PERFORMANCE ASPECTS OF SBS MODIFIED ASPHALT ROOFING MEMBRANES

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Modified bituminous roofing materials are predicted to be one of the fastest growing segments of the North American single-ply roofing market.[1] These membranes provide excellent compatibility with present roofing application practices, and due to their high strength and elasticity, they are able to accommodate the movements of thicker insulations and unstable roof decks.

Adding elastomers, particularly thermoplastic elastomers, significantly upgrades the properties of conventional asphalt. These asphalt/elastomer blends have a wide useful temperature range, from −30 to 120C, and elasticity up to 2000 percent. The superior strength of these membranes is attributable to inorganic or synthetic reinforcements, such as non-woven polyester, glass or films.

Long-term durability is the main performance criterion of these membranes. Therefore, selection of the proper elastomers/asphalt blend is critical.

It should be noted that most of the products presently marketed in this continent are either imports, or are manufactured using technology developed in Western Europe. The work by Building Products of Canada Ltd. was directed towards developing a modified asphalt formulation particularly suitable for North American application conditions.

OBJECTIVES

The objectives of the work summarized in this paper were:

- to highlight the importance of selecting the right formulation to ensure long-term performance, and
- to compare the results of accelerated aging tests to actual weathering performance and to the performance of conventional, unmodified roofing asphalts.

ASPHALT/SBS ELASTOMER BLENDS—GENERAL CONSIDERATIONS

The literature and those involved in this technology agree that the performance of asphalt/elastomer blends is most affected by the nature and composition of the asphalt. While the characteristics of SBS elastpmers and the thermo/mechanical operating conditions are also important parameters, they are usually well known and controllable.

Chemically, asphalts are extremely complex mixtures of high molecular weight hydrocarbons and polar compounds usually containing oxygen, nitrogen and sulfur. The most common method of chemical characterization of asphalt is the Corbett analysis, which is performed by adsorption/elution chromatography on alumina.

The composition is defined in terms of arbitrarily defined components as follows:

- **saturates** eluted with n-heptane, containing saturated hydrocarbons;
- **napthene aromatics** eluted with toluene;
- **polar aromatics** eluted with MeOH/toluene and TCE; and
- **asphaltenes** insoluable in n-heptane.

The first three fractions are commonly called maltenes.

Asphalt used for elastomeric modification behaves like a colloidal substance. The dispersed phase, the asphaltenes surrounded by the polar compounds, is suspended in the saturates or oil phase.

Once the elastomers are added to the hot asphalt, the colloidal structure can be disturbed by the polystyrene and polybutadiene components of the polymer. These parts either dissolve or disperse in such a way that, in hot storage conditions, phase separations do not occur. When cooled to ambient temperatures, the polystyrene endblocks are reformed to serve as crosslinks for the dispersed polybutadiene phase.

It is critical that these midblocks be finely dispersed in the asphalt to prevent phase separation either during cooling or in service. This is accomplished by selecting an asphalt with just sufficient aromaticity to provide a fine, filament-type network within the asphalt at service temperatures.

It is important to note that natural aging of asphalt results in volatile losses and changes in the balance of saturates/napthenes and asphaltenes content. As the asphaltene content increases, the solvating power of the asphalt decreases. Therefore, the aromaticity of the asphalt has to be selected to accommodate the changes caused by both the elastomers and natural aging. Asphalts that meet this criteria, can be called compatible.

Microscopic examination of aged, compatible samples reveals a homogeneous, continuous, highly swollen elastomer lattice with the asphalt absorbed in the form of almost spherical droplets.

THE IMPORTANCE OF ASPHALT SELECTION

The selection criteria developed in Europe reflected the fact that the asphalt situation there, as in North America eight to ten years ago, was predictable and consistent. These criteria usually included limitations on asphaltene content, aromaticity and polarity.

In Europe, a predictive model was developed for asphalts. Accordingly, to have a compatible asphalt/SBS elastomer blend:

- the solvent power of maltenes (fa) had to be higher than $0.28 + 0.004A$, in which A is percent asphaltenes, and
- the ratio of fa/MW had to be between 3 to 7×10^{-4}, in which MW is the molecular weight of the maltenes.[2]

However, this model is feasible only when the asphalt supply has consistent composition, a very rare occurrence in North America.

The situation is further complicated by the fact that the world resources of crude oils are becoming heavier and many refiners avoid the increased heavy bottom output by cracking and coking. This further reduces the choice of asphalts available.

It should also be noted that approximately 80 percent of asphalt production is manufactured to paving specifications. Based on our own experience, most of these asphalts are unsuitable for elastomeric blends. Obtaining a special grade limits refining and production flexibility and is generally much more expensive.

The majority of all asphalts tested exhibited excellent initial physical and rheological properties. Were they to be used to manufacture roofing membranes, most would likely pass all the existing specifications for modified bituminous roofing materials.

Accelerated aging tests on compatible and incompatible blends, however, soon produced dramatic differences in performance. Key properties, such as elasticity, almost totally disappeared in incompatible blends after the samples were subjected to less than three to four months of heat aging at 70C. This highlights the importance of selecting the proper asphalt.

After testing dozens of different Canadian asphalts, it was realized that, in order to have a compatible formulation of exceptional durability, a special grade was needed. This asphalt was developed for us by ESSO Petroleum Canada Ltd.

LABORATORY PROCEDURE

Over three dozen different asphalt/elastomer compositions were tested throughout our work. The elastomers were styrene-butadiene-styrene (SBS) types with either radial or comb-shaped structures. The asphalts were mostly of Canadian origin and included compatible and incompatible types. Common grade limestone was used as a filler.

Blends were mixed in a high-shear mixer at 1500 rpm for one hour with temperature maintained at 190C maximum. The level of elastomer addition ranged from 10 to 20 percent, depending on the type used.

Initial testing to determine the degree of compatibility included a hot storage phase stability test, consisting of storing the samples for 5 days at 160C in 100mm diameter, 1 litre containers. Following a cooling period, the top and bottom parts were separated by cutting the cans in two, and softening points (S.P.) and penetrations (pen) at 25C were determined for each portion.

The blends were defined as follows:

- Compatible I less than 5 percent difference in S.P. and pen.
- Compatible II, more than 5 percent and less than 20 percent difference in S.P. and pen.
- Incompatible, more than 60 percent difference in pen and more than 40 percent difference in S.P.

All blends then were cast into 2mm thick sheets and stored in air at 70C for 0, 2, 4 and 6 months. After aging, samples were cut in order to test tensile properties, permanent set and low temperature flexibility.

Additional samples were remelted for rheological and analytical testing, such as softening point, penetration and gel permeation chromatography GPC.

Since the oxidation of the films is diffusion controlled, remelting could have affected possible changes induced by aging, such as phase separation or crystallization. However, tests of tensile properties, permanent set, and cold temperature properties took the physical and chemical changes into account, as the measurements were taken on the original samples without further processing.

Whenever possible, the accelerated test results were compared with the properties of naturally aged asphalt/elastomer samples recovered from roofing materials exposed in Germany since 1968. The samples were collected from the same roof over a period of eight years.

Laboratory aging of type II roofing asphalts also were included in the experiments as a basis for comparison.

THE EFFECT OF AGING ON SOFTENING POINT

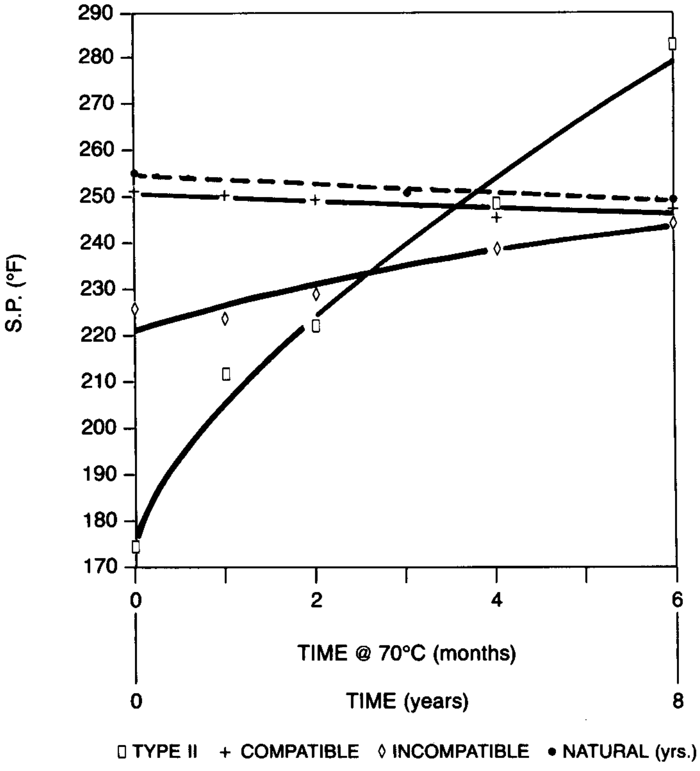
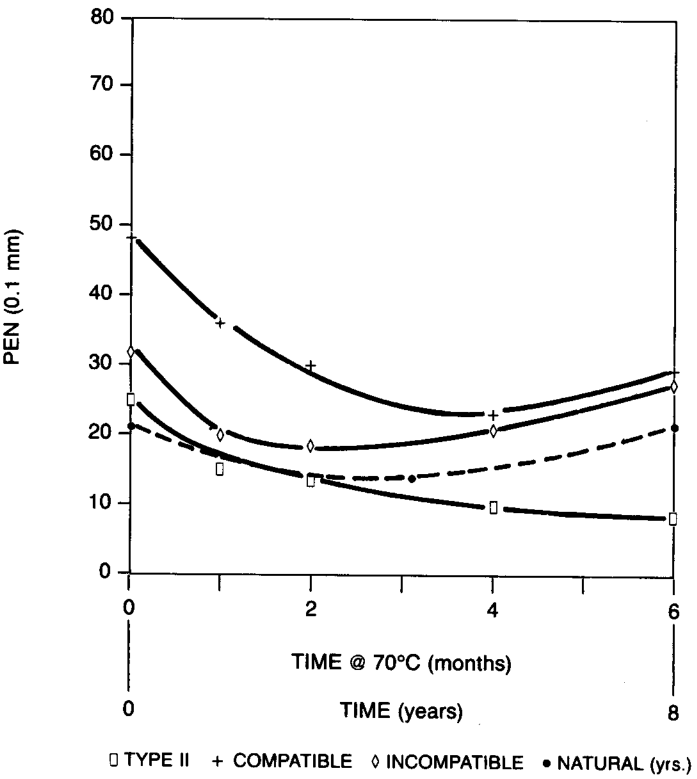


Figure 1 Effect of aging on softening point

The softening point (S.P.) of compatible blends remained virtually unchanged after six months. That of the incompatible blend increased from 225F to 250F.

The S.P. of a conventional type II oxidized roofing asphalt changed dramatically from 175F to 285F. This represents a 500 percent faster rate of hardening than obtained even with an incompatible blend.

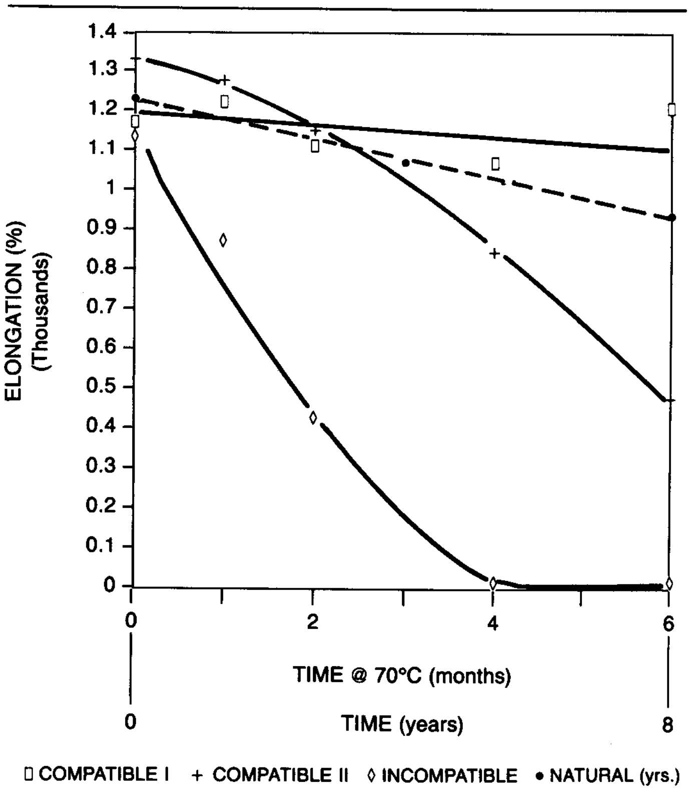
Compatible asphalt/elastomer blends recovered from membranes exposed in Germany for eight years exhibited very slight decrease in S.P.



THE EFFECT OF AGING ON PENETRATION

Figure 2 Effect of aging on penetration

All blends behaved similarly. Penetration changes could not be used to differentiate between asphalts. There was an initial drop in penetration due to hardening of the asphalt as it aged. After approximately three months penetration started to increase again. This was most likely due to depolymerization of the elastomers. The same phenomenon took place with the naturally exposed samples.



THE EFFECT OF AGING ON ELONGATION

Figure 3 Effect of aging on elongation

Elongation was found to be the most useful to differentiate between compatible and incompatible blends. With a highly compatible asphalt, elasticity remained unchanged at 1200 percent after six months.

Marginal compatibility (Compatible II in Figure 3) reduced the elongation from 1300 to 500 percent and incompatible blends lost almost all their elasticity, from 1100 to 20 percent in less than four months.

Optical microscopic examination of incompatible blends after accelerated aging revealed extremely poor morphologies. The asphalt had wide areas of incompatibility with the elastomer. The spatial lattice was irregular with many areas of discontinuity, which explains the poor elastic properties.

The compatible blends, however, still maintained their initial morphologies after aging. The lattices were continuous and very homogeneous. The asphalt was absorbed in the form of approximately spherical droplets.

It should be noted that no differences were found in morphologies between compatible and incompatible blends before accelerated aging.

The elasticity of blends recovered from actual roofing membranes exposed in Germany, changed only slightly, declining from 1200 to 1000 percent after eight years. Again, under the microscope, the globular distribution of the asphalt in the continuous lattice of elastomer was very obvious.

The penetration of the unmodified asphalt decreased continuously from 25 to 10 and at the end of six months it was less than one-third that of the compatible blend. These results on unmodified asphalts are similar to those obtained by the Ruberoid International Technical Committee. Their findings indicated that a 30-pen oxidized asphalt would harden to 15 pen in 10 years.[3]

With a compatible asphalt blend, penetration was approximately 20 pen after eight years, with an increasing trend.

THE EFFECT OF FILLER ON ELONGATION

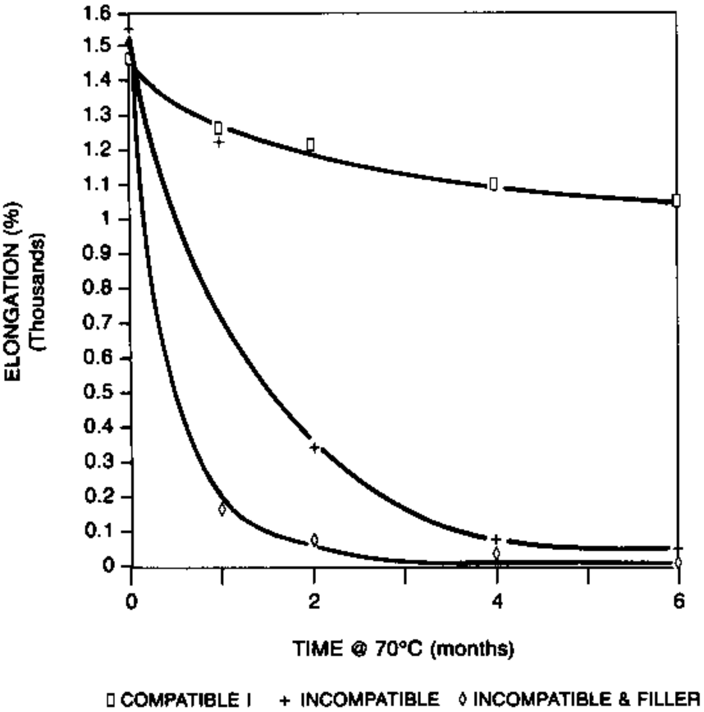


Figure 4 Effect of filler on elongation

The addition of limestone fillers had very little effect on the elongation performance of compatible blends. When added to incompatible blends, however, it accelerated the rate of degradation. After two months at 70C the elasticity decreased from 1450 to 100 percent with filler and to 350 percent without.

Use of fillers such as limestone could further upset the balance of incompatible blends, since it absorbs some of the asphalt components. The effect of reinforcing or non-absorbing fillers on property changes is presently being studied.

THE EFFECT OF AGING ON PERMANENT SET

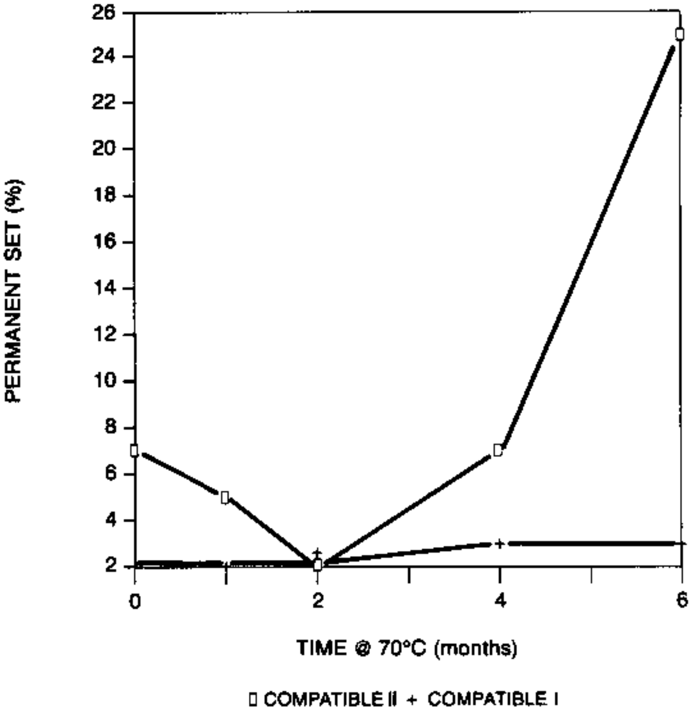


Figure 5 Effect of aging on permanent set

These results were similar to the elongation results. Permanent set after 50 percent elongation was almost negligible for a compatible blend, while it increased to 25 percent with a marginally compatible blend after six months. The test could not be performed with incompatible blends due to the rapid decrease in elongation.

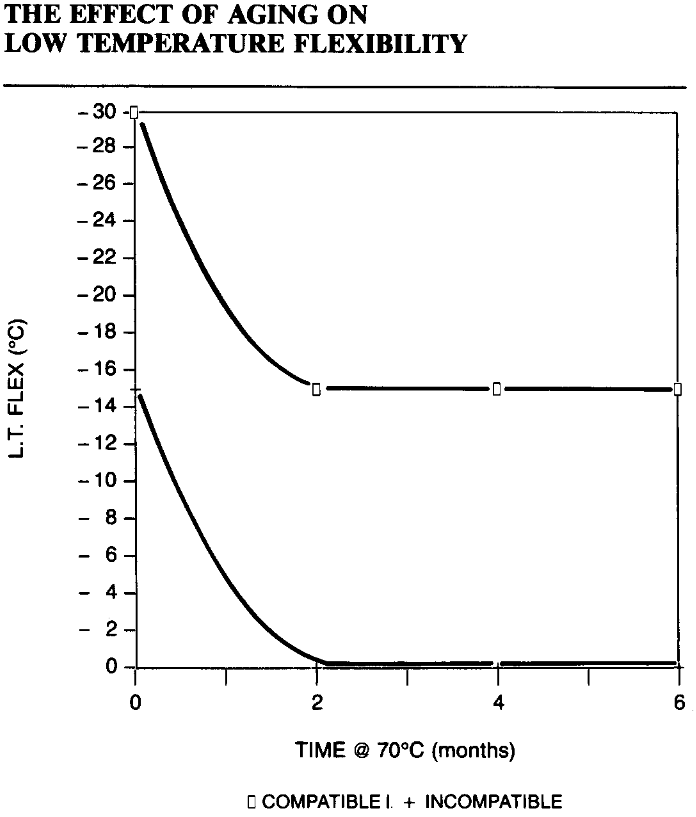

THE EFFECT OF AGING ON LOW TEMPERATURE FLEXIBILITY

Figure 6 Effect on aging on low temperature flex

In all instances, there was a relatively rapid drop in low temperature flexibility. With a compatible blend, it decreased from −30C to −15C in two months. The incompatible blend dropped from −15C to 0C. The values seemed to stabilize at those levels.

Optical microscopy of the aged blends confirmed that a significant phase change took place in the incompatible blend during the first 60 days. The morphology of the originally homogeneous and continuous elastomer matrix had changed to a highly discontinuous one with unevenly dispersed and large, agglomerated asphalt particles.

No significant change in morphology was found in the compatible blends.

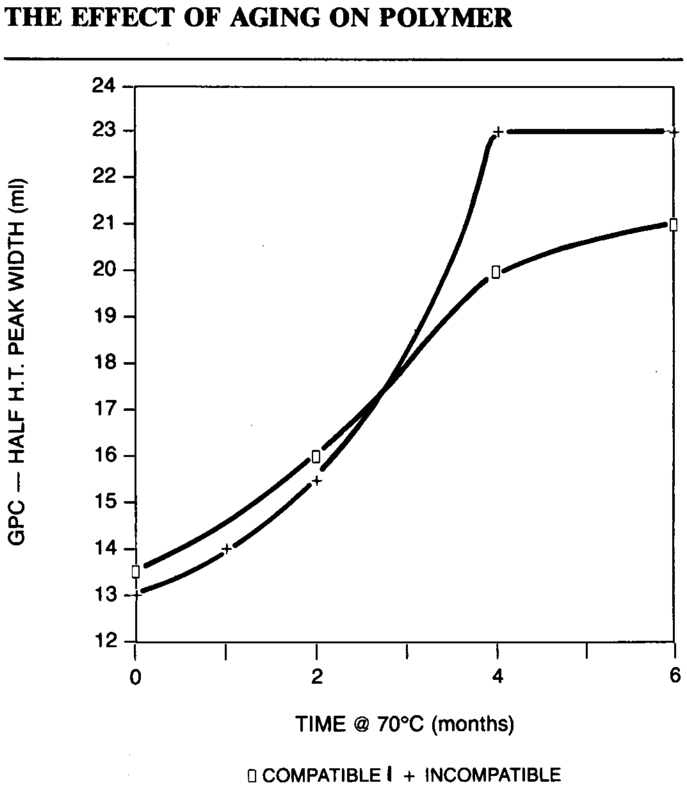

THE EFFECT OF AGING ON POLYMER

Figure 7 Effect of aging on the polymer

Long-term exposure of asphalts to heat and oxygen causes volatile losses and changes in composition by polymerization and/or oxidation. These result in hardening.

The results of gel permeation chromatography (GPC) have shown that, at least in the initial phase of the aging process, chain scission of elastomers predominates. The polymer peak broadened and shifted towards the lower molecular weight asphalt peak. This was indicated by an increase in the polymer peak elution volume from 106ml to 114ml, and by an increase in the half-height peak width from 13ml to 20ml.

The amount of degradation appeared independent of whether the asphalt was compatible or incompatible.

As shown in Figure 2, depolymerization of the elastomer does not necessarily adversely affects hardness or softening point. Softening of the polymer could counteract the hardening of the asphalt, resulting in relatively steady maintenance of those properties.[4] It could, however, affect properties such as elongation, elastic recovery and low temperature flexibility, particularly when incompatible asphalts cause significant time-dependent charges in blend morphologies.

SUMMARY

Accelerated aging of compatible and incompatible elastomer/asphalt blends revealed significant differences in key properties, in spite of acceptable and similar initial values.

Selection of the correct asphalt is critical in North America because the asphalt supply is inconsistent and rapidly changing.

The superior performance of modified bituminous membranes was confirmed by testing roofing materials exposed to natural weathering for up to eight years, and by comparing the performance of modified asphalts to standard oxidized roofing grades.

APPENDIX

Testing of elastomer/asphalt blends

Softening Point:	ASTM D36
Penetration:	ASTM D5, equivalent to the penetration of a standard needle into the sample, under a load of 100g during 5 sec. at 25C, measured in 0.1mm.
Low Temperature Flexibility:	A 2 × 25 × 150mm strip is bent over a 25mm diameter cylinder across a 90° angle in 5 sec.
Permanent Set:	A 2 × 20 × 100mm strip is stretched at 5mm per min. at 50 percent elongation. After 24 hours the strip is allowed to recover.
Elongation at Break:	A 2 × 15 × 50mm sample is stretched in an Instron at a speed of 8.5mm per sec. until failure.
Gel Permeation Chromatography:	This technique yields the molecular weight distribution of a product.

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