Technical Paper

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DuPont Advanced Fibers Systems

KEVLAR® Engineered Elastomer for Tire Reinforcement

by

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KEVLAR® Engineered Elastomer for Tire Reinforcement

ABSTRACT

KEVLAR® engineered elastomer, a composite of KEVLAR® pulp and elastomer, enables incorporating high-surface-area para-aramid reinforcement to tire compounds. Extensive laboratory studies of the effects of this material on typical tire compounds demonstrate its potential for reinforcement of several tire components.

INTRODUCTION

DuPont™ KEVLAR® brand fiber was introduced in the 1970's. KEVLAR®, the world's first para-aramid fiber, is known for its high strength to weight ratio, high modulus, and excellent chemical and thermal stability. Initially, it was offered in continuous filament form, and soon found applications in tires, mechanical rubber goods, bullet resistant vests, and composites. In the 1980's, short forms of the fiber - staple, floc, and pulp - were introduced and quickly found acceptance in cut-resistant protective apparel, gaskets, and friction materials. Photographs of these three product forms are shown in **Figure 1**.

Once short forms of KEVLAR® and Akzo's (now Teijin Twaron's) para-aramid TWARON® were introduced, they were evaluated for rubber reinforcement. Using short fibers (such as cellulosics, cotton, denim, polyester, and nylon) to reinforce rubber is common in rubber goods. They improve green strength, provide dimensional stability prior to cure, and improve mechanical properties of the vulcanizate. Compounders found that they could incorporate para-aramid floc (we define floc as short fiber less than 6 mm long) into rubber using an internal mixer or a roll mill, often with difficulty. An electron photomicrograph showing floc in a rubber compound may be found in **Figure 2**. Incorporating the high-surface-area pulp product (**Figure 3**) proved to be exceedingly difficult. Only a few people were able to adequately disperse pulp into a rubber compound. However, their work did demonstrate the superior reinforcement potential of aramid pulp once the dispersion limitation was overcome. An electron photomicrograph showing pulp in a rubber compound may be found in **Figure 4**.

DuPont initiated studies to define a method to disperse para-aramid pulp into rubber, and this effort led to development of a unique new technology platform for dispersing pulp into an elastomer matrix. Products produced via this technology showed superior dispersion of aramid pulp in rubber. Samples of rubber compound of identical composition were analyzed using an ultrasonic scanning technique that measures relative porosity are shown in **Figure 5**. In the sample on the left, the pulp was introduced using engineered elastomer; in the sample on the right, the pulp was added directly into the rubber. A uniform color indicates a homogenous mixture. The sample made by compounding pulp directly into the rubber shows significant color differences indicating relatively poor fiber dispersion; the sample prepared using engineered elastomer is nearly a uniform color, demonstrating its excellent dispersion.

Product made via this new technology enabled dispersion of pulp into rubber so well that it was given a new name, 'KEVLAR® engineered elastomer.' Initial evaluation in the rubber industry confirmed that engineered elastomer was far easier to process than dry para-aramid pulp, and confirmed the improved dispersability of pulp made possible by using this offering. Initial adoptions for engineered elastomer were in power transmission belts; the PT belt industry had experience with short-fiber reinforcement; a common part of a belt formulation.

The tire industry had less experience with short-fiber reinforcement; we initiated a fundamental study to determine the effect of para-aramid pulp reinforcement on properties of typical tire compounds. The study included both static and dynamic tests. A second study was initiated to determine the effect on compound properties by varying the concentrations of para-aramid pulp and carbon black reinforcement.

The two studies were quite extensive. Only a summary will be included in this paper.

EXPERIMENTAL

Fundamental study:

A ‘hard’ compound formulation was selected for the fundamental study. A ‘precompound’ of the following composition was prepared in an internal mixer:

SMR 10	89.96
Renacit 11	0.10
ZnO	7.00
Stearic Acid	2.00
TMQ	1.00
6PPD	0.75
N326	60.00
Durez 32333	1.00
Resorcinol	1.25
Aromatic Oil	5.00

Compounds for testing and evaluation were then prepared by adding the para-aramid (via KEVLAR® engineered elastomer) and remaining natural rubber on a roll mill, then adding the cure package on the mill. The final compositions were:

Sample Identification	Reference	F1NR	F3NR
Precompound (above)	89.96	89.96	89.98
Engineered Elastomer	0.00	4.35	13.04
SMR 10	10.04	6.70	0.00
Cristex OT33AS	4.00	4.00	4.00
HMMM	3.00	3.00	3.00
TBBS	0.40	0.40	0.40
DCBS	0.50	0.50	0.50
PVI	0.20	0.20	0.20
Total	186.2	187.2	189.2
(para-aramid pulp concentration)	0	1	3

Test work was conducted by the MRPRA (now Rubber Consultants) in the UK.

Compound formulation study:

A heavy-duty tread formulation was selected to determine the effect of pulp and carbon black concentrations on compound properties. All mixing was done on an internal mixer. A two-stage mixing protocol was employed:

Stage 1

Add ½ NR, fibers, then remaining ½ NR
Add remaining ingredients

Stage 2

Add ½ stage 1, cure package, then remaining ½ stage 1

The detailed formulations were:

SBR 1502	60.00	53.30	39.90	46.60	39.90	53.30
PB 1207	40.00	40.00	40.00	40.00	40.00	40.00
EE 1F724		8.70	26.10	17.40	26.10	8.70
CB N-110	24.00	24.00	24.00	16.00	8.00	8.00
CB N-234	20.00	20.00	20.00	14.00	7.00	7.00
Aromatic Oil	8.00	8.00	8.00	8.00	8.00	8.00
Zinc Oxide	4.00	4.00	4.00	4.00	4.00	4.00
Stearic Acid	2.00	2.00	2.00	2.00	2.00	2.00
Agerite Resin D	1.00	1.00	1.00	1.00	1.00	1.00
Antozite 67	1.00	1.00	1.00	1.00	1.00	1.00
Vantard PVI	0.25	0.25	0.25	0.25	0.25	0.25
Amax	1.00	1.00	1.00	1.00	1.00	1.00
Unads	0.20	0.20	0.20	0.20	0.20	0.20
Sulphur	1.90	1.90	1.90	1.90	1.90	1.90
Total	163.35	165.35	169.35	153.35	140.35	136.35
phr Carbon Black	44.0	44.0	44.0	30.0	15.0	15.0
phr Aramid	0.0	2.6	7.8	5.2	7.8	2.6

Compounding and testing were conducted by the Akron Rubber Development Laboratory.

FUNDAMENTAL STUDY

Static stress-strain:

A typical stress-strain curve for a compound reinforced with para-aramid pulp is shown in **Figure 6**. The tensile modulus at up to 50% strain is about three times that of a corresponding non-fiber reinforced compound. Above 50% strain, the stress-strain response of a compound reinforced with para-aramid pulp is similar to the reference compound. The stress-strain response is not affected by strain rate as shown in **Figure 7**.

When subjected to shear, the fiber in a para-aramid pulp reinforced compound can be oriented; and the properties of the rubber compound are different in the direction of fiber orientation. The effects of fiber orientation and concentration are shown in **Figures 8 and 9**. Tensile modulus in the direction of fiber orientation (machine direction - MD) is higher than that perpendicular to the direction of orientation (cross-machine direction – XMD.) The MD/XMD modulus difference (anisotropy) of the compounds peaks near 50% strain. In **Figure 10**, shows the relationship between modular anisotropy, strain and fiber content where anisotropy is calculated from the absolute stress values at a given strain. Anisotropy peaks at about 60% strain for the compound reinforced with 1 phr of para-aramid pulp, and at about 50% strain for the compound with 3 phr reinforcement. **Figure 11** shows an identical plot where modular anisotropy is calculated by the tangential stiffness at a given strain. Anisotropy peaks at about 40% for the compound with 1 phr of pulp, and at about 30% for the compound containing 3 phr pulp.

An indication of the additive effects of carbon black and para-aramid pulp reinforcement is shown in **Figure 12**. The lower stress-strain curve shows the response of a ‘gum rubber’ compound. The next three curves show the effect of addition of carbon black (N330) at 30, 45 and 60 phr. The following two curves illustrate the effect of adding 1 and 3 phr pulp to a compound containing 60 phr carbon black. The large increase in modulus obtained by low concentrations of pulp is readily apparent.

The stress-strain curves of compounds reinforced with para-aramid pulp are nearly linear with ‘high modulus’ at low strain, and at again with ‘lower modulus’ at high strain. The transition or inflection in the stress-strain curve occurs at around 50% strain. Acoustic emission tests were conducted in triplicate on the three compounds prepared in this study. Specimens were pulled at a constant rate of 2 inches per minute, and the acoustic output monitored throughout. Key observations made during the testing included:

- Each material (non-pulp-reinforced and pulp-reinforced) showed detectable acoustic activity.
- The amount of acoustic activity, as measured by the total number of events, was roughly proportional to the amount of pulp present (**Figure 13**).
- The amplitude (intensity) of the acoustic events was similar; that is, the fiber compounds reinforced with pulp did not produce louder events, just more of them.

The peak acoustic activity was determined by plotting the data as 'hits' per strain interval (**Figures 14 and 15.**) We found that peak acoustic activity occurs in the range 40-60% strain; this corresponds to the region where the stress-strain curve changes slope. The onset and peak of acoustic activity for the three compounds is summarized below:

Pulp concentration (phr)	0	1	3
Onset of acoustic activity			
% Strain	14-38	26-36	24-37
Stress (lbs)	<10	16-18	26-30
Peak of acoustic activity			
% Strain	51-85	60	47-54
Stress (lbs)	8-15	22-23	38-40

We hypothesize that reinforcement of elastomers by para-aramid pulp involves association between charged groups on the fibril surfaces and those in the elastomer(1), a mechanism similar to bound rubber theories for carbon black(2). It is our belief that acoustic emission testing is recording the disruption of the association between the charged groups on fibrils and elastomers.

Cycled Stress Stain Measurements:

Compounds reinforced with para-aramid pulp are used in dynamic applications; cyclic and dynamic properties are those important in the end-use.

The cyclic stress-strain behavior of para-aramid pulp reinforced compounds was observed over 10 cycles up to 2.5, 10, and 50% strain. In these tests, the first cycle was at the given strain, and subsequent cycles at the (constant) force required to achieve this strain in the first cycle. Some of the test details are described in **Figure 16**. Typical curves from the test at 10% ultimate strain are shown in **Figure 17**; the curves for the first and tenth cycle are shown.

The energy loss fraction (fraction of energy dissipated in each cycle as shown in **Figure 18**) was calculated from the stress-strain curves for each cycle (**Figure 19**.) The energy loss fraction was:

- Nearly constant after the first cycle;
- Nearly the same in the machine and cross-machine direction, and
- Nearly independent of the fiber concentration in the compound (**Figure 20**.)

The stress-strain behavior of para-aramid pulp reinforced compounds after cycling was also measured. These tests were conducted at 10, 30, 50 and 100% strain, and after 2, 10 and 100 cycles. Measurements were made in both the machine and cross-machine direction (with and against fiber orientation.) A description of the test is shown in **Figure 21**. The stress-strain curves in the machine direction for the reference (no fiber compound) after 2, 10 and 100 cycles at 10% strain and for the compound containing 1 phr para-aramid pulp are shown in **Figures 22 and 23**. The effect of cycling on stress-strain behavior is nearly identical for both compounds. Similar nearly identical results were obtained with samples cycled to other strains, and those measured in the cross-machine direction.

Short Term Dynamic in Compression:

Short-term dynamic properties in compression were measured using plied-up cylinders (disks.) The specimens were precompressed to 10%. Samples were measured from 0.1% to 5% dynamic strain at 1, 10 and 100 Hz, and at 20° and 100°C.

Curves for compound containing 1 phr aramid are shown in **Figures 24** (20° C) **and Figure 25** (100°C). Stiffness at 1 and 3 phr aramid content at 1% dynamic strain is shown in **Figure 26**. Stiffness, as expected, increases with increasing fiber content. Loss angle was almost totally independent of fiber content as shown in **Figure 27**.

Short term dynamic properties in tension:

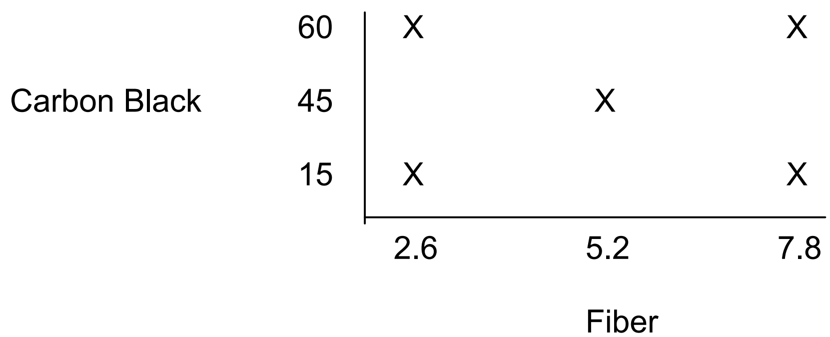
Short-term dynamic properties in tension were measured using molded strips prestressed to 5%. Samples were measured at 0.1% to 5% dynamic strain at 1, 10 and 100 Hz, and at 20° and 100°C.

Results were quite similar to those of the short-term dynamic properties in compression. Curves at 20° and 100°C are shown in Figures 28 and 29. Stiffness increased with increasing fiber content (**Figure 30**) while loss angle was relatively independent of fiber content (**Figure 31**.)

Both dynamic tests, compression and tension, showed that loss angle was nearly independent of fiber content. This is in contrast to carbon black reinforcement where loss angle is quite dependent upon concentration **Figure 32**.

COMPOUND FORMULATION STUDY

A series of compounds were prepared to determine the interaction between carbon black and para-aramid pulp concentrations on compound properties. A two-level factorial type design with a center point was used.



The effect of carbon black and fiber content on low-strain modulus is shown in **Figure 33**. Modulus in the machine direction increased dramatically with increasing fiber content, as expected. Little effect was seen in the machine direction. Modular anisotropy, as mentioned before is a consequence of fiber orientation. The degree of anisotropy – fiber orientation – is dependent upon the amount of shear in processing. Higher anisotropy and orientation are achieved by calendering the stock to a thin gauge, or extruding to a thin profile.

Tear resistance, as measured by both trouser tear and die C tear improved with increasing fiber content. Surprisingly, the improvements were seen in both machine and cross-machine direction (**Figures 34 and 35**.) This isotropic improvement in tear properties suggests that para-aramid pulp reinforcement may lead to improved life in off-road tires. Formulations are possible showing improvement in tear resistance and higher modulus without dramatic increase in hardness (**Figure 36.)**

CONCLUSIONS

- Para-aramid pulp can be used to significantly reinforce rubber compounds for engineering applications.
- The reinforcement efficiency is significantly greater than that of other commonly used reinforcing materials such as carbon black and silica.
- A high level of anisotropy can be introduced to a compound by conventional processing techniques.
- Hysteretic properties are nearly unaffected by the concentration of para-aramid pulp used in the compound.
- Stress-strain and acoustic emission data suggest that association between elastomer and fiber exists up to ~40% strain.
- Tear resistance can be improved by incorporation of para-aramid pulp into a tire compound.
- Para-aramid pulp reinforcement should be considered for low strain – constant stress tire components.

REFERENCES

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2. J. L. Leblanc, *J. Applied Polymer Science*, **66**, 2257 (1997).

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Web Address: www.kevlar.com

Figure 1

Commercial Forms of KEVLAR®

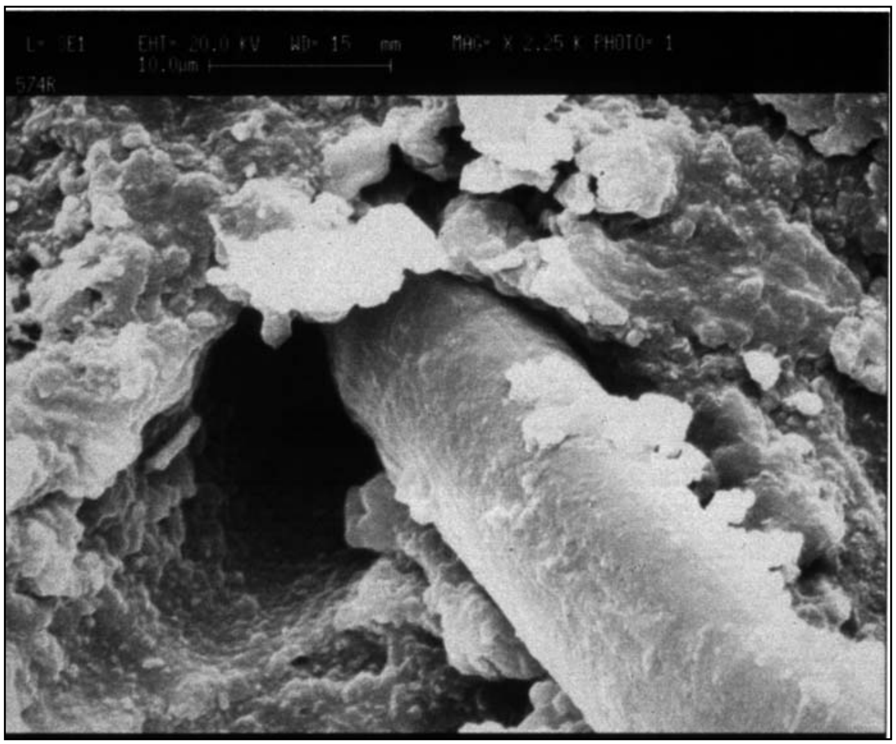
Pulp

Filament

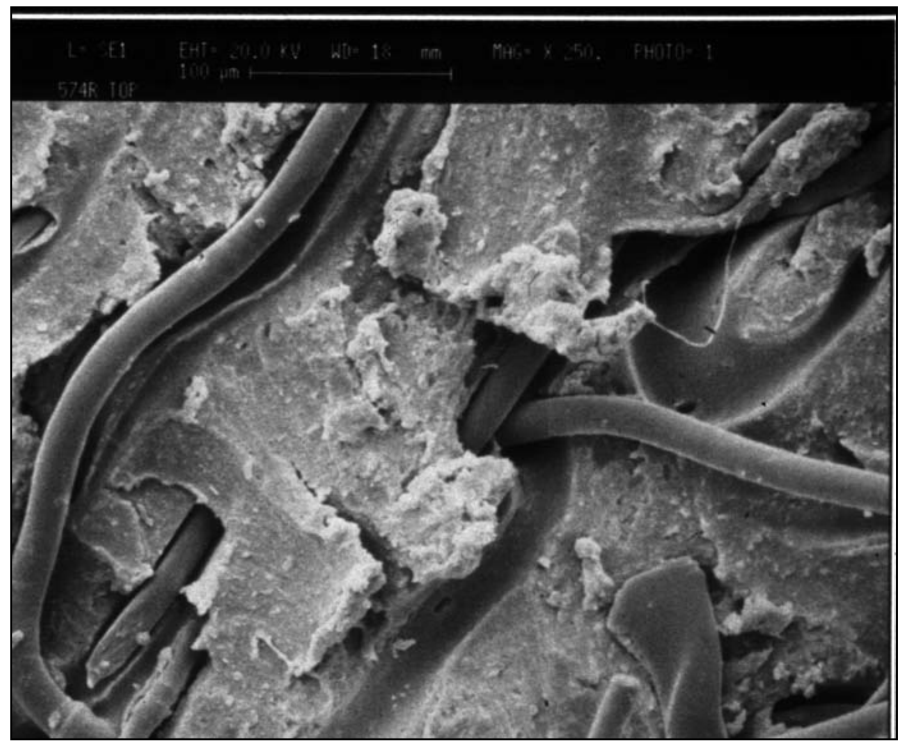
Staple

Figure 2

Aramid Floc in Rubber



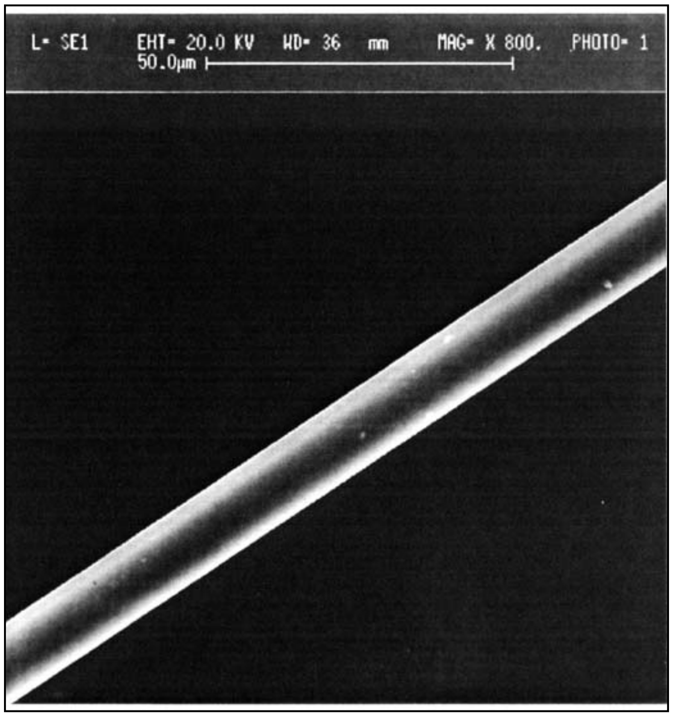
Staple on V-belt surface



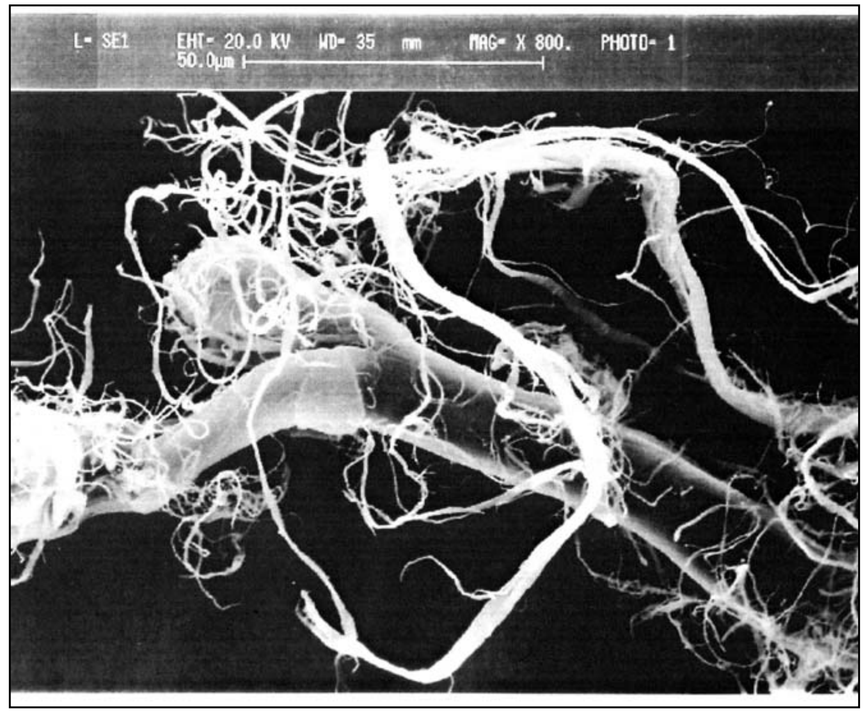
Staple in V-belt compound

Figure 3

Pulp Versus Floc Fiber Form



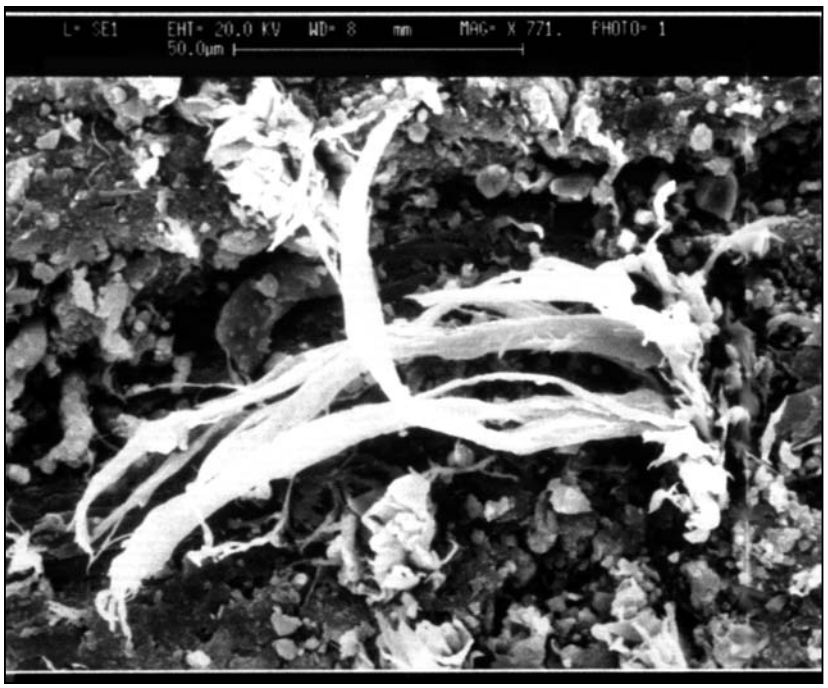
0.1-0.3 m^2/g



7-9 m^2/g

<u>Figure 4</u>

Pulp Fiber in Rubber



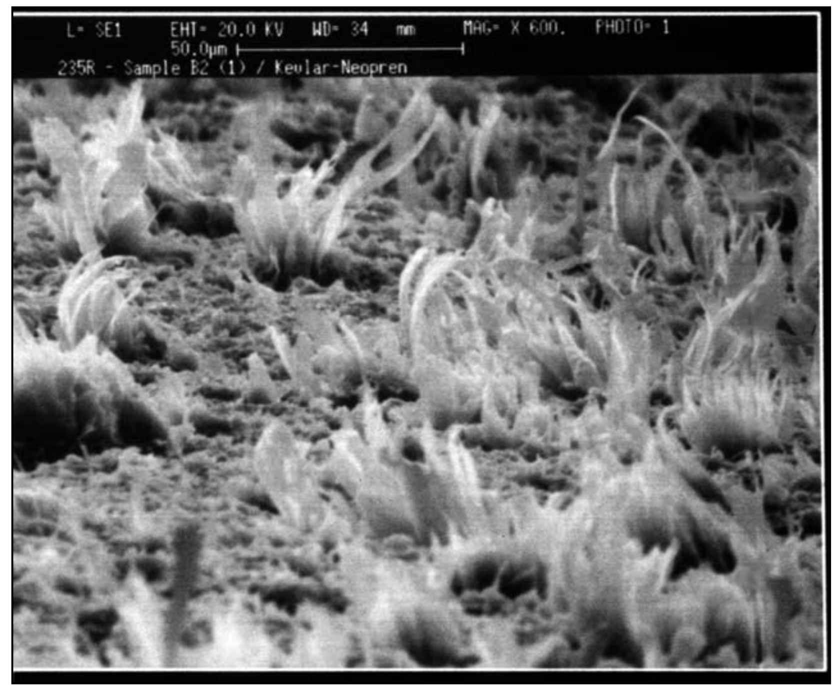


Figure 5

Fiber Dispersion and Uniformity with and without use of KEVLAR® Engineered Elastomer

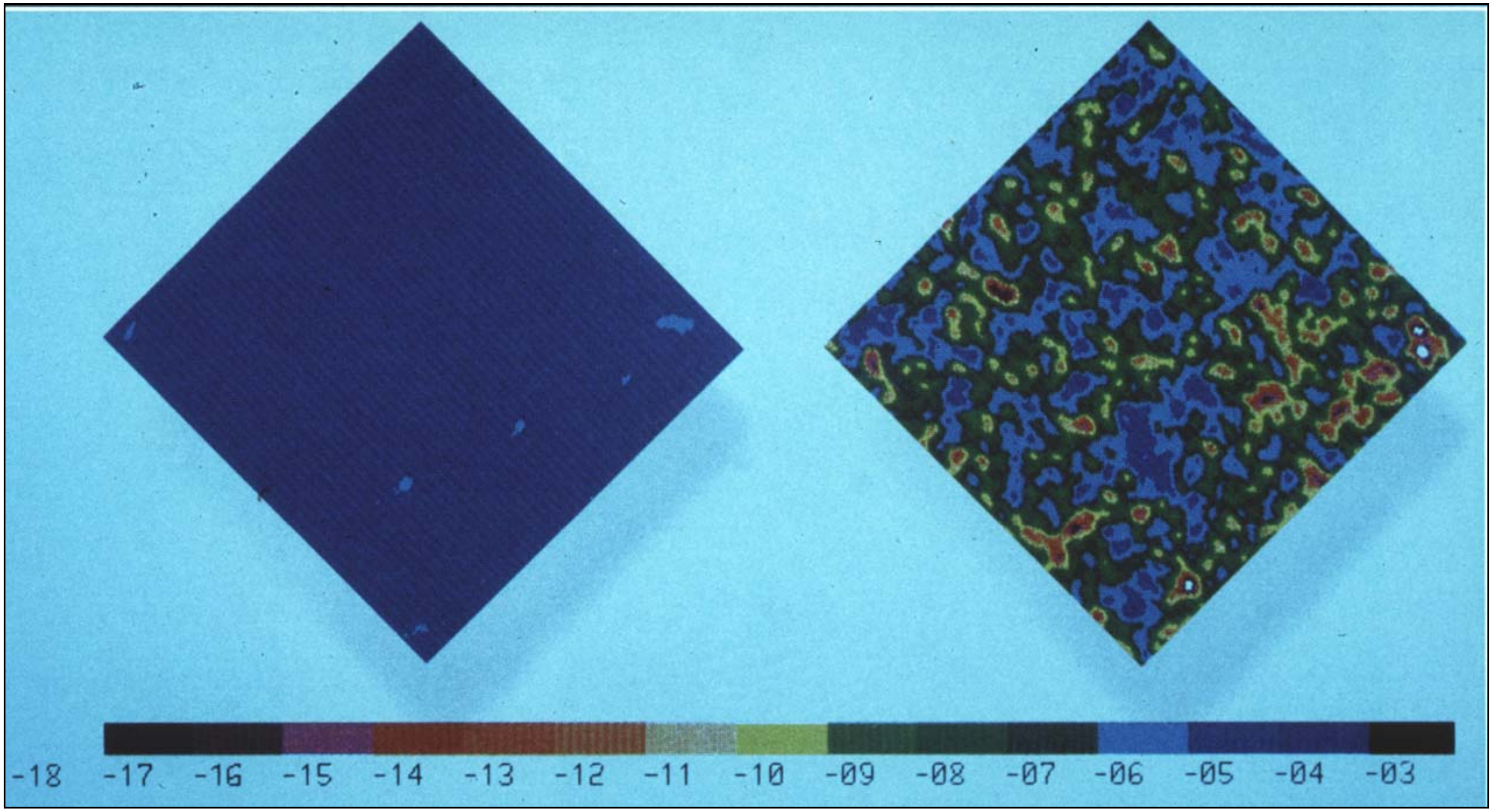
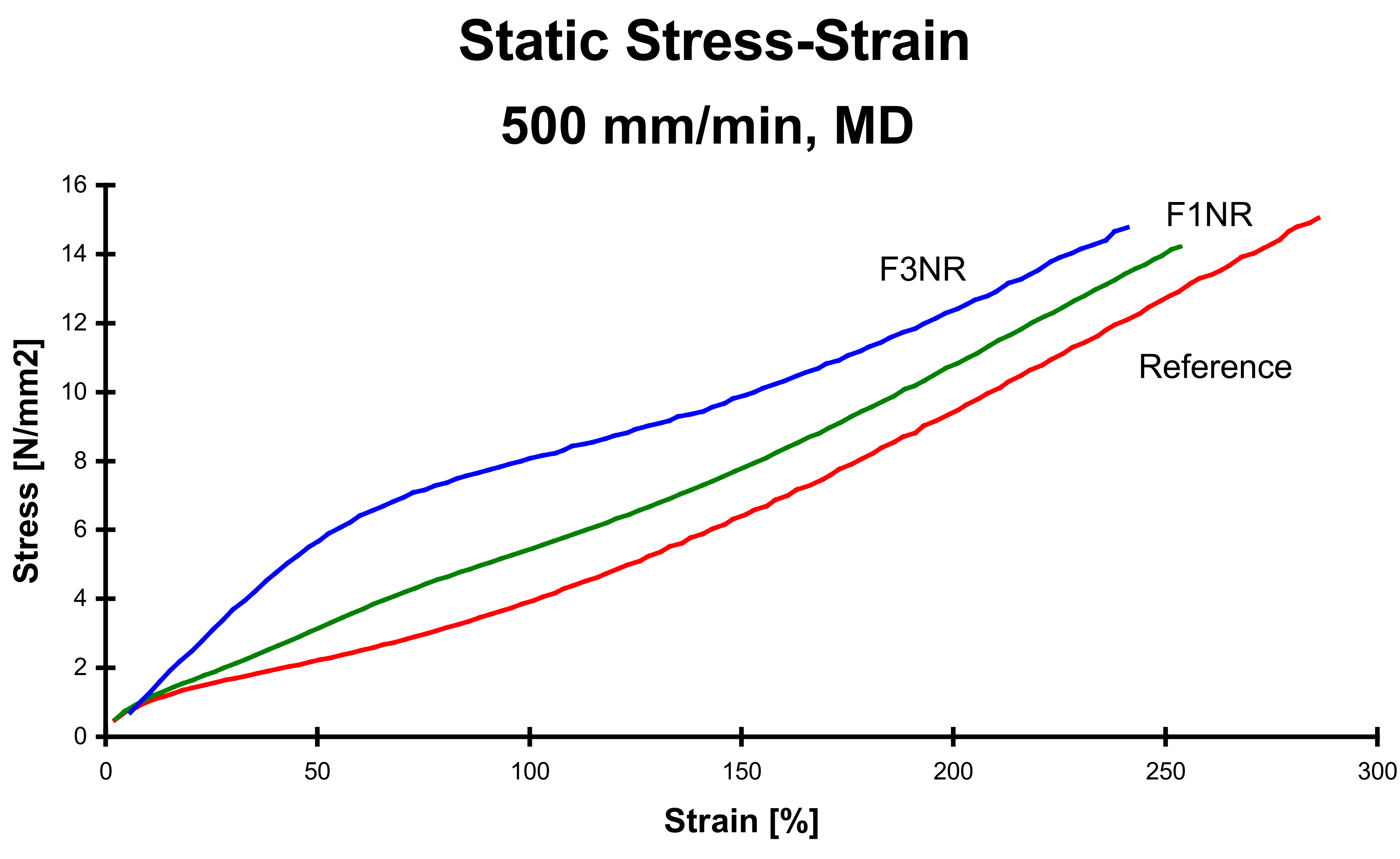


Figure 6



Static Stress-Strain
500 mm/min, MD
Stress [N/mm2]
0
2
4
6
8
10
12
14
16
Strain [%]
0
50
100
150
200
250
300
F3NR
F1NR
Reference

Figure 7

Static Stress-Strain
Effect of Pulling Speed (MD only) F3NR Compound

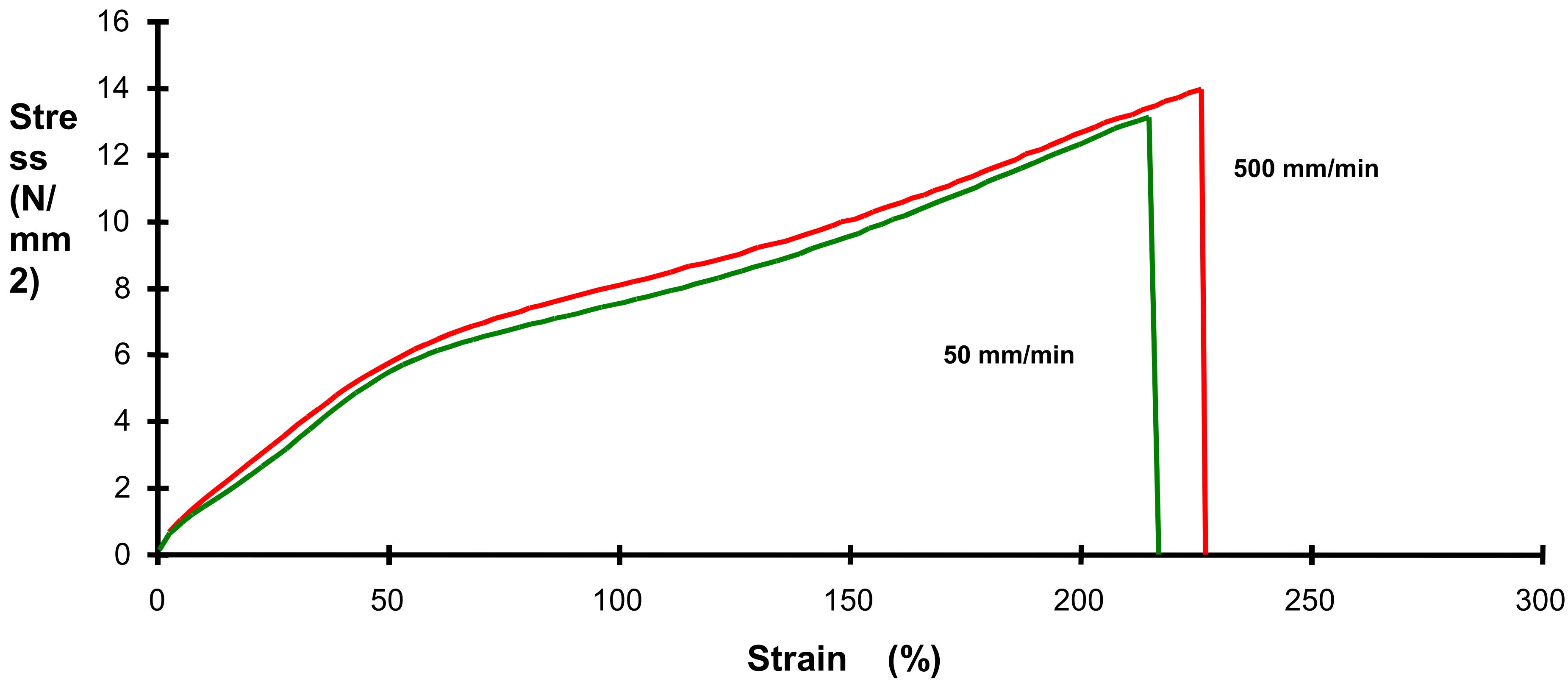


Figure 8

Static stress-strain at 25mm/min.
Effect of fiber loading upon stress-strain curves

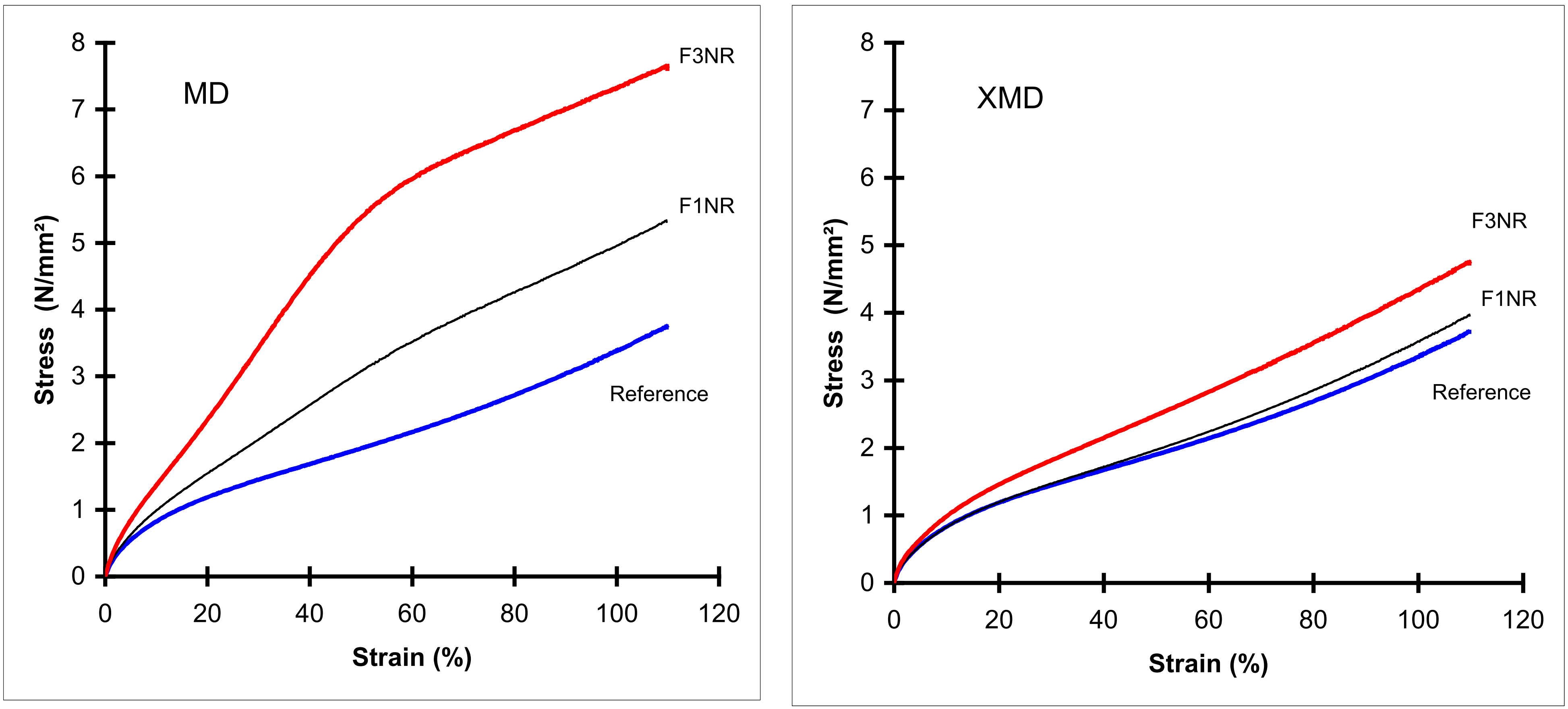


Figure 9

Static stress-strain at 25mm/min
Anisotropy Effects

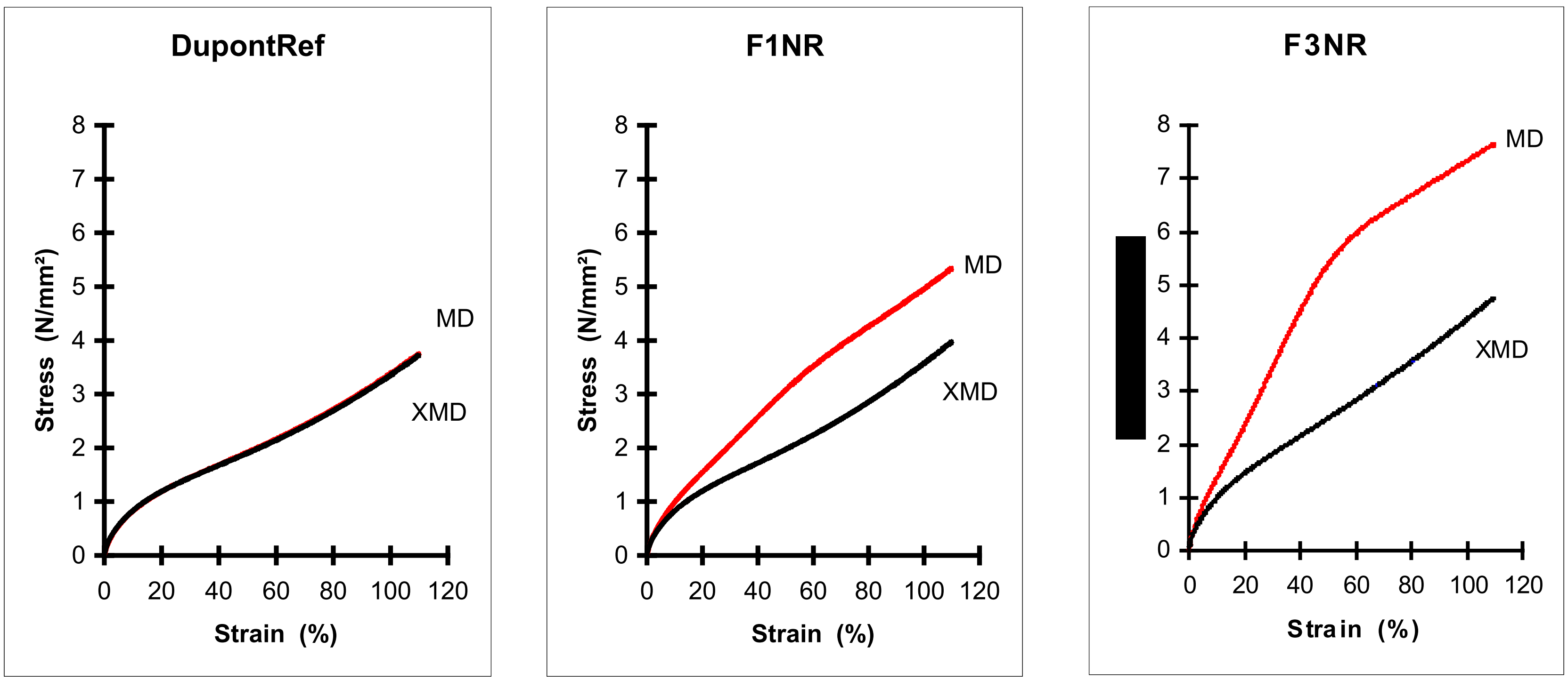


Figure 10

Stress Ratio Anisotropy vs. Strain

Stress ratio anisotropy is the ratio of MD/XMD absolute stress values at a given strain

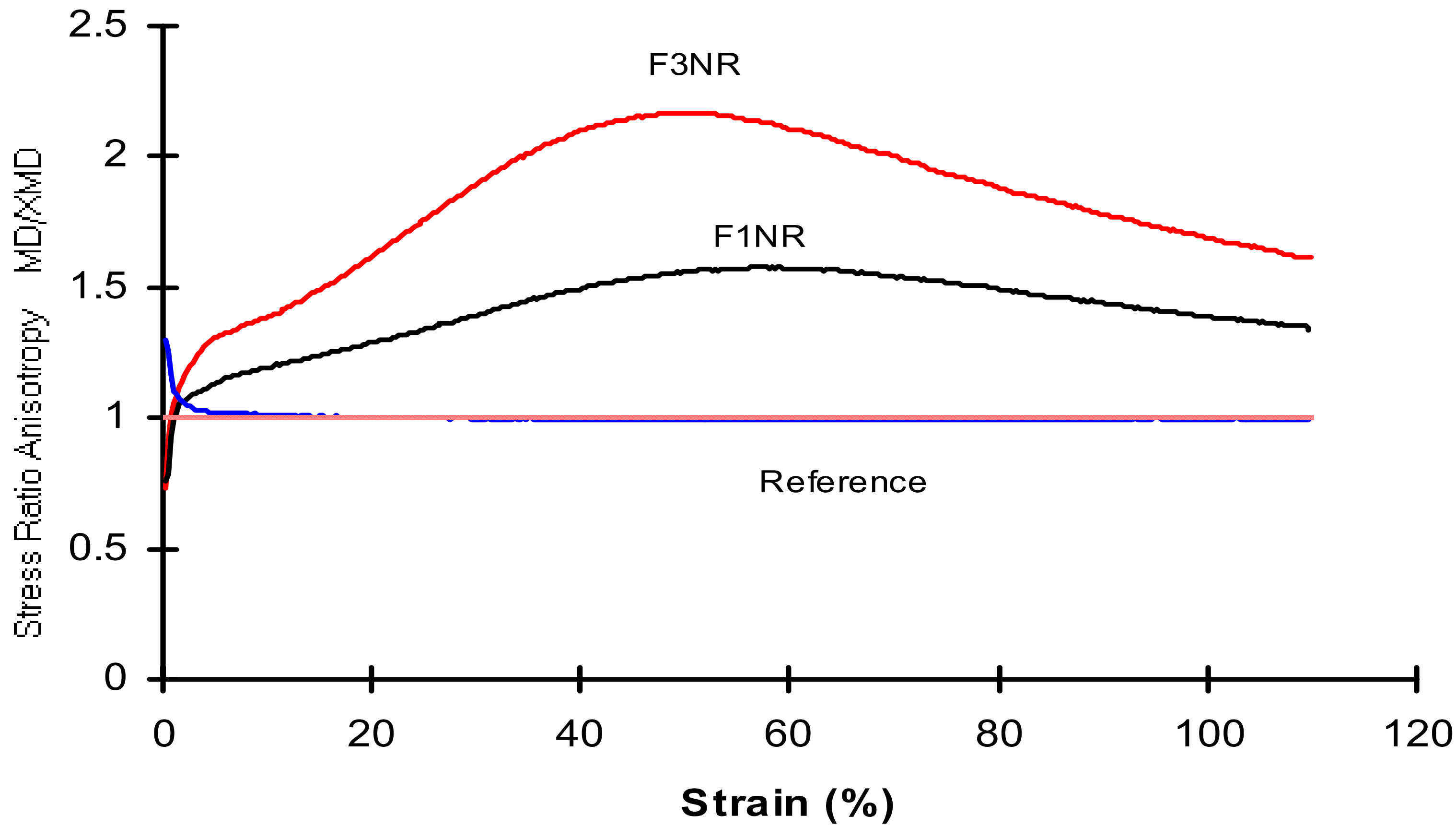


Figure 11

Modular Anisotropy vs. strain

Modular anisotropy is ratio of MD/XMD tangential stiffness at a given strain

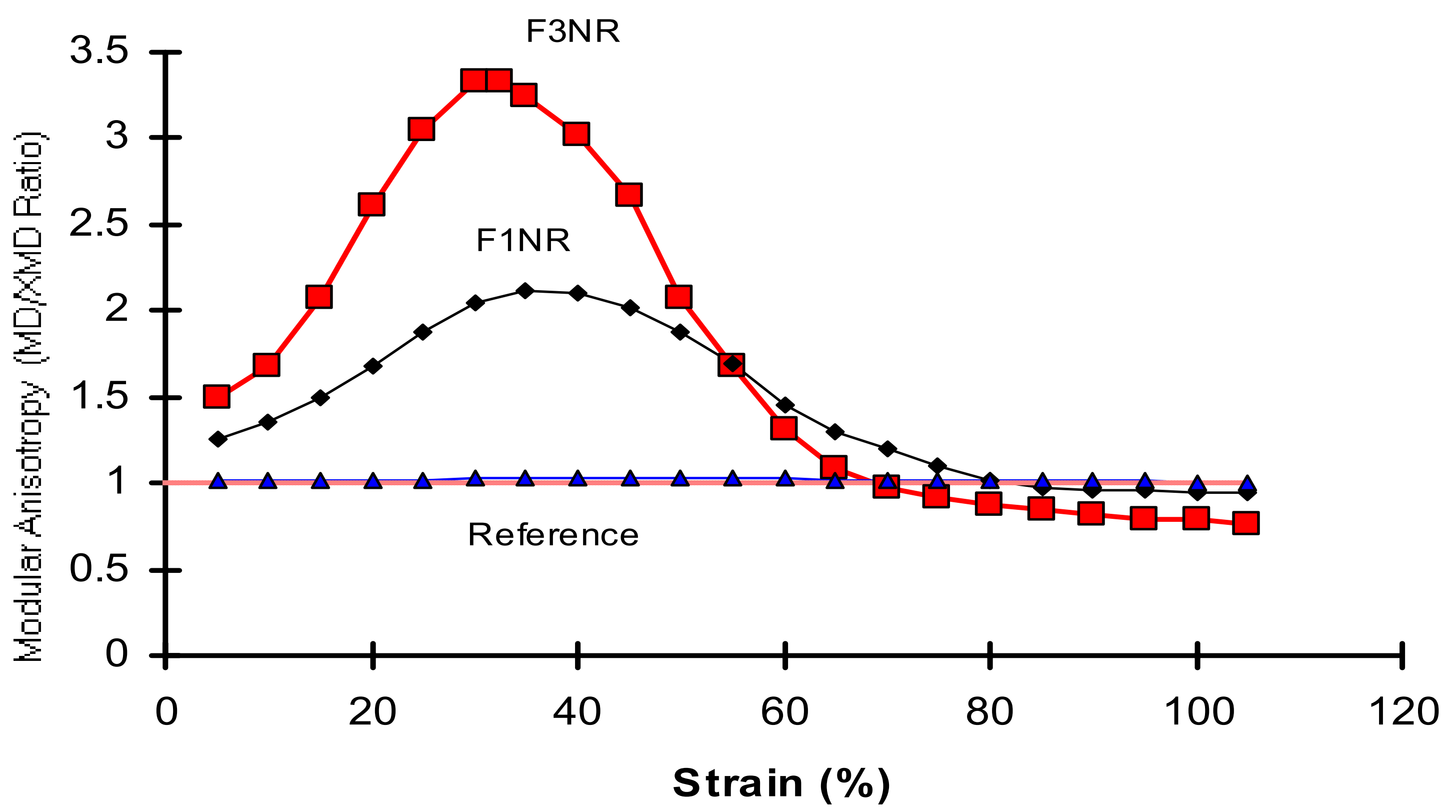


Figure 12

Comparison between carbon black and p-aramid pulp reinforcement of NR

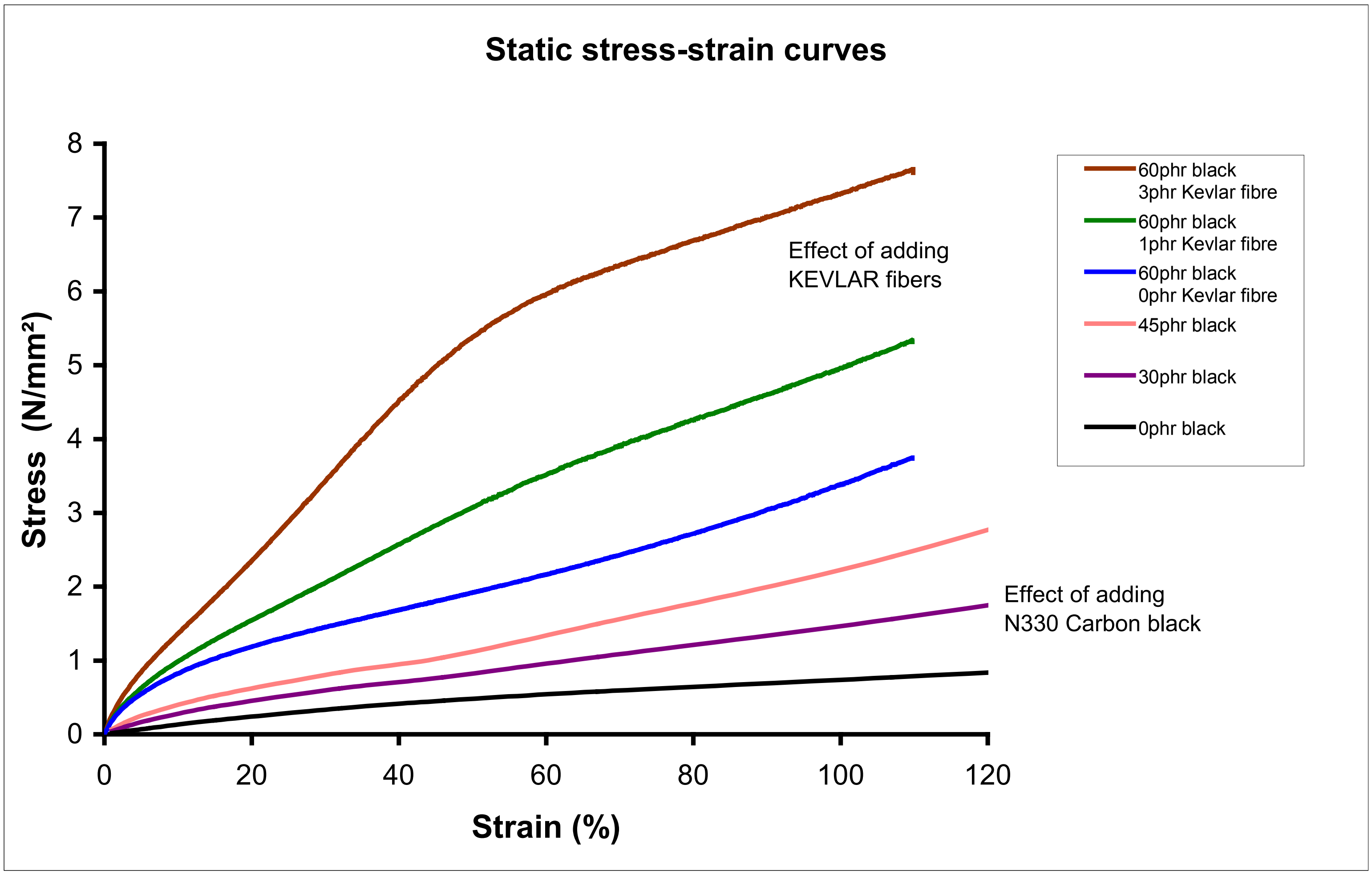


Figure 13

Acoustic Emission Tests

Acoustic Events are proportional to Fiber Loading

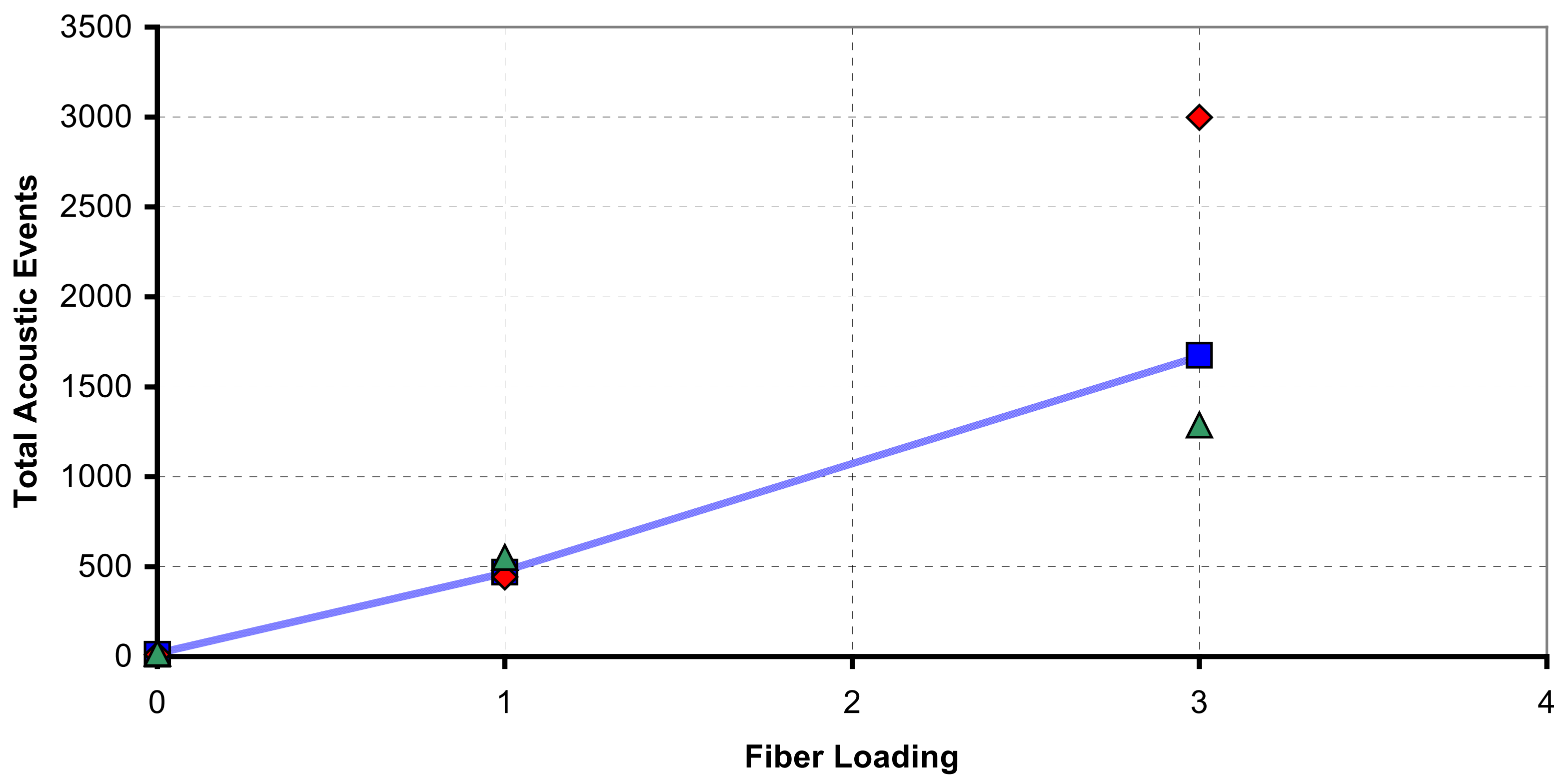


Figure 14

Acoustic Emission Tests
Acoustic Activity for F3NR

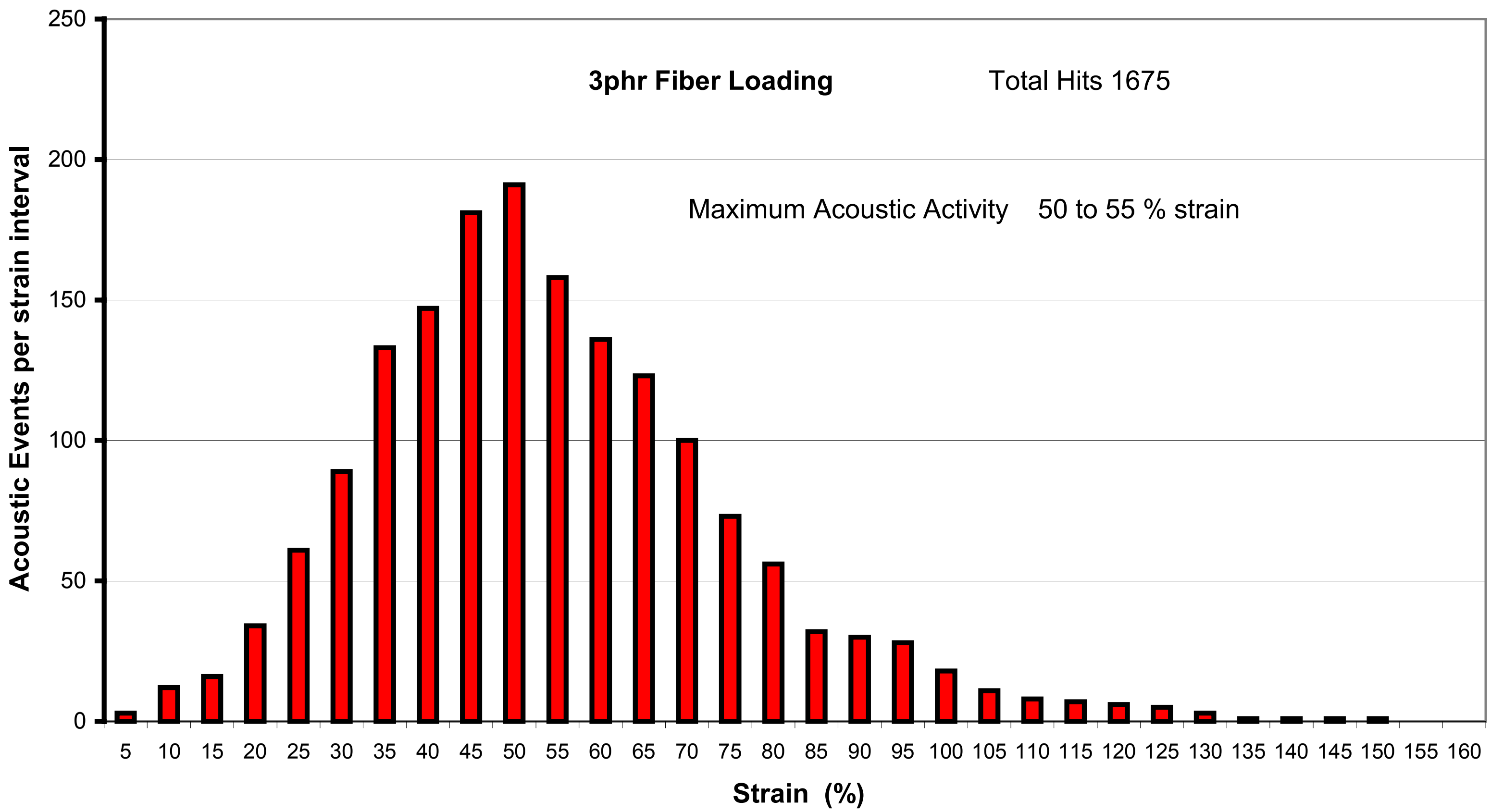


Figure 15

Acoustic Emission Tests
Acoustic Activity for F1NR

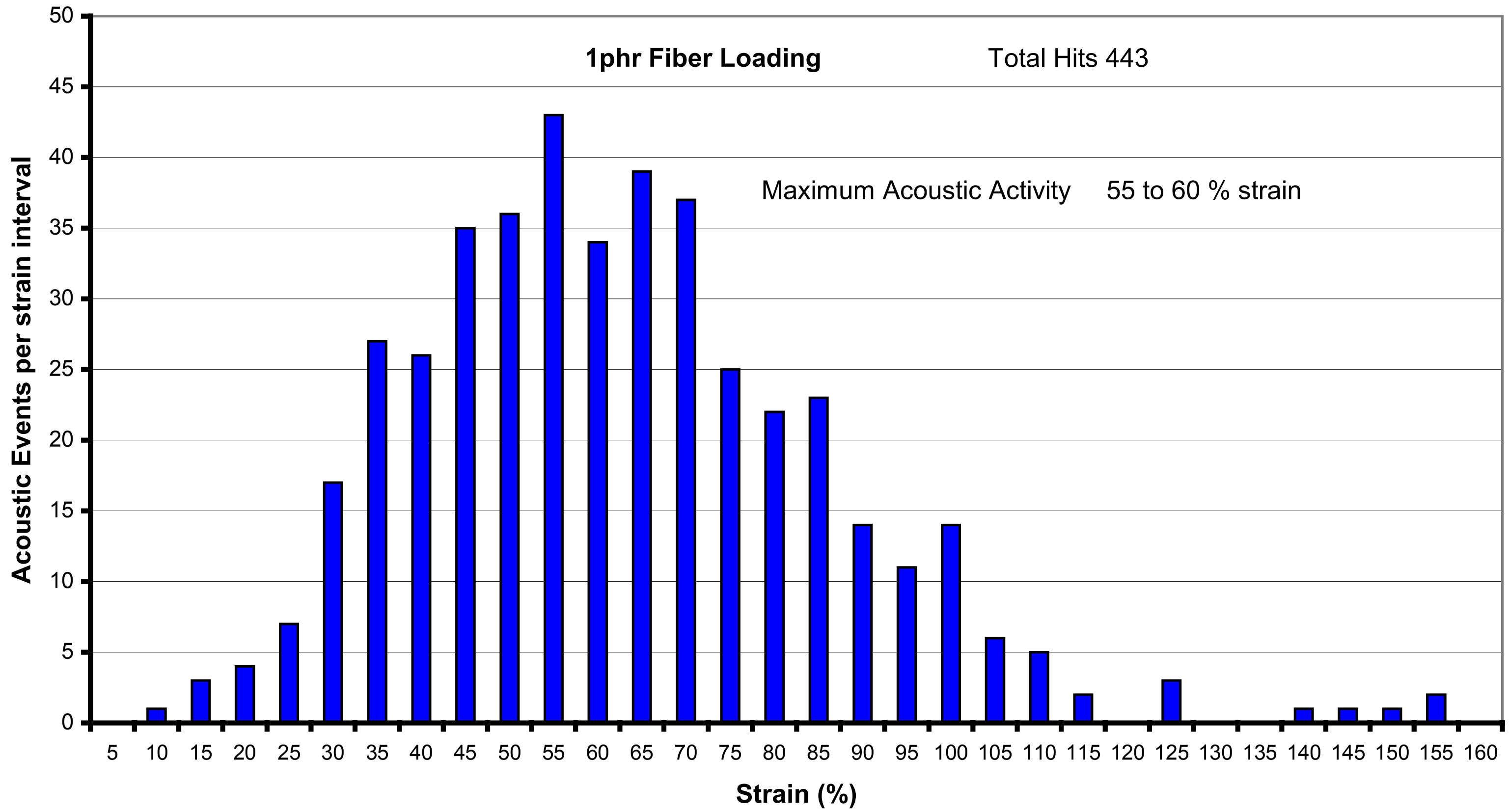


Figure 16

Cyclic Stress-strain Conditions

- Pull Speed: 25mm/min
- Position: cross-head displacement calibrated for pull speed
- First Cycle at constant Strain
- Subsequent Cycles at constant Force
- Test pieces: Bongos

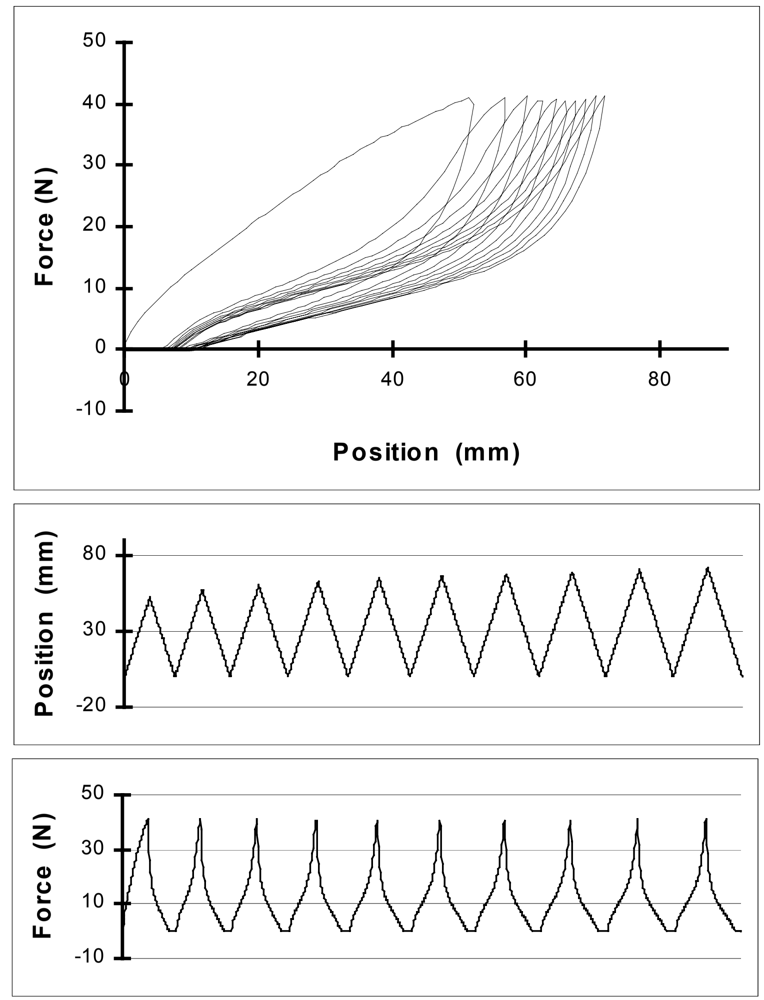


Figure 17

Cyclic stress-strain

Effect of fiber loading on 1st and 10th hysteresis cycles, cycled up to 10% strain

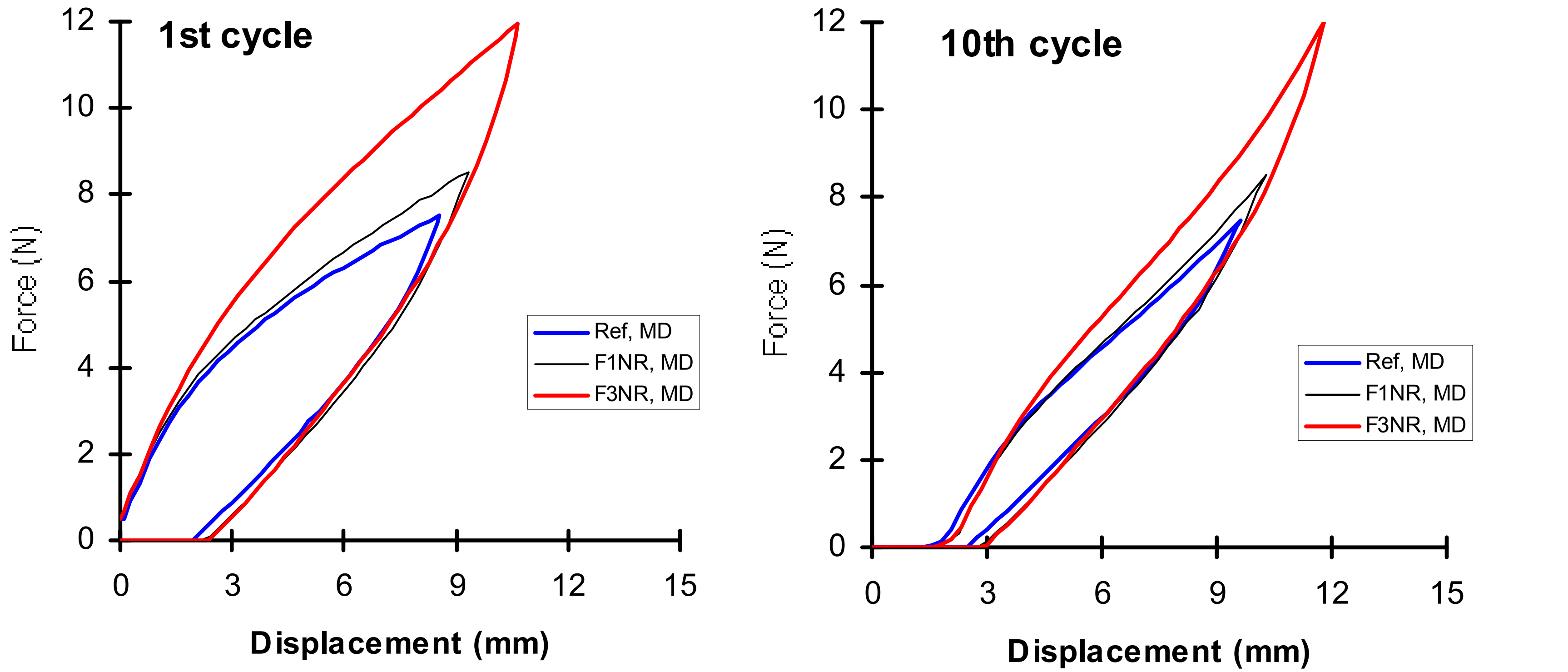


Figure 18

Definition of Energy Loss Fraction

Energy Loss Fraction = A1 / (A1+A2) =Hysteresis Energy / Stored Elastic Energy

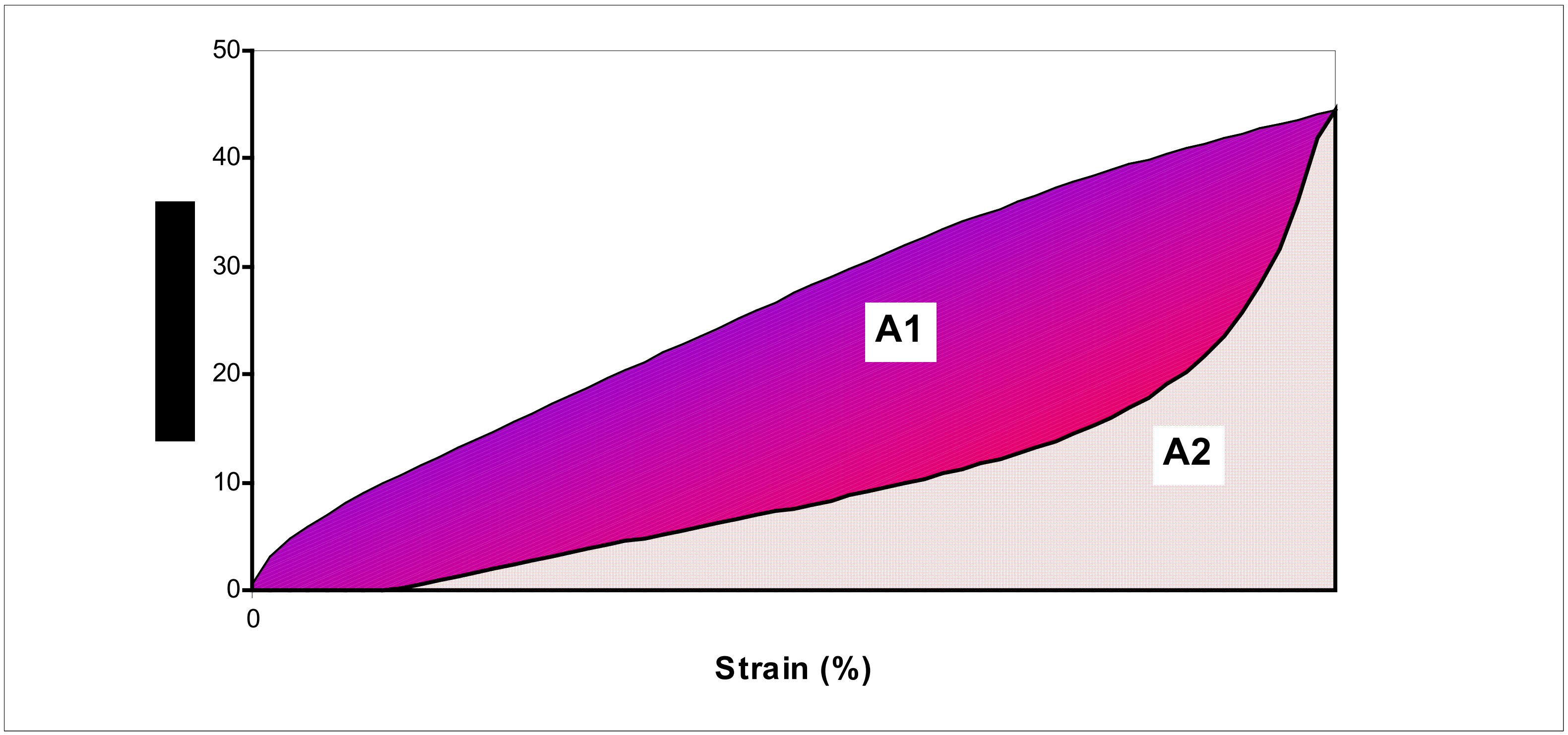


Figure 19

Cyclic stress-strain
Effect of number of cycles upon Energy Loss Fraction

F1NR Compound – Cycles up to 10% Strain

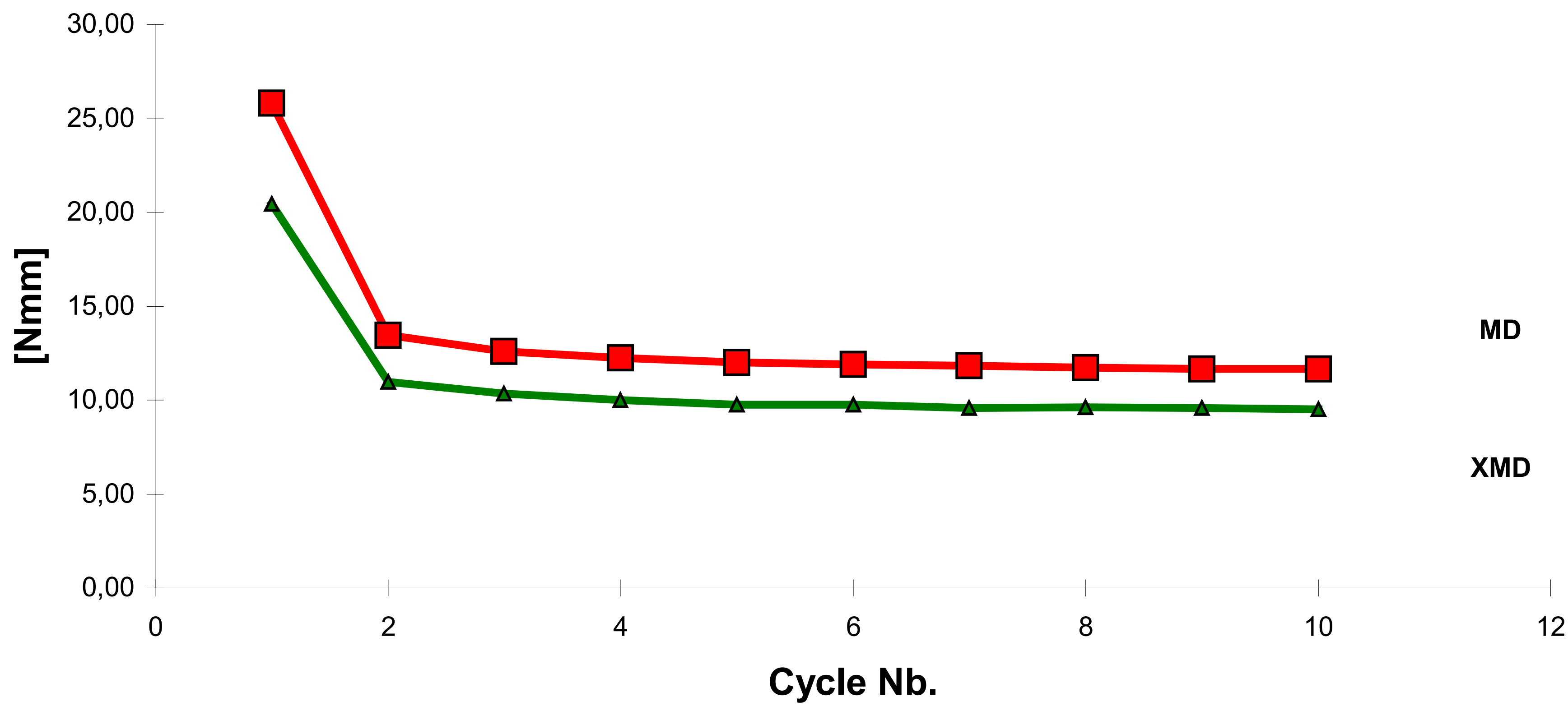


Figure 20

Cyclic stress-strain Energy loss fraction vs. fiber loading
Cycled up to 10% strain

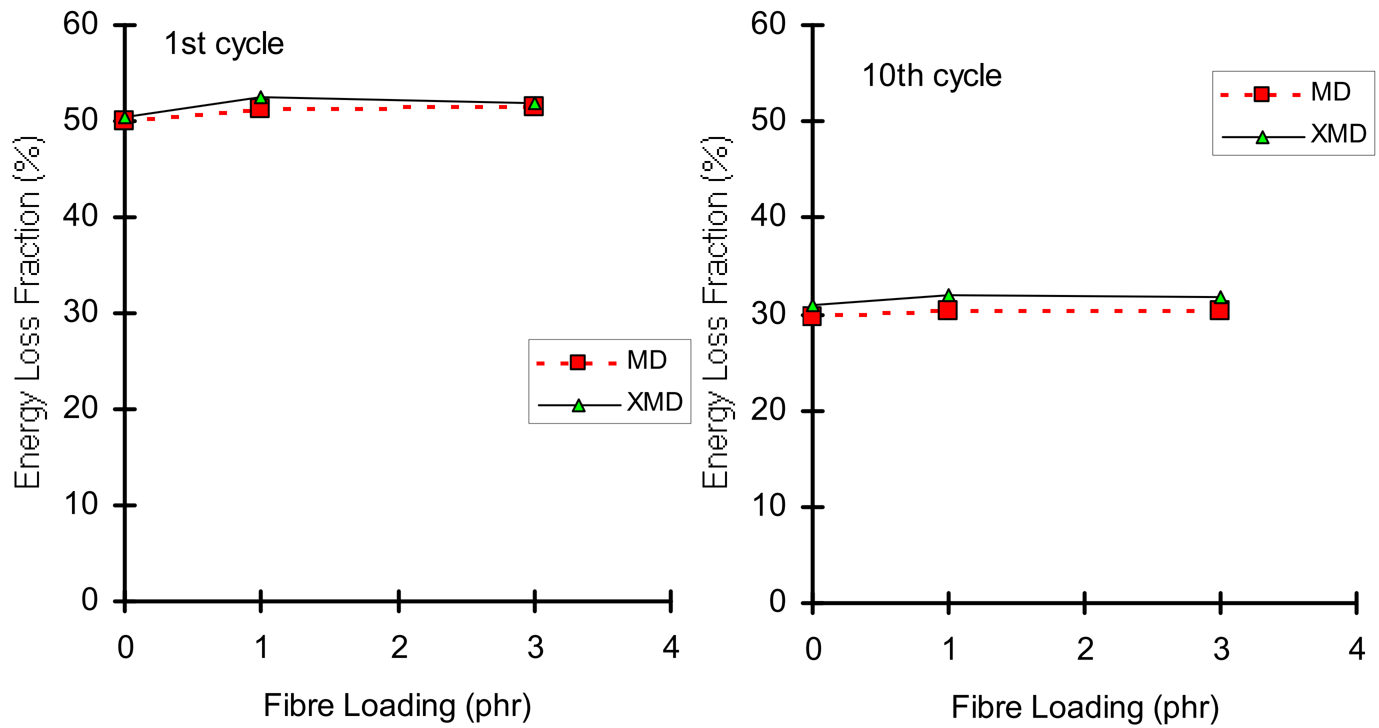


Figure 21

Cycles Were Performed At Constant Force

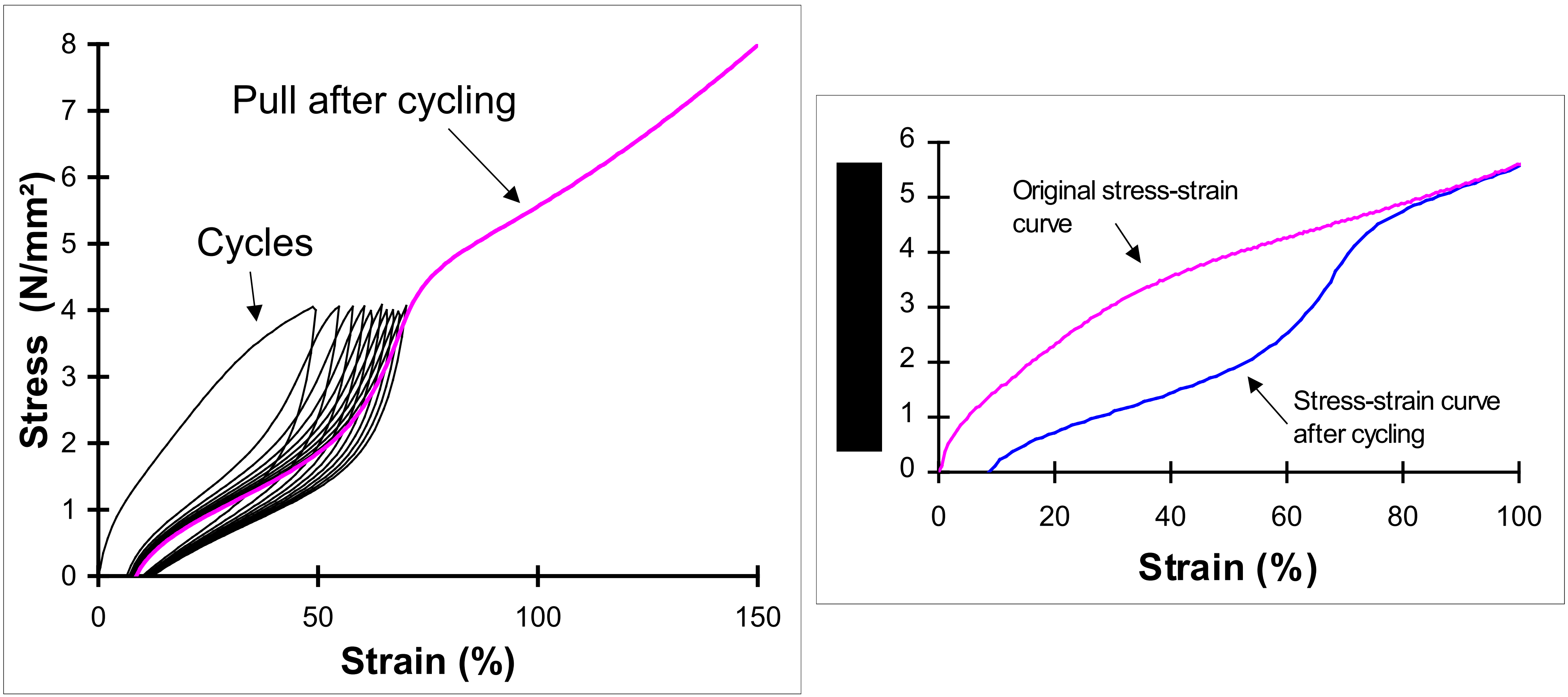


Figure 22

Ref MD cycled at 10% for 2, 10 and 100 cycles

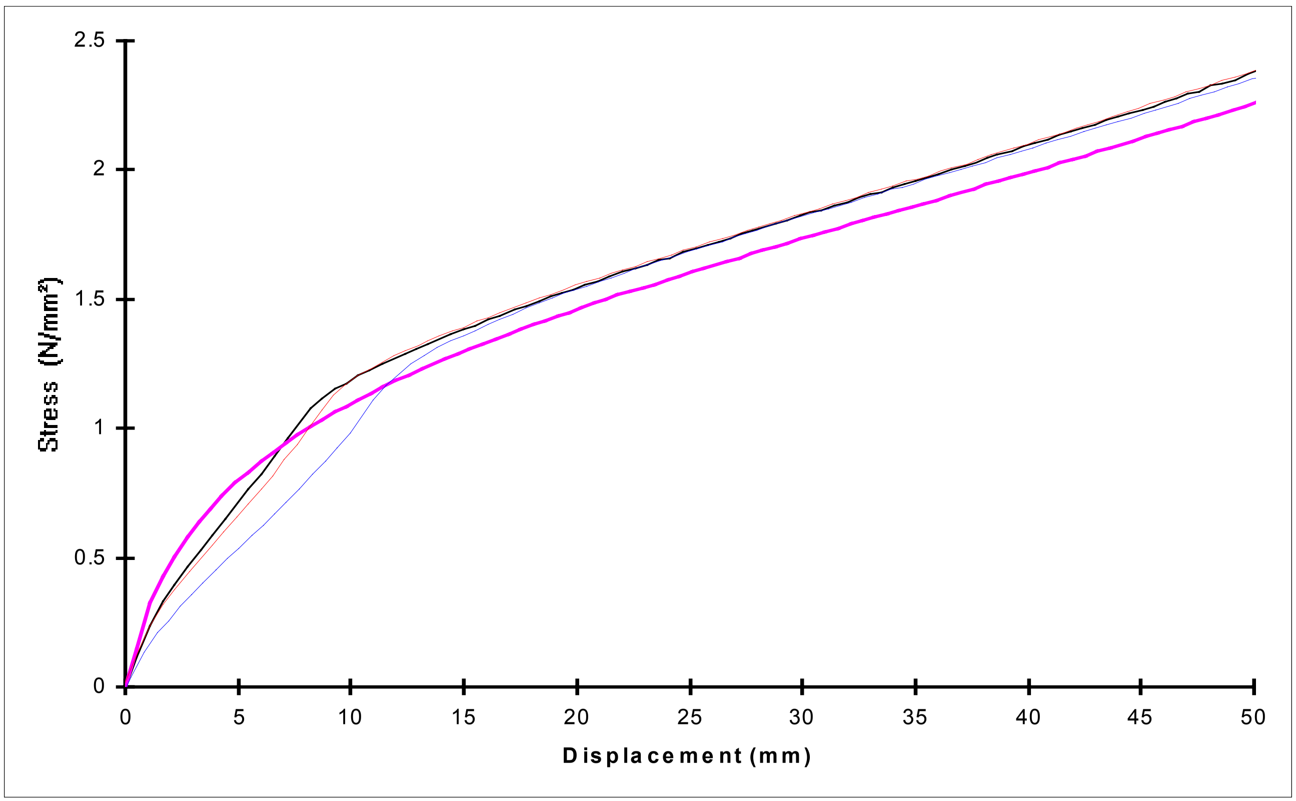


Figure 23

F1NR MD cycled at 10% for 2, 10 and 100 cycles

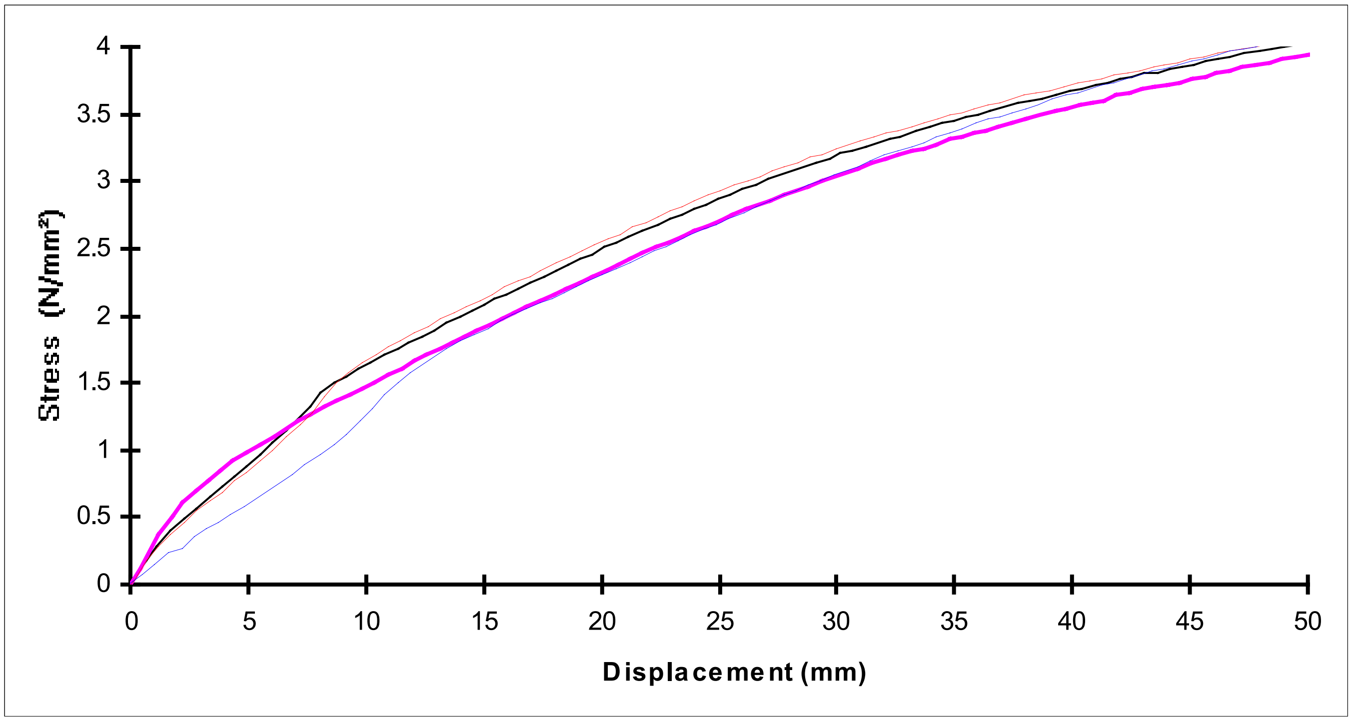


Figure 24

Short-Term Dynamic Compression
F1NR Compound 20°C Plied Up Discs

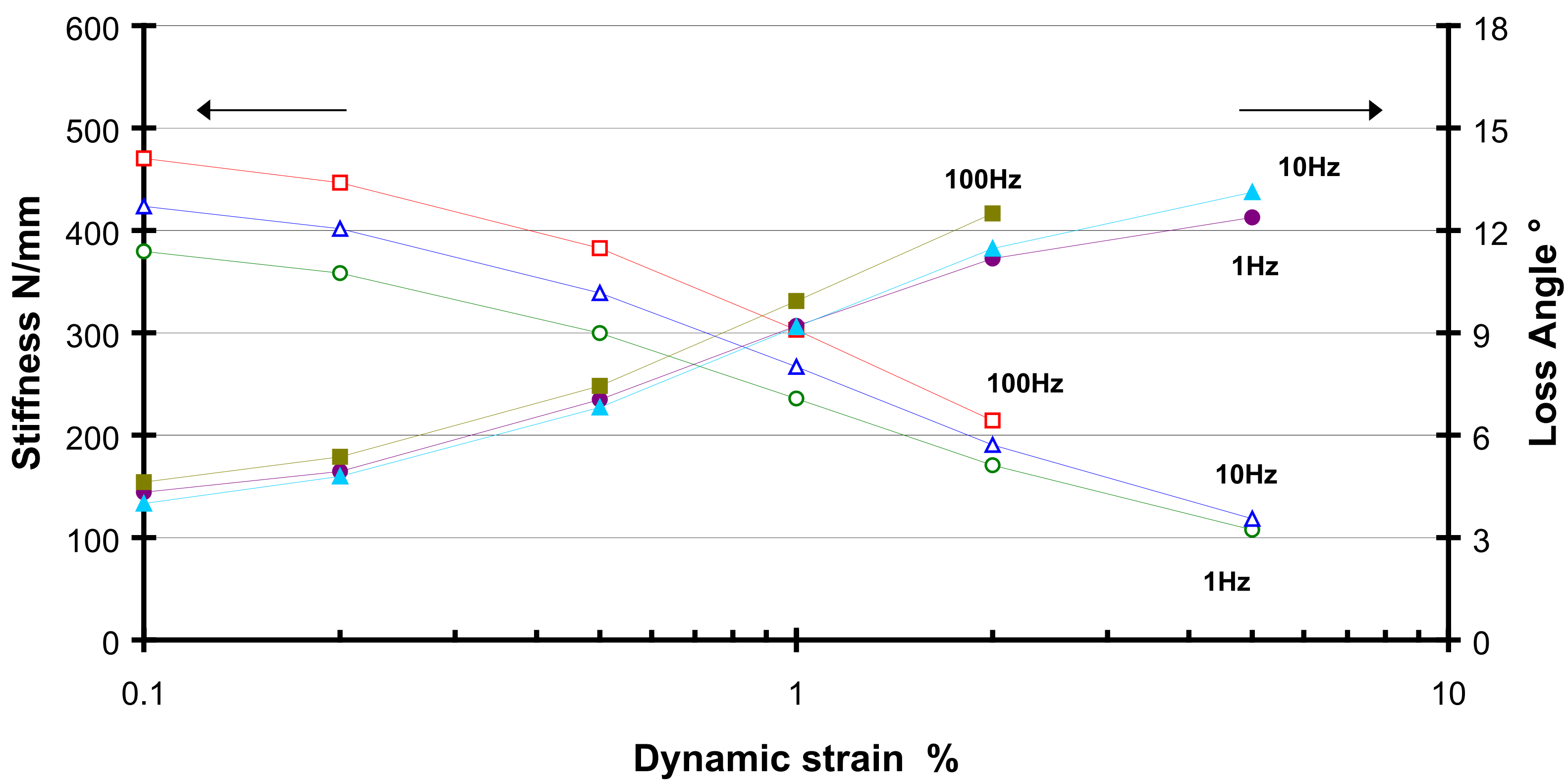
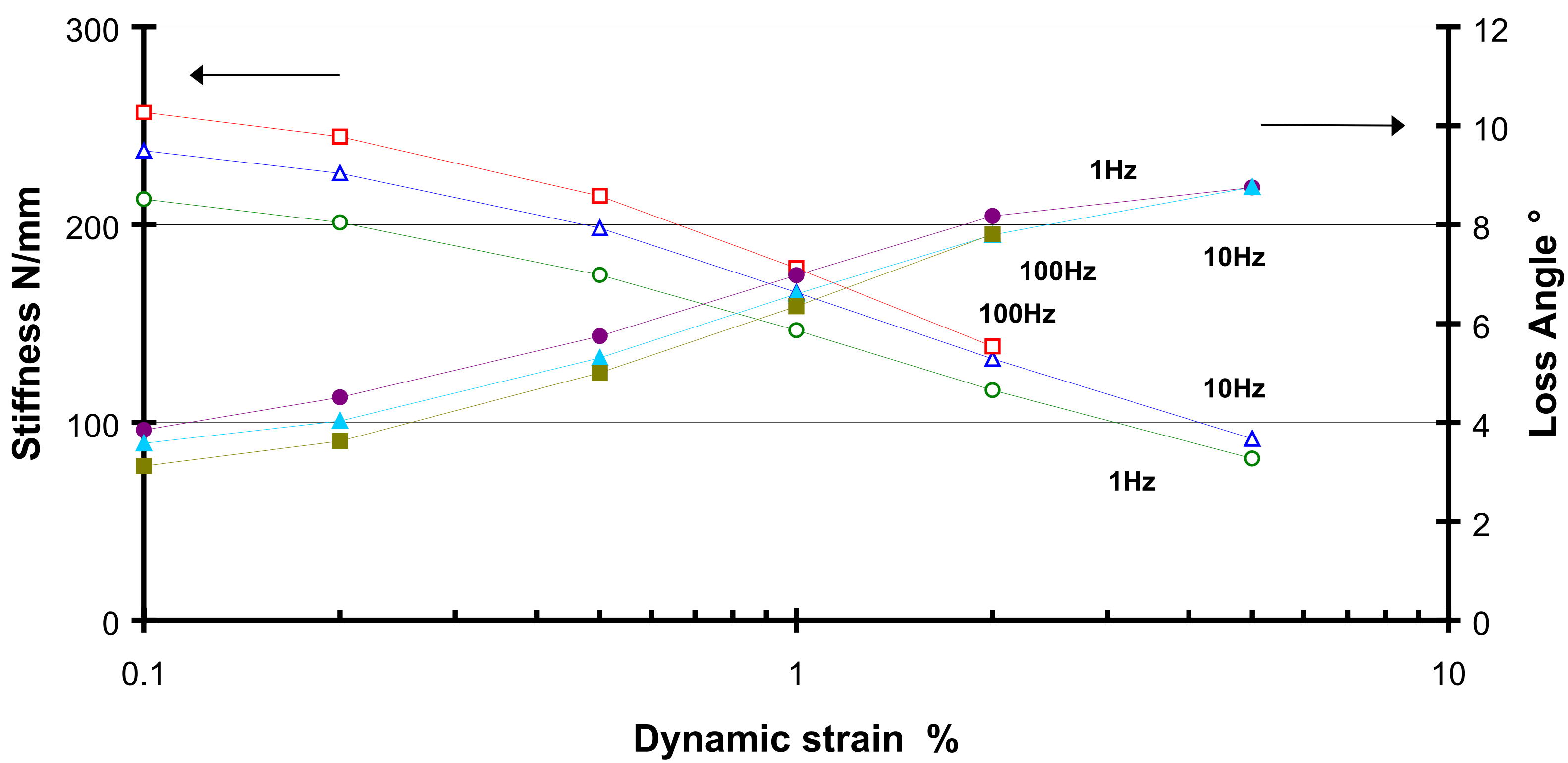


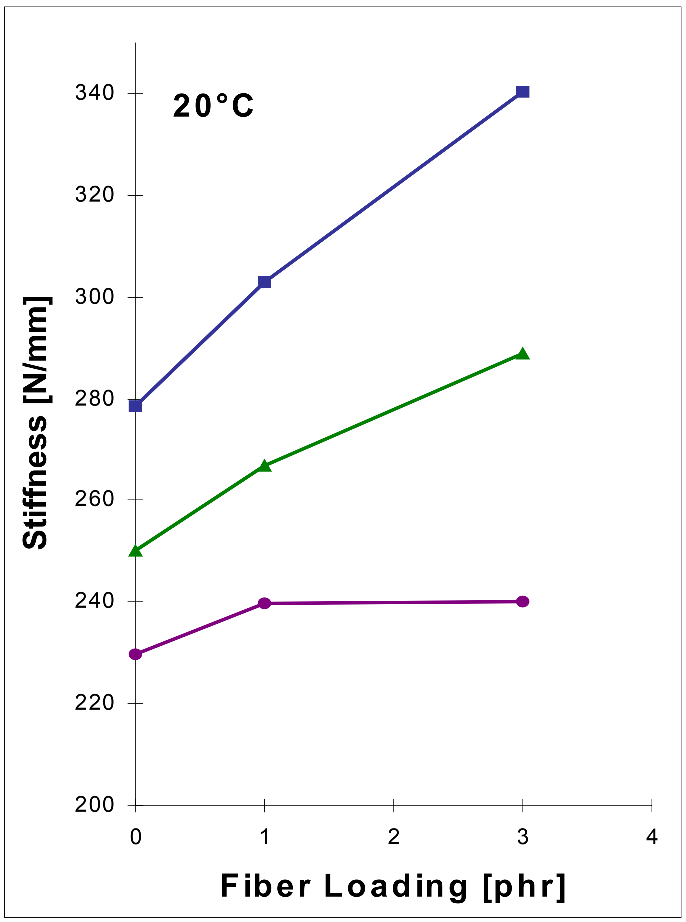
Figure 25

Short-Term Dynamic Compression
F1NR Compound 100°C Plied Up Discs



<u>Figure 26</u>

Short-Term Dynamic Compression
Stiffness vs. Fiber Loading
Piled Up Discs 20°C and 100°C at 1% Dynamic Strain



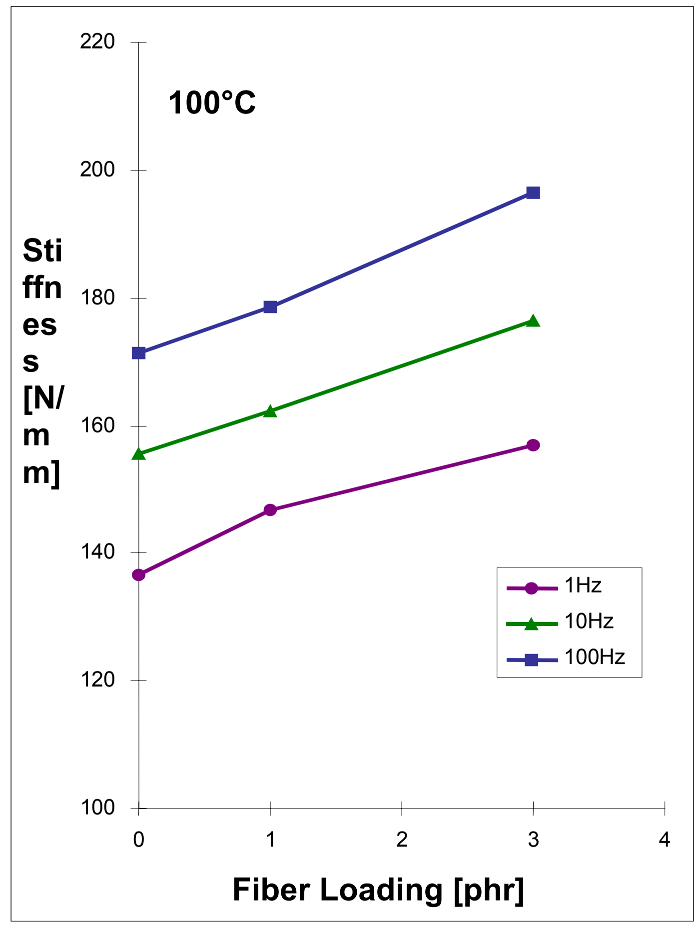
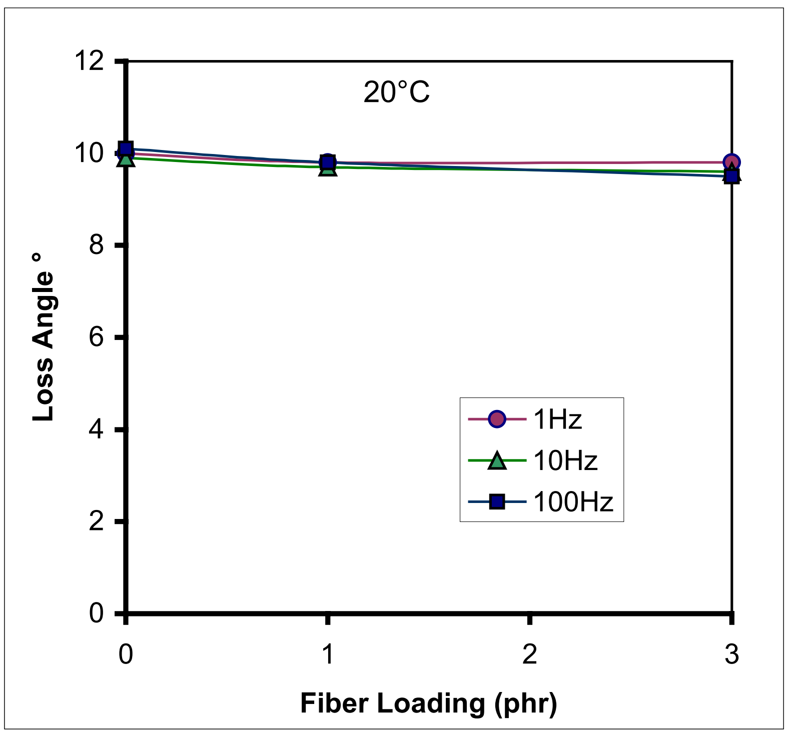


Figure 27

Short-Term Dynamic Compression
Loss Angle vs. Fiber Loading
Piled Up Discs 20°C and 100°C at 1% Dynamic Strain



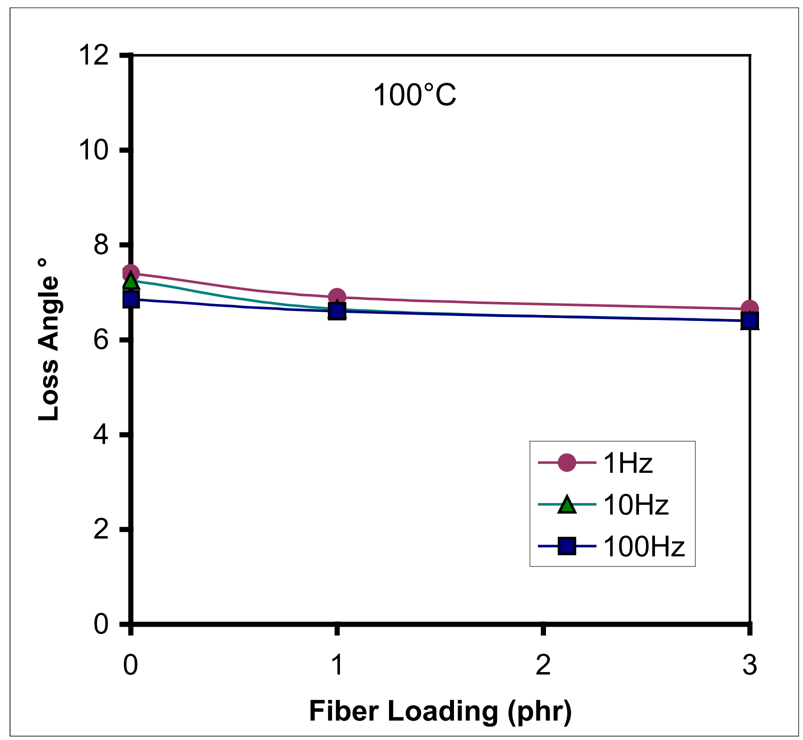


Figure 28

Short-Term Dynamic Tension
F1NR Compound 20°C Moulded Strip

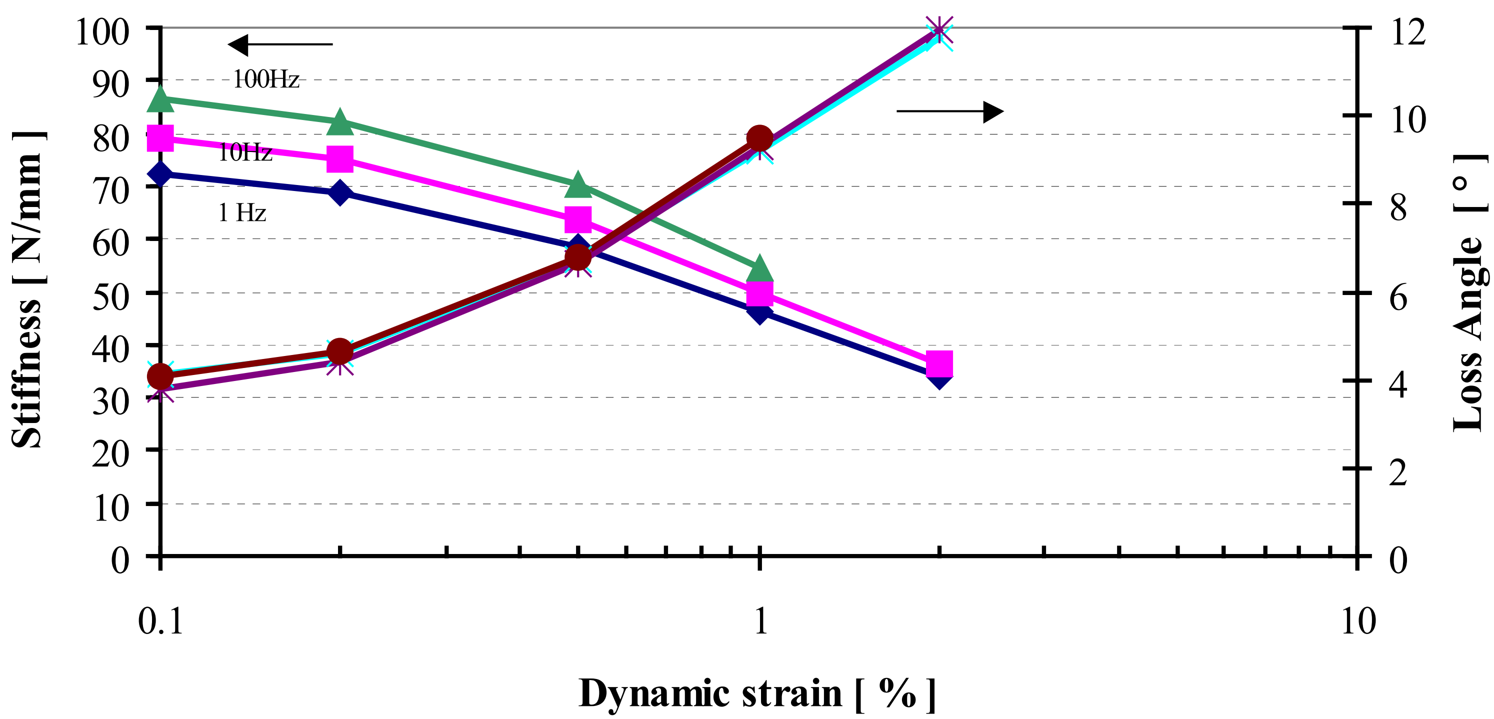


Figure 29

Short-Term Dynamic Tension
F1NR Compound 100°C Moulded Strip

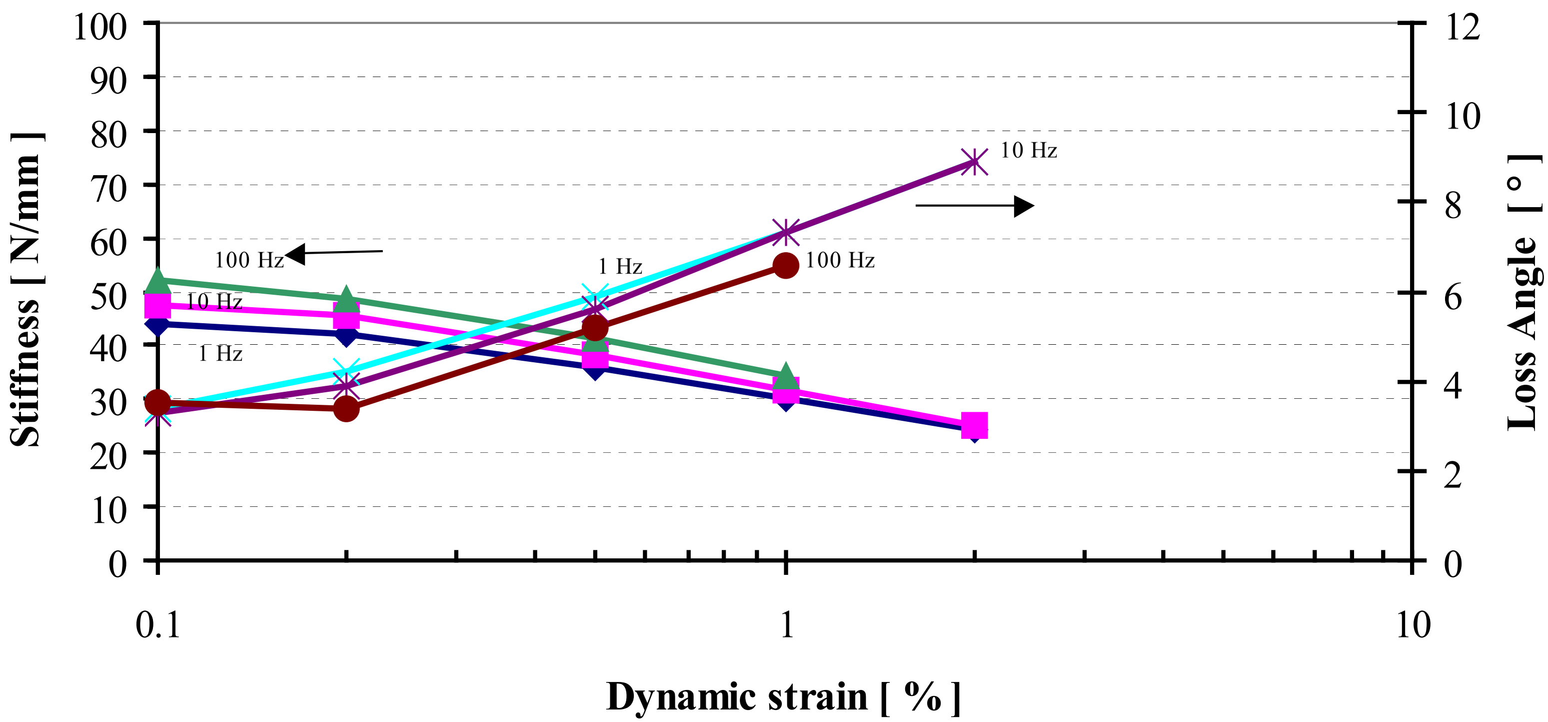


Figure 30

Short-Term Dynamic Tension Stiffness vs. Fiber Loading Moulded strip at 1% Dynamic Strain

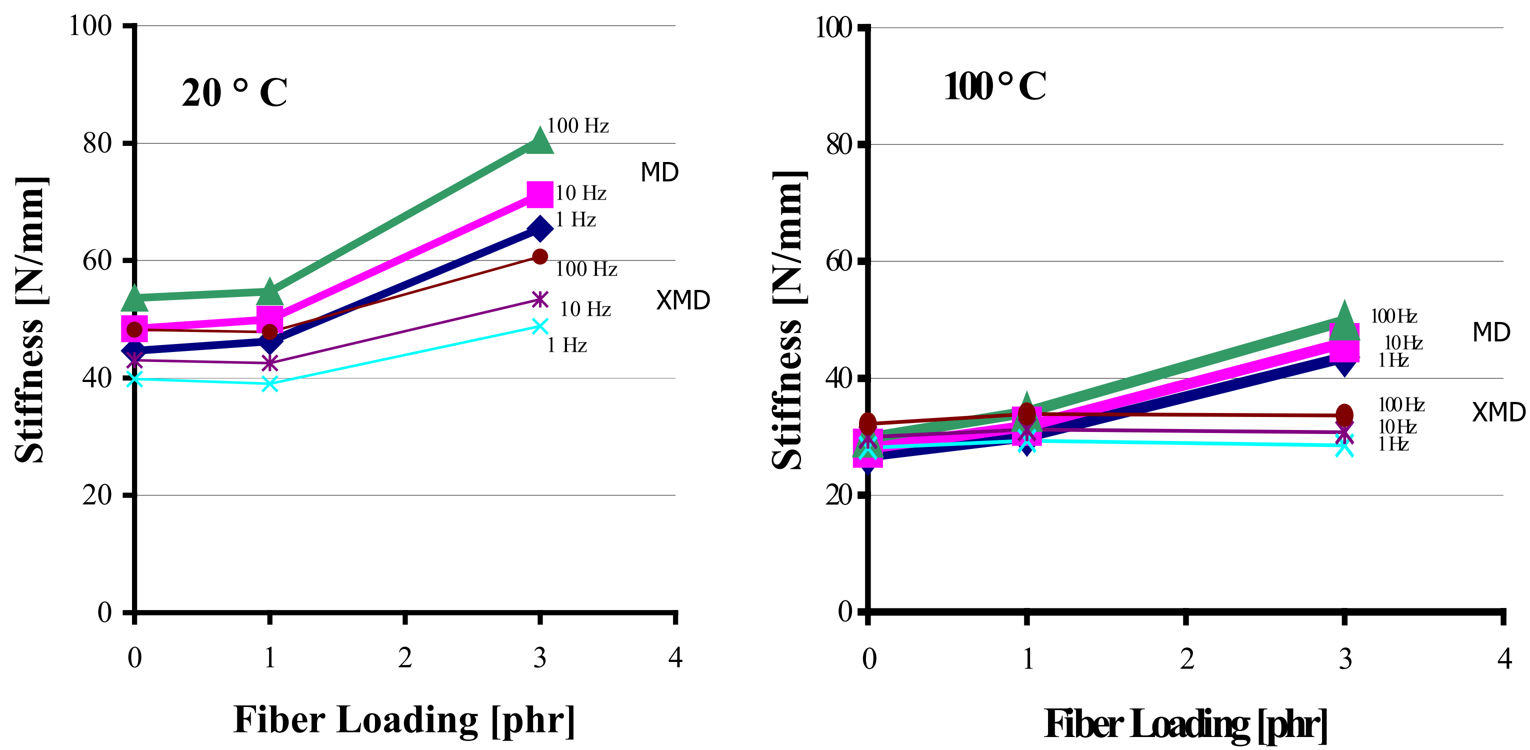


Figure 31

Short-Term Dynamic Tension
Loss Angle vs. Fiber Loading (MD only)
Moulded strip at 1% Dynamic Strain

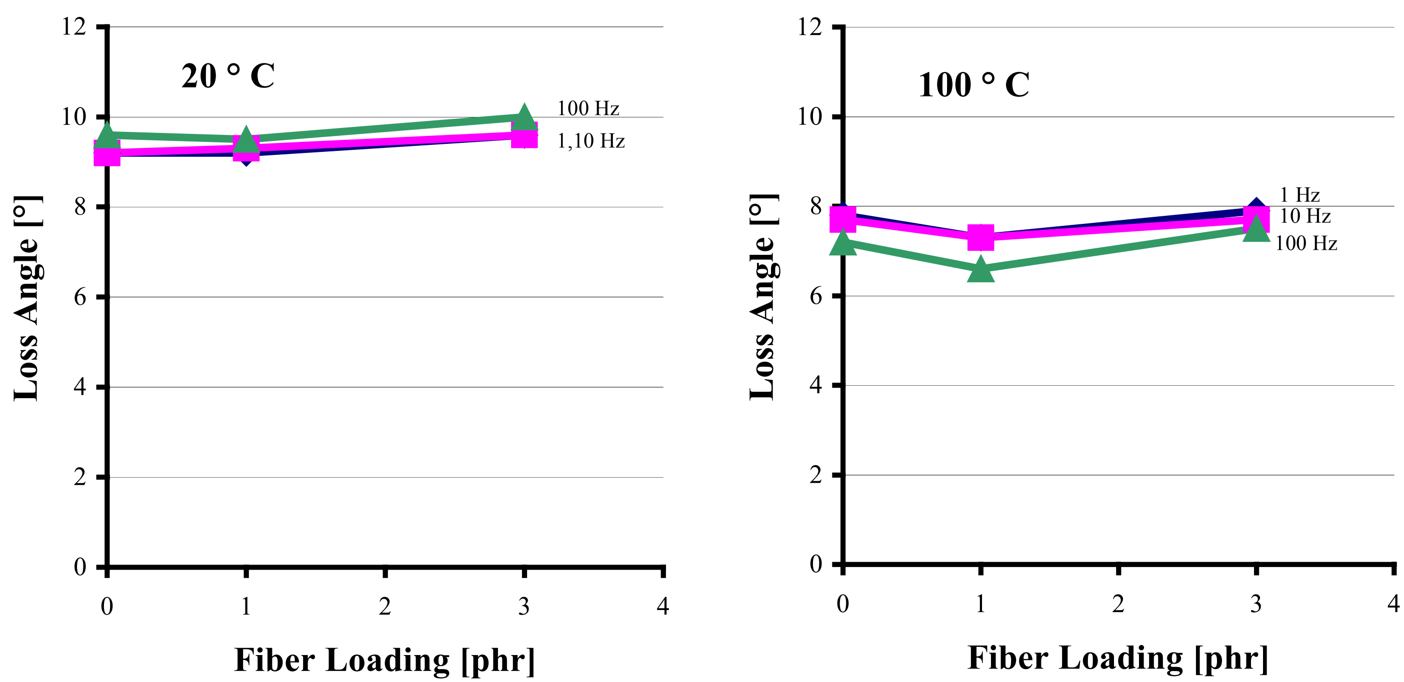
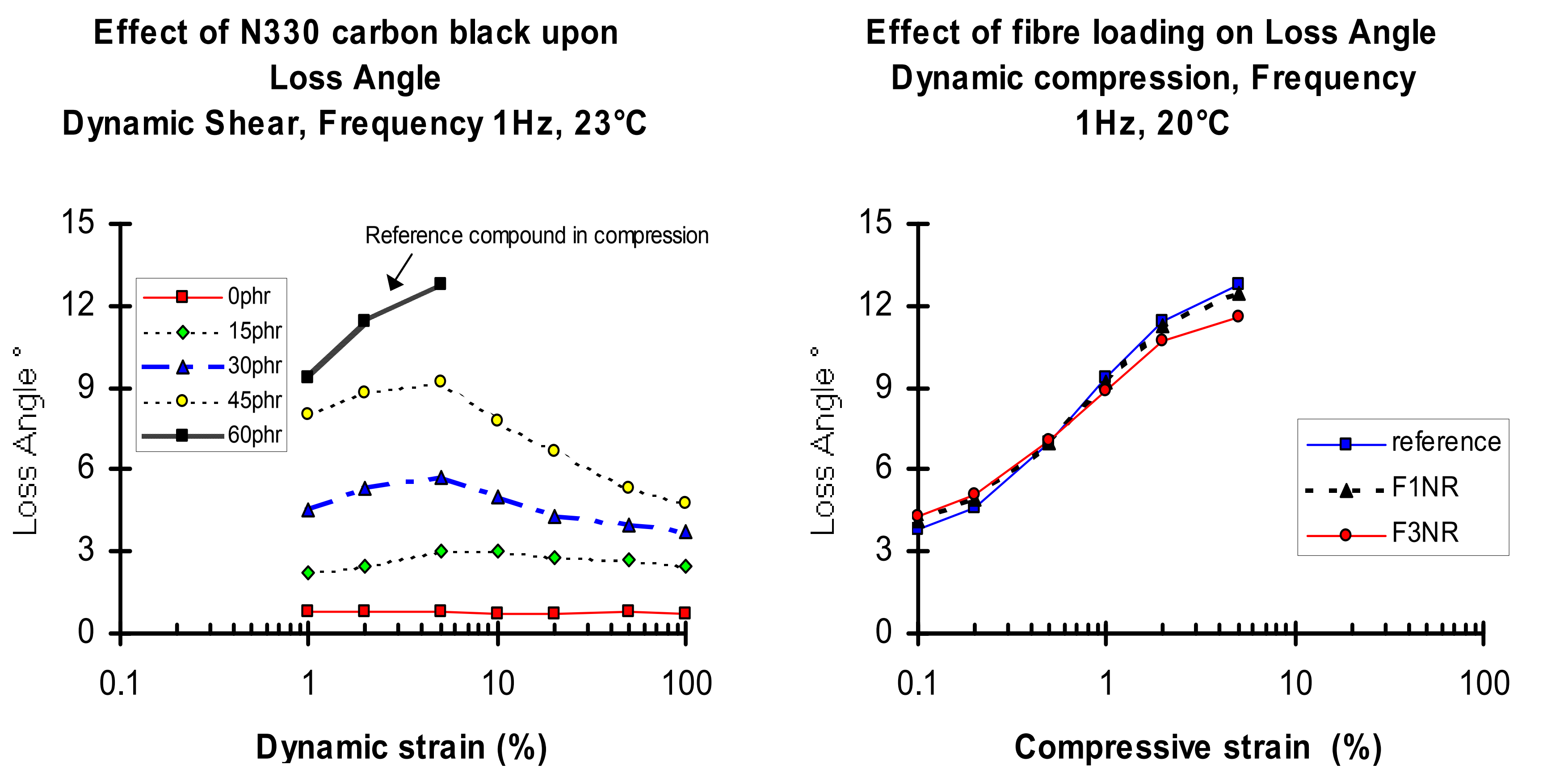


Figure 32

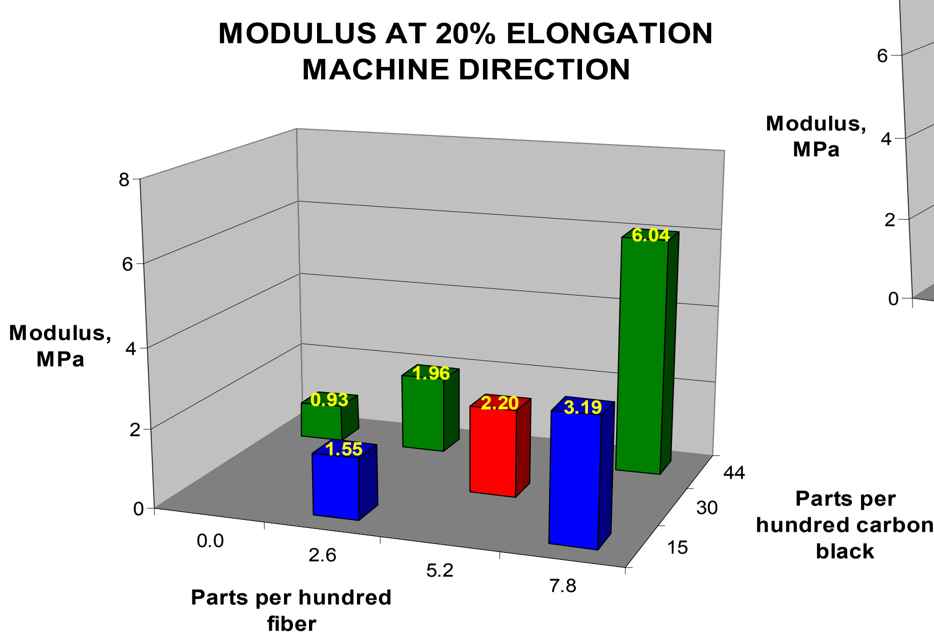
Comparison between effects of carbon black and para-aramid fibers upon loss angle



Data from MRPRA, Engineering Data Sheets©

Figure 33

Effect of fiber and carbon black loadings on modulus at 20% elongation



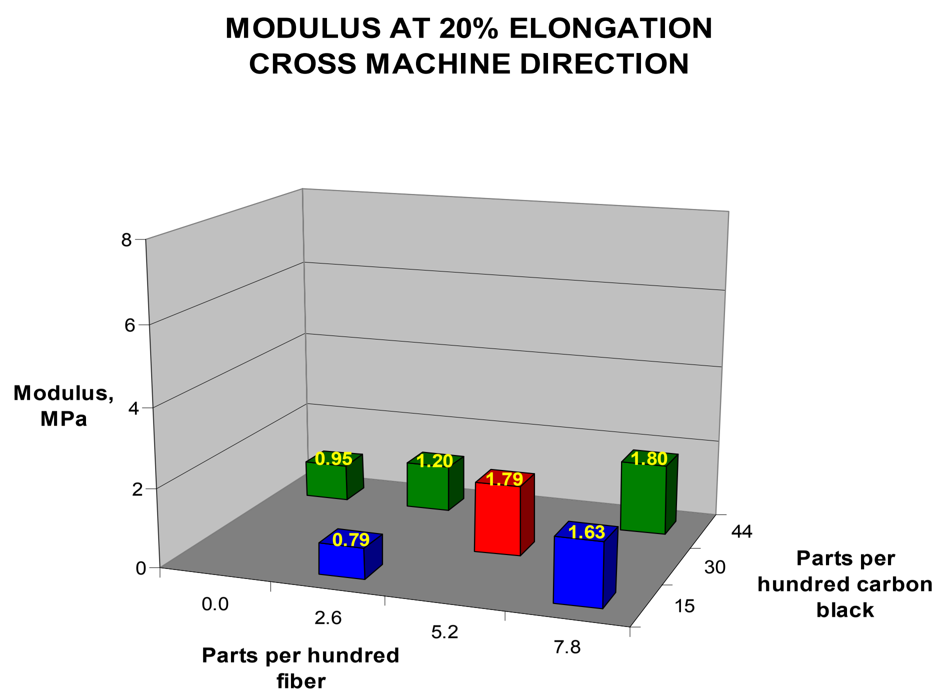
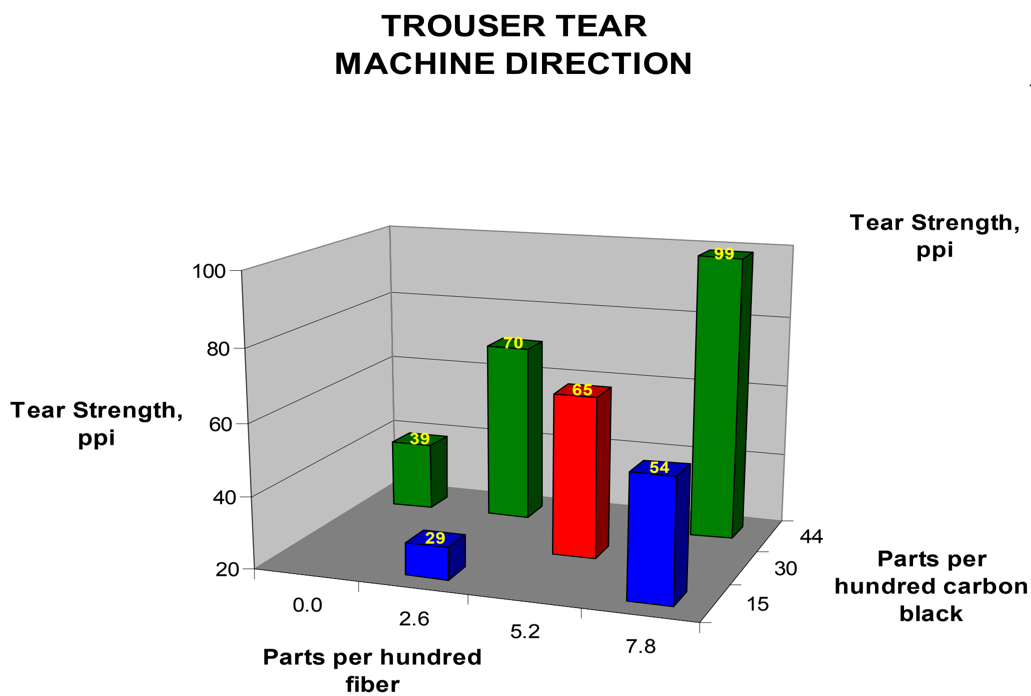


Figure 34

Effect of fiber and carbon black loadings on trouser tear



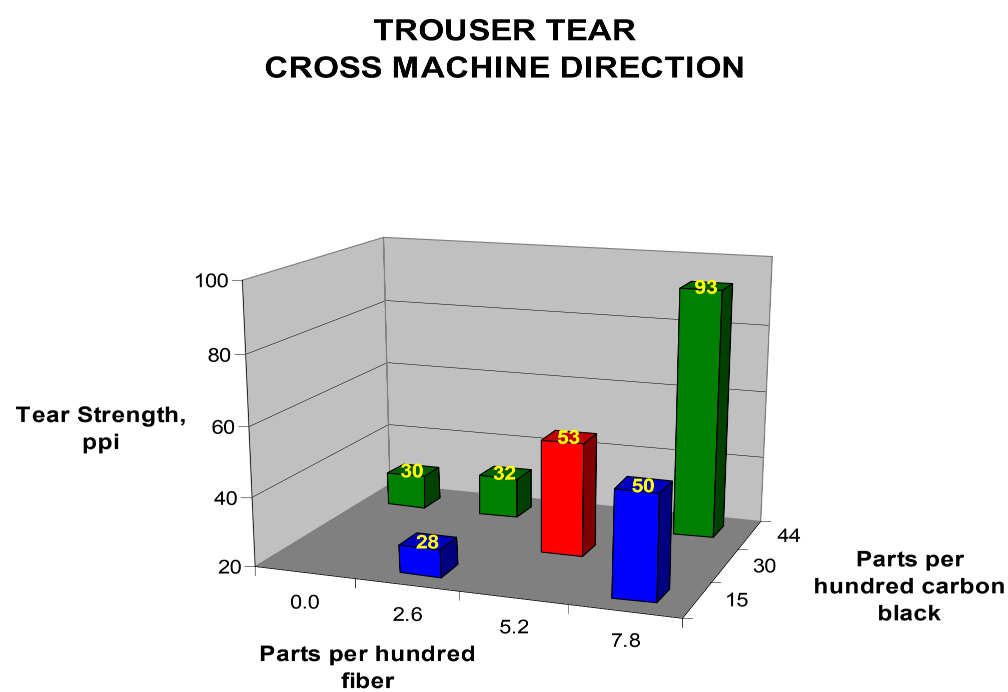


Figure 35

Effect of fiber and carbon black loadings on die C tear

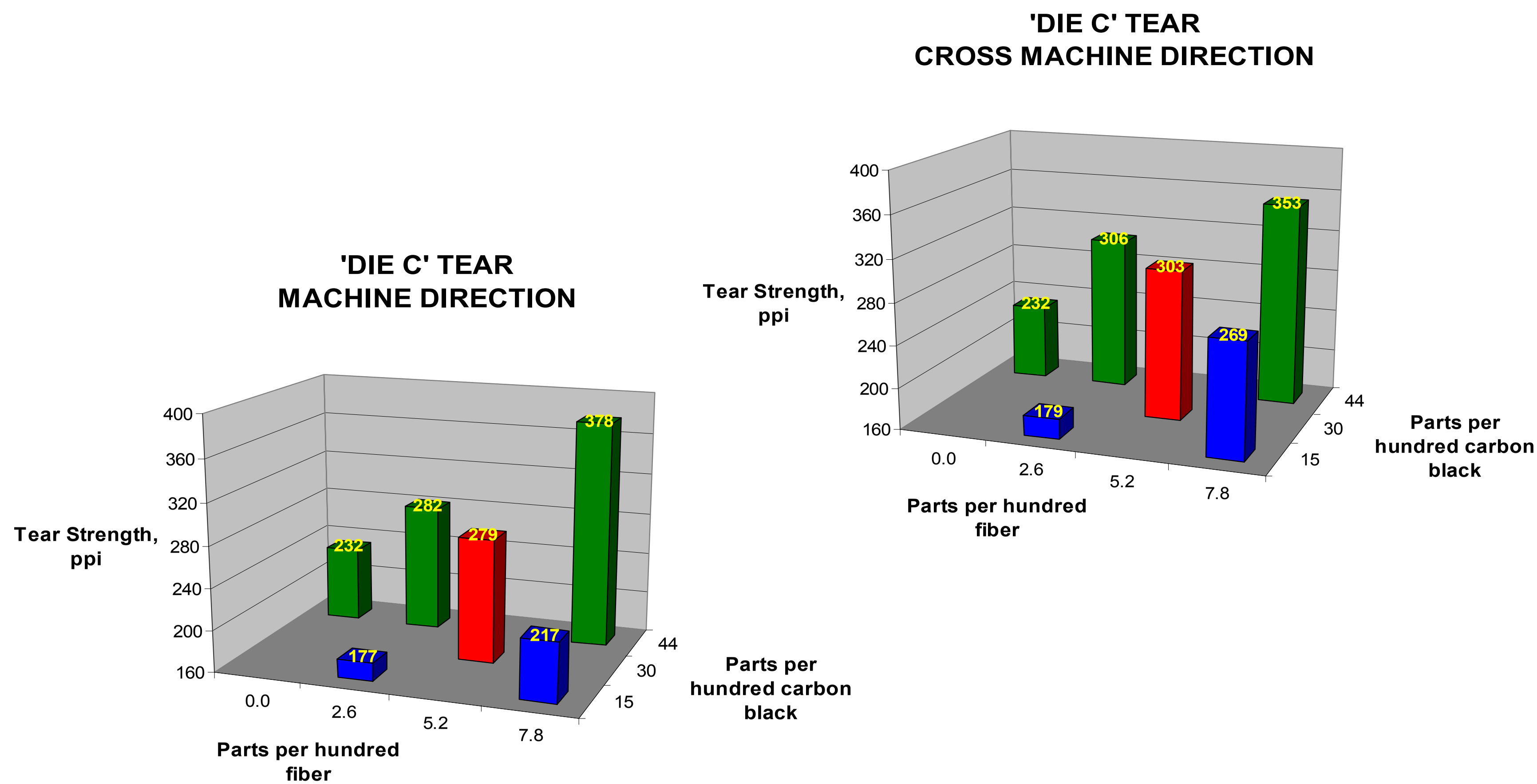


Figure 36

Hardness, Modulus, Tear Balance as affected by pulp and carbon black loadings