FORCED VIBRATION TESTS ON BITUMEN AND POLYMER-BITUMEN MEMBRANES TO DETERMINE THEIR FUNDAMENTAL PROPERTIES WITH RESPECT TO FREQUENTLY USED POLYMERS

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Fundamental tests are necessary to adequately describe the behavior of factory-made, reinforced bitumen and polymer-bitumen membranes. Their mechanical properties are essentially influenced by environmental conditions, loading time and loading intensity. Consequently, the fundamental properties have to be determined over wide temperature and frequency ranges.

The forced vibration tests allow the determination of the fundamental properties such as complex moduli and thus enable a description in physical terms of the behavior of bitumen and polymer-bitumen membranes under realistic environmental loading conditions.

The characteristics determined by forced vibration tests allow a comparison of the properties of the tested materials. Bitumen- and polymer-bitumen membranes were tested which were modified with atactic polypropylene (APP) and styrene-butadiene-styrene (SBS). Their behavior differed significantly at high temperatures and low frequencies.

A method for measuring SBS in polymer-bitumen quantitatively is included to suggest behavior of prefabricated polymer-bitumen membranes and polymer content. A diagram was developed in which the original SBS percentage of a SBS-bitumen mix can be found.

The results of the mechanical tests described combined with the determinations of polymer percentage is considered an important element in optimizing polymer-bitumen behavior for various applications.

KEYWORDS

Bitumen membrane, dynamic mechanical analysis, forced vibration test, high-pressure liquid-chromatography, polymer-bitumen membrane, styrene-butadiene-styrene content.

INTRODUCTION

Factory-made, reinforced bituminous membranes are frequently used for roofing or waterproofing. In Switzerland, these materials are delivered in the form of rolls and consist of bitumens or polymer-bitumens with a reinforcement of suitable mats, fabrics etc. During the past 10 years, the usage of polymer-bitumens has continuously increased. In Switzerland, factory-made and reinforced polymer-bitumen sheets are applied mostly as waterproofing material on bridges.

MATERIALS

Reinforced membranes are flexible or semiflexible roof coverings or waterproofing layers reinforced with felts, mats, fabrics or chopped fibers. Their primary function is to prevent water penetration in buildings, i.e., the exclusion of water. In Switzerland, reinforced bitumen membranes or reinforced polymer-bitumen membranes are normally obtained from factory-made sheetings of these materials.

This paper describes test results from a bitumen membrane consisting of a blown and oxidized bitumen with a jute fabric, and a polymer-bitumen membrane consisting of a bitumen modified by either atactic polypropylene or styrene-butadiene-styrene and reinforced with a polymer fleece.

Traditional tests were carried out on the binders themselves. For the penetration at 25°C (Pen) and the softening point by the ring and ball method (R & B) the mean values are reported in Table 1.

FORCED VIBRATION TESTS

The principle of forced vibration tests consists of applying either repeated equal loads or repeated forced displacements on a test specimen. Tests on bituminous materials have to be carried out under various, but precisely maintained temperatures.

Forced vibration tests were carried out on bitumen and polymer-bitumen membranes over wide temperature and frequency ranges typically from −10°C up to +40°C and between 0.1 and 32 Hz (see Figure 1).

The forced displacements and the resulting material behavior enable the characterization of the viscoelastic materials. Figure 2 schematically shows a vertical section of the coaxial cylinders with a test specimen in place. This kind of shear test allows the determination of the ratio of viscous modulus and elastic modulus as components of the complex modulus in shear as follows.

Complex modulus in shear $\vec{G}^* = \vec{G}' + i\,\vec{G}''$

- G^* dynamic shear modulus
- G' elastic modulus or storage shear modulus
- G'' viscous modulus or loss shear modulus
- $\emptyset$ phase angle

The imaginary part of the complex modulus in shear is also called the viscous modulus G''. This viscous modulus is then described by the relationship of its components G' and G^*.

$$G'' = G^* \cdot \sin(\varnothing)$$

G″ is a degree of the lost energy, which is transformed into heat, observed in the temperature rise of the specimen during the test at high frequencies.

The real part of the complex modulus in shear (which is the elastic modulus in shear as well) can be presented as

$$G' = G^* \cdot \cos(\varnothing)$$

G′ is a degree of recoverable energy of displacement and therefore a measure of elasticity.

MEASUREMENTS

The goal of the development of such a test method was to be able to efficiently measure physical values such as the complex modulus in shear, viscous modulus, elastic modulus and phase angle of different kinds of bituminous materials over a wide range of temperature and frequency.

During the test, there is no need to use more than one specimen for a complete series of measurements. Mechanical strain is minimized and there is no flow (creeping) allowed of the specimen throughout the test because a computerized procedure always resets the equipment to the initial conditions. In this procedure, during the time when the temperature is changed to another level and the specimen adapts the new temperature, a computer always controls displacement of the centered metallic body (see Figure 2) and invokes the hydraulics to keep it in initial position. Initial position is the position before any loading ocurs.

The test series repeated 14 times with the same specimen resulting in less then 1 percent standard deviation, and less than 5 percent when the test was repeated with two to three different specimens. However, the same test procedure was used.

Automating the test procedure, greatly facilitates the collection of data, its evaluation, presentation, calculation and presentation of the master curves. The WLF-equation [1,2] enables a shifting of the curves for each modulus and for the different temperatures in such a manner as to obtain a unique curve for one reference temperature (e.g., 20°C). The master curves for the different test specimens allow a direct comparison of the materials tested.

RESULTS OF FORCED VIBRATION TESTS

A comparison of the different master curves of the bitumen and polymer-bitumen membranes described leads to the following interpretation.

The dynamic shear modulus G* and the elastic modulus G′ are:

- Almost equal, for the three materials at high frequencies.
- Significantly higher for the polymer-bitumen membrane than for the bitumen membrane.
- Significantly more curved at the curves for the bitumen membrane than for the polymer-bitumen membrane (e.g., higher temperature susceptibility of the bitumen membrane than for the polymer-bitumen membrane).

This last conclusion is drawn from the phase angles Ø too, shown as a function of frequency and for different temperatures (see Figure 3). Especially for temperatures above 15°C and/or low frequencies, the bitumen membrane is significantly more temperature dependent than the polymer-bitumen membrane.

The forced vibration tests described above allow the determination of essential properties and thus enable a realistic description of the behavior of bitumen and polymer-bitumen membranes.

MEASUREMENTS OF SBS IN SBS-MODIFIED BITUMENS BY MEANS OF HIGH-PRESSURE LIQUID-CHROMATOGRAPHY

This study was performed to determine a method for measuring SBS in SBS-modified bitumens.

Four different SBS and six bitumens of different penetration grade were combined to produce commonly used mixes in the range of 3 to 30 percent SBS. Some SBS contents of these mixes were measured by high-pressure, liquid-chromatography.

The integration of the peak areas of the chromatographs is computed as percentage of the total peak areas and then plotted against the original SBS percentage of the mix. A diagram was developed in which the original SBS percentage of a SBS-bitumen mix can be found: A vertical line is erected on the X-axis at the value of SBS percentage found by the regression equation and this point is connected horizontally to the Y-axis. The value of original SBS percentage is thus obtained.

MATERIALS

SBS Polymers

A polymer-bitumen manufacturer supplied four SBS polymers numbered from one to four for this work. SBS 1 was delivered with some oil content. However, in this paper, only the percentage of SBS is discussed.

Bitumen

Different penetration graded bitumens of crude oil of various origins were used to prepare the SBS-bitumen mixes (see Table 2).

EXECUTION OF MEASUREMENTS

Detecting the Chromatographs

The measurements were performed with the high-pressure, liquid-chromatography apparatus. Chromatographs of bitumen and SBS-bitumen mixes are detected exclusively with newly distilled tetrahydrofuran.

Mobile Phase	**Tetrahydrofuran**
Flow rate	1 ml/min.
UV detector	
Low-pressure mercury source	254 nm

Flame ionization detector			
heating range		6	
flame	H2	140	
	air	0	
cleaning flame		H2	600
		02	300
injection volume		20 μl	

PREPARING THE SOLUTIONS OF SBS AND STRAIGHT-RUN BITUMEN

In this paper the term molecular mass is used exclusively for the formerly used expression molecular weight.

Defined quantities are taken from the above-mentioned SBS-polymers and bitumens in a 25ml calibrated, graduated cylinder and dissolved in tetrahydrofuran without mixing it previously. The total mass of SBS and bitumen is 0.5g. Only solutions prepared on the same day are measured.

RESULTS

Molecular Mass Determination of Polystyrene Calibration Standard

A mix of polystyrene calibration standards was prepared which contained all polystyrene calibration standards with their differing molecular mass in the same quantity in a single sample.

To check the retention time of the ultraviolet detector and the flame ionization detector, dichloromethane was used as solvent. The chromatographs obtained with the ultraviolet detector and flame ionization detector show that the retention times of each polystyrene calibration standard are similar.

Molecular mass of SBS is assumed to be between 2,750,000 g/mol. and 35,000 g/mol. (83 = molecular mass of dichloromethane). The molecular mass of the solvent dichloromethane used is easily detected by the ultraviolet detector, but is not visible by the flame ionization detector. Therefore, only the data of the flame ionization detector are used for the interpretation of the chromatographs. This makes it easier for the laboratory assistant to control the baseline for peak calculations.

PERCENT SBS IN BITUMEN

The percentage of SBS measured in the bituminous mixes conforms to the range expected in industrial products for road construction and waterproofing materials. Figure 4 summarizes all the results of the measurements of SBS in bitumen (plotted on the X-axis) vs. the added SBS-percent (Y-axis).

The computer produced a curve representing the cubic regression equation [y = b0 + b1X + b2X*X + b3X*X*X] which fit slightly better than the quadratic one. Two other dotted lines are drawn representing confidence limits at the 95th percentile.

From this diagram, the original SBS percentage of a SBS-bitumen mix is found when a vertical line is erected on the X-axis at the value of SBS percentage found by the regression equation; this point is connected horizontally to the Y-axis. The value of original SBS percentage can then be recorded. Table 3 shows the chromatography determinations of SBS in straight-run bitumen.

REPRODUCIBILITY OF THE MEASUREMENT OF THE SBS PERCENTAGE

Based on the results of the measurements of SBS in bitumen as shown in Figure 4, the confidence limits at the 95th percentile represent an acceptable accuracy at the present time. The measurements already performed show thE SBS percentage of a bituminous mix can in all probability be determined to an accuracy of 1 percent.

CONCLUSIONS

The characteristics determined by the forced vibration test allow a comparison of the properties of the tested materials and lead to the following conclusions.

Compared with the bitumen membranes, the polymer-bitumen membranes show:

- Significantly higher dynamic and elastic moduli at high temperatures and/or low frequencies, i.e., slow-load applications (static load).
- Significantly lower temperature susceptibility.

High-pressure, liquid-chromatography may be used to determine the SBS percentage in modified bitumen. It is easy to run and gives reasonably accurate results very rapidly. This makes it suitable for supervising a continuous production of SBS-modified bitumen.

A method of analyzing the percentage of atactic polypropylene (APP) is still in evaluation.

Investigation of the polymer percentage in combination with the determination of the mechanical properties is considered an important element in optimizing polymer-bitumen behavior for various applications.

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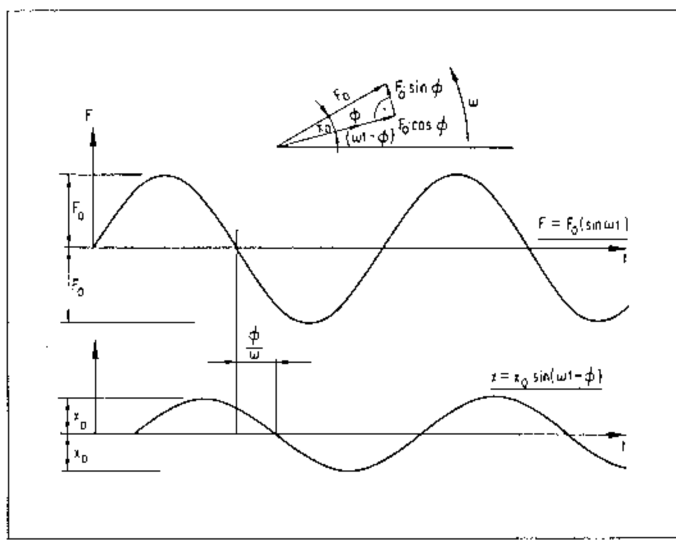

Figure 1 Forced vibration tests—Sinusoidal displacements (X), recorded force (F) and phase angle (Ø).

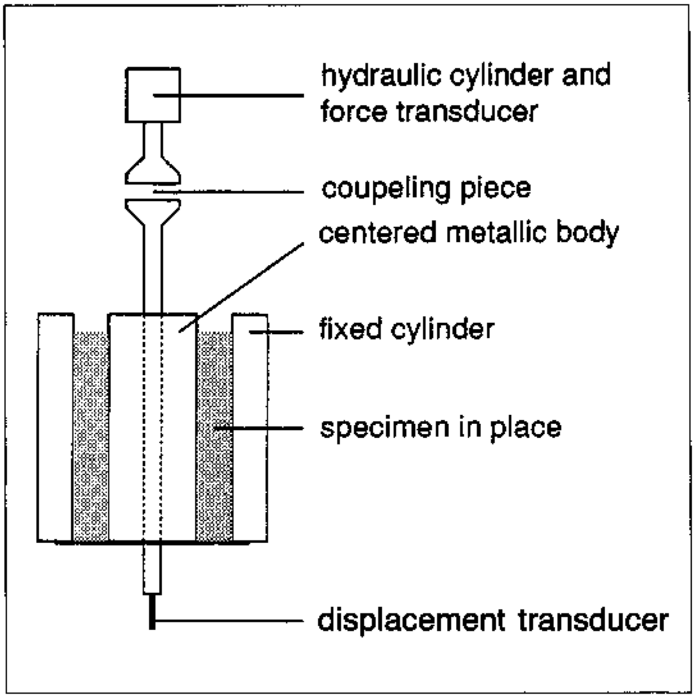

Figure 2 *Vertical section of the coaxial cylinders with a test specimen in place.*

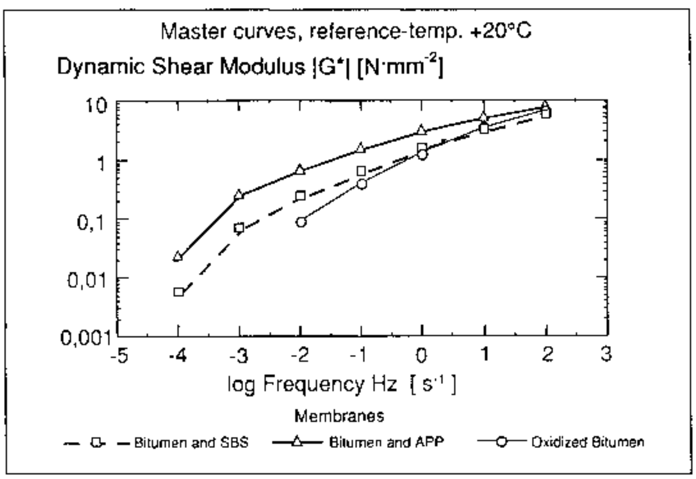

Figure 3 *Master curves for the different test specimens.*

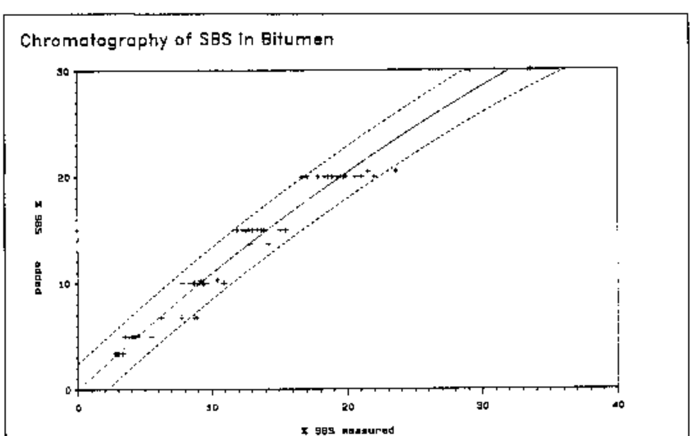

Figure 4 *SBS percentage determined as function of the added SBS percentage with the regression line and the confidence limits at the 95th percentile.*

	Ring and Ball	Penetration
Oxidized Bitumen	116°C	19 10^{-1}mm
Polymer-Bitumen modified by APP	152°C	36 10^{-1}mm
Polymer-Bitumen modified by SBS	120°C	39 10^{-1}mm

Table 1 *Results of traditional tests on the bituminous coatings.*

Bitumen	Penetration range at 25°C	Origin of crude oil
1	B 180/220	Venezuela
2	B 180/220	Near East
3	B120/150	Unknown
4	B 80/100	Arabia heavy
5	B 80/100	Safaniyah (Near East)
6	B 60/70	Unknown

Table 2 *Bitumens used to prepare the SBS-bitumen mixes.*

Chromatography determinations of SBS in straightrun bitumen					
Number of Determinations	%-SBS added	Mean %-SBS obtained	Minimal Value	Maximal Value	Standard-deviation
6	3.4	3.03	2.74	3.37	0.3
9	5.0	4.18	3.49	5.49	0.6
4	6.8	7.90	6.24	8.89	1.2
14	10.0	9.28	7.82	10.96	0.9
2	10.3	9.82	9.16	10.47	0.9
2	13.7	13.56	12.89	14.22	0.9
12	15.0	13.64	11.87	15.51	1.2
14	20.0	19.16	16.66	22.00	1.5
2	20.5	22.56	21.54	23.58	1.4
8	30.0	31.57	28.81	33.73	1.9

Table 3 *Number of determinations, added SBS percentage, SBS obtained, mean value, minimal value, maximal value, standard deviation.*