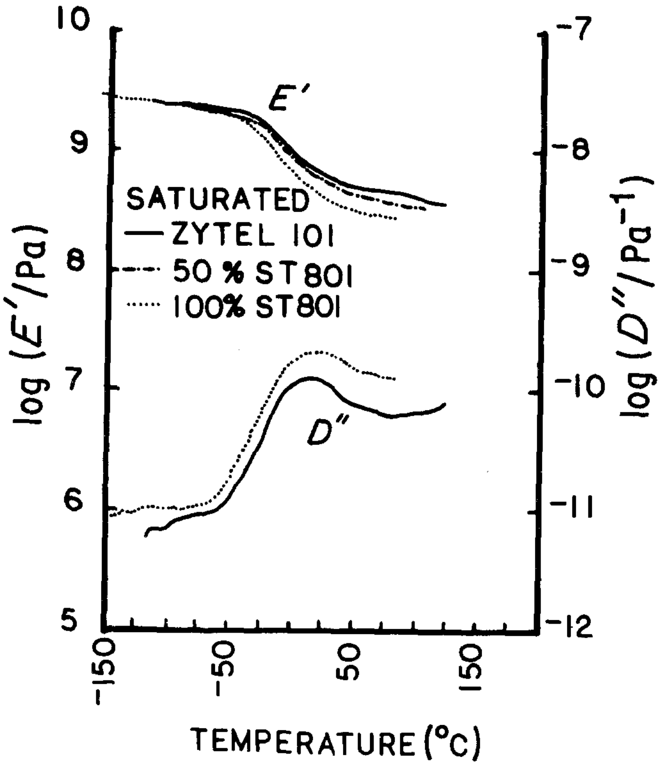

Figure 12 Dynamic spectra of Zytel 101, 50% Hi-N66 and 100% Hi-N66, saturated with water (elevated temperature).

the water-saturated (elevated temperature) condition. As in the unmodified nylons, the water shifts the glass transition to lower temperatures and increases the glassy modulus. Note that the change in moduli with increasing amounts of rubbery phase is less for the saturated material than for the dry as-moulded material. This is due to the fact that nylon with 8.5% water has a much lower T_g than nylon in the dry as-moulded condition. The addition of a rubbery phase to such a material has less effect than in the dry material, because there is less difference in the moduli. Note the absence of a visible glass transition of the modifying phase, in contrast to Fig. 11. Since the T_g of the water-saturated nylon phase is close to that of the rubber-modifying phase, the contribution of the latter is not visible.

4. Summary

The rubber-modified nylon 66 (ST801) contains approximately 20 vol% of a rubbery phase which is composed of 0.2 to 0.8 μm diameter spherical domains of EPDM. The nylon phase in Hi-N66 is semicrystalline in character and contains spherulites with a diametral size range of 0.1 to 0.2 μm. The size range of the spherulites in unmodified nylon 66 is approximately ten times larger (10 to 20 μm). At the same time, the degree of crystallinity in the modified nylon (approximately 31%) does not differ markedly from that of the unmodified nylon and does not vary with rubber content. Dynamic modulus data of the modified nylon reflect the effect of the rubbery phase more strongly than the differences in the nylon phase.

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