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Effect of heat-ageing on the thermal and mechanical properties of APP- and SBS-modified bituminous roofing membranes

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The effect of heat-ageing on four bituminous roofing membranes, two modified with atactic polypropylene (APP) and two modified with styrene–butadiene–styrene (SBS) was studied using tensile testing and dynamic mechanical thermal analysis (DMA). The samples were heated at 80°C for 7, 28, 84 and 168 days and were tensile tested at 23, 0, −10, −20 and −30°C. Each heat-aged sample was also subjected to thermomechanical testing to find its glass transition temperature T_g. The results show significant variation in the effect of heat-ageing on tensile strength and elongation of membranes. T_g values differ with the modifiers and other ingredients of the membranes and are affected by heat-ageing. The influence of the glass transition zone measured by DMA is also reflected in the tensile test results.

1. INTRODUCTION

Polymer-modified bituminous membranes were developed in Europe in the mid-1960s and have been in use in North America since 1975. Bitumen, polymers and other ingredients used for the manufacture of these membranes have to be carefully selected and compounded in the manufacture of the coating. Also, reinforcing mats like glass fibre and polyester are specifically designed to meet the membrane requirements for successful performance in a roofing system. The modifying polymers, such as atactic polypropylene (APP) or styrene–butadiene–styrene (SBS), impart flexibility and elasticity, improve cohesive strength, resistance to flow at high temperatures and toughness [1,2]. Typical compositions of modified bituminous roofing membranes are shown in Table 1.

Mechanical testing and dynamic mechanical thermal analysis (DMA) can be applied to predict the durability and performance of bituminous roofing membranes [3]. In the laboratory, heat-ageing and u.v. exposure are used to accelerate the effects of exterior weathering of the membrane on the roof. The results obtained after ageing may provide useful information as to the performance of the membrane, but may not have a direct correlation with the actual changes in physical and chemical properties that may occur during natural weathering [4,5].

Tensile strength and elongation are the most commonly used mechanical properties that provide information about the performance of the membranes. Tensile strength relates to the ability of a membrane to withstand stresses that might be imposed by building movement, wind uplift and thermal loading. Elongation measures the ability of a membrane to accommodate movement in the substrate or structure without rupturing.

In general, thermal and mechanical properties provide information as to the effective life and why some roofing

Table 1 Typical compositions of APP- and SBS-modified bituminous roofing membranes

	Approx. content (wt %)		
Ingredients	APP	SBS	Function
Bitumen	38.0	50.0	Waterproofing agent
Polymer	15.0	4.4	Imparts elastomeric or plastomeric properties
Reinforcement	3.5	3.5	Provides tensile strength
Mineral granules	36.0	31.0	Protect against u.v. radiation
Filler	7.4	9.0	Provides rigidity
External plastic layer	0.1	0.1	Avoids stickiness during storage

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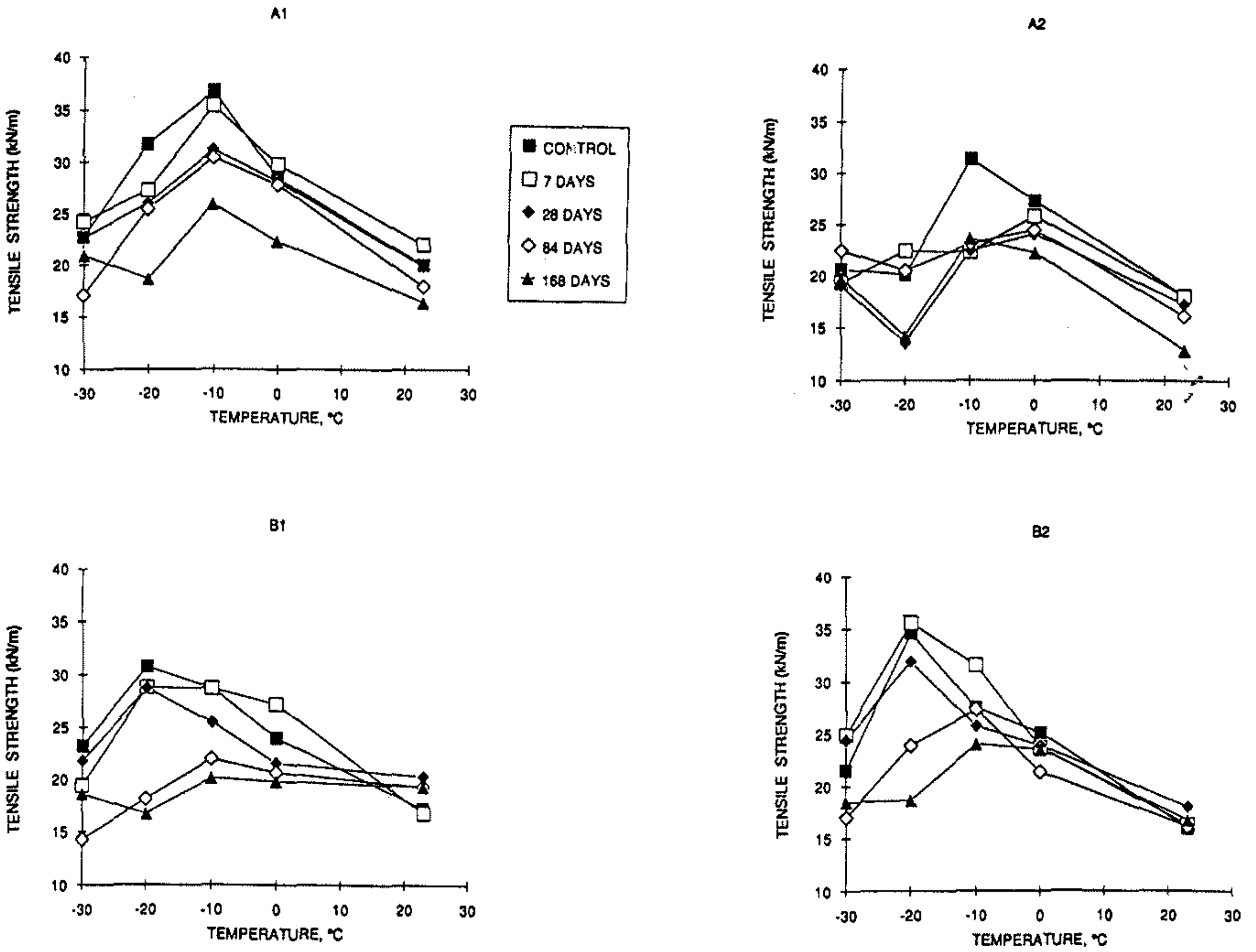

Fig. 1 Strength–temperature.

membranes fail faster than others. DMA can be used routinely to determine some properties of membranes, e.g. glass transition temperatures below which they tend to become stiff and lose flexibility. The objective of this study is to evaluate the significant properties of butuminous membranes modified with different modifiers and different intensities of accelerated weathering. Their glass transitions and tensile properties were compared for correlation [6].

2. EXPERIMENTAL PROCEDURE

2.1 Heat-ageing

Four commercially available modified bituminous membrane samples (A1, A2, samples modified by APP and B1, B2 modified by SBS) were selected. Their weights were 4.0, 4.2, 5.5 and 4.9 kg m^{-2}, and thickness 3.8, 4.1, 5.1 and 4.2 mm, respectively. Polyester mats, placed in the centre of the membranes with weights 318.3, 253.8, 211.0 and 197.0 g m^{-2}, were used as reinforcements. For each ageing period (7, 28, 84 and 168 days), twelve pieces of approximately 150 mm × 250 mm were cut. Two pieces of each material were used as controls and ten were placed in air-circulating ovens preheated to 80°C.

2.2 Tensile testing

The specimens were conditioned at 23, 0, −10, −20 and −30°C for a minimum of 24 h prior to testing. The control and heated specimens were cut using a dumbbell-shaped die in a hydraulic press. A universal test apparatus (Instron model 1122) connected to a computer and provided with an environmental chamber and nitrogen cooling device was used. The test conditions were: gauge length 75 mm, crosshead speed 75 mm min^{-1}, chart speed 100 mm min^{-1} and grip spacing 75 mm. Five replicates for each sample were tested at each temperature. The load–elongation curves were recorded on the machine chart recorder as well as being stored in the computer.

2.3 Dynamic mechanical analysis

A Rheometrics Solids Analyzer RSA II dynamic mechanical thermal analyser with RHIOS software and equipped with a Polycold gas chiller model PGC-100 was used. The bituminous samples were cut in the machine direction 48 mm long and 12 mm deep and were run in the DMA in three-point-bending mode. A fixed frequency of 1 Hz and heating rate of 2°C min^{-1} was used to study the samples between −70 and 40°C. In

Table 2 Tensile strength values of modified bituminous membranes

Testing temp. (°C)	Heat-ageing (days at 80°C)	Tensile strength (kN m^{-1})							
		A1		A2		B1		B2	
		TS	%	TS	%	TS	%	TS	%
23	0	20.0	100	18.1	100	17.2	100	16.0	100
	7	22.0	110	18.0	100	16.8	97	16.3	102
	28	19.9	99	17.2	95	20.3	118	18.0	112
	84	17.9	90	16.1	89	19.3	112	16.1	101
	168	16.4	82	12.9	71	19.3	112	16.7	105
0	0	28.4	100	27.2	100	24.0	100	25.1	100
	7	29.8	105	25.7	95	27.2	113	23.6	94
	28	28.1	99	24.0	88	21.6	90	23.9	95
	84	27.8	98	24.4	90	20.6	86	21.3	85
	168	22.3	79	22.2	82	19.8	83	23.5	94
−10	0	36.8	100	31.3	100	28.8	100	27.5	100
	7	35.5	96	22.3	71	28.7	100	31.6	115
	28	31.2	85	22.4	72	25.5	89	25.7	94
	84	30.5	83	23.1	74	22.0	76	27.3	99
	168	25.9	70	23.6	75	20.1	70	24.0	87
−20	0	31.7	100	20.1	100	30.8	100	34.6	100
	7	27.3	86	22.4	112	28.8	93	35.6	103
	28	26.0	82	13.5	67	28.7	93	31.9	92
	84	25.4	80	20.5	102	18.1	59	23.9	69
	168	18.6	59	14.2	70	16.7	54	18.6	54
−30	0	22.7	100	20.6	100	23.2	100	21.5	100
	7	24.2	107	19.3	94	19.4	84	24.9	116
	28	22.6	100	19.0	92	21.8	94	24.4	113
	84	17.1	75	22.4	109	14.3	62	17.0	79
	168	20.9	92	19.8	96	18.6	80	18.5	86

this system, a sinusoidal stress imposed upon the specimen is directly related to the amount of current delivered to the vibrator. The samples are also subjected to strain via the induced displacement. The glass transition temperature (α-transition) values were obtained for the maximum in the loss modulus (E'') versus temperature curve.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties

Fig. 1 shows the variation of the tensile strength with the temperature and ageing. At room temperature the tensile strength values (Table 2) are always higher for A1 and A2 (20 and 18 kN m^{-1}, respectively) than those for B1 and B2 (17 and 16 kN m^{-1}). These values are controlled by the weight of the reinforcement used. After 168 days of ageing, there is a decrease (18 and 29%) in the tensile strength values for membranes A1 and A2. Membranes made with SBS show a slight increase in these values after 168 days of ageing, i.e. 12% for B1 and 5% for B2. The minimum value obtained is 12.9 km m^{-1} for A2.

At 0°C, tensile strength values for control samples increase to about 1.5 times the values obtained at room temperature. After 7 and 28 days of ageing these values do not change appreciably. After 168 days of ageing the values are higher than those obtained for the same age period measured at 23°C. The tensile strength increases 1.7 times in the case of A2. As the age increases, the tensile strength of all the materials decreases. The lowest value obtained was 19.8 kN m^{-1} for B1 after 168 days of ageing.

At −10°C, tensile strength values for control samples increase to about 1.7 times the room-temperature values. The maximum value obtained is 36.8 kN m^{-1} for A1. After 168 days of ageing the values are higher than those obtained for the same ageing at 23 and 0°C. With the ageing process the strength decreases, the minimum value being 20.1 kN m^{-1} for B1.

At −20°C, tensile strength values of the control samples in the A1 and A2 series start to decrease in relation to the values at −10°C, but are still higher than those obtained for the same materials at room temperature. In the case of samples B1 and B2, tensile strength values for control samples increase to 1.8 and

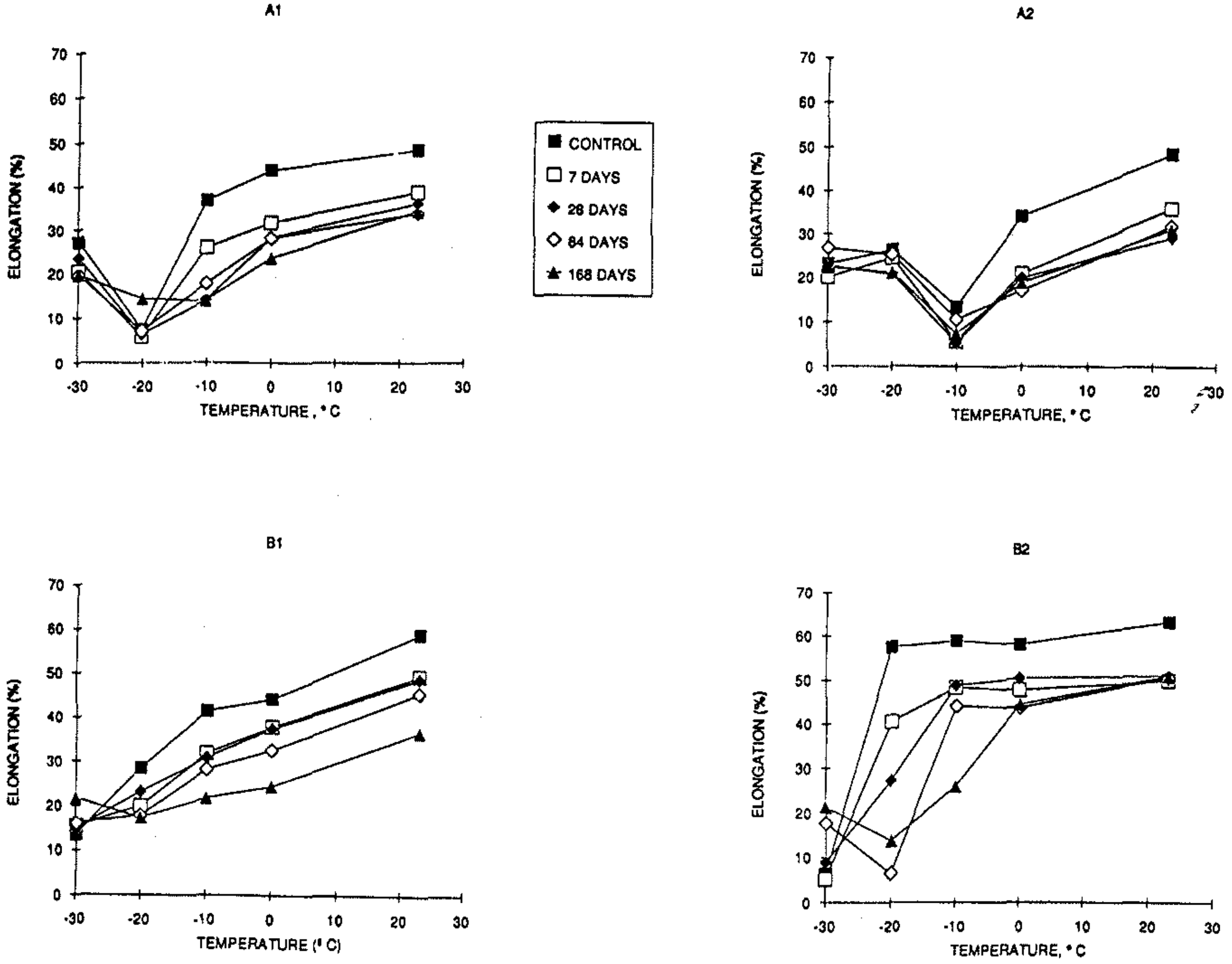

Fig. 2 Elongation–temperature.

2.1 times the values obtained at room temperature. After 168 days of ageing the strength values decrease, the minimum being 14.2 kN m^{-1} for A2.

At −30°C the values of tensile strength decrease for all the materials, but are higher than those obtained at room temperature. After ageing, the values slightly diminish. The minimum value obtained was 18.5 kN m^{-1} for B2.

Fig. 2 shows the elongation after ageing at different temperatures. In general, the elongation values for the control samples A1 and A2 are lower than for B1 and B2, except at −30°C (Table 3). After 168 days of ageing, at room temperature, elongation values for A1 and A2 decreased by 30 and 35%, respectively; elongation for B1 decreased by 37% and B2 by only 20%. The minimum value of elongation was 30.9% for A2.

At 0°C, elongation values decrease in all cases. For control samples, the minimum value was 33.9% for A2. After 7, 28 and 84 days of ageing, elongation values diminish gradually. After 168 days of ageing, elongation values for samples A1, A2 and B1 decrease by 45%. For sample B2 elongation decreases by only 23%.

At −10°C, elongation values for control samples tend to diminish. The minimum value obtained for control samples is 13.4% for sample A2. After ageing, a general tendency towards lower values of elongation is observed. The minimum value obtained is 7.4% for sample A2, after 168 days of ageing.

At −20°C, elongation values for control samples show a decreasing trend except for sample A2, where the elongation value doubles in comparison with the value obtained at −10°C. After ageing, the general tendency of the values is to decrease. The minimum value obtained is 14.4% for sample A1.

At −30°C, elongation values for control samples decrease except for A1 sample where the elongation value increases to 3.6 times the value obtained at −20°C. The minimum value obtained is 6.4% for sample B2. After ageing, elongation values decrease in the case of sample A1. For sample A2 the elongation is kept quite balanced. For samples B1 and B2 the elongation values increase.

3.2 Thermal properties

Table 4 represents the results for glass transition temperatures and Fig. 3 shows the variation of the glass transition temperature with heat-ageing period. Samples A1 and A2 exhibit higher glass transition temperatures

Table 3 Elongation values of modified bituminous membranes

Testing temp. (°C)	Heat-ageing (days at 80°C)	Elongation (%)							
		A1		A2		B1		B2	
		E	%	*E*	%	*E*	%	*E*	%
23	0	48.5	100	48.2	100	59.1	100	63.3	100
	7	38.8	80	35.7	74	49.5	84	49.9	79
	28	36.2	75	29.0	60	48.8	83	51.1	81
	84	33.8	70	31.7	66	45.6	77	50.6	80
	168	34.4	71	30.9	64	36.6	62	50.9	80
0	0	43.9	100	33.9	100	44.4	100	58.2	100
	7	31.8	72	20.8	61	37.9	86	47.9	76
	28	28.2	64	19.9	59	37.5	85	50.5	80
	84	28.1	64	17.0	50	32.7	74	43.8	69
	168	23.6	54	18.8	55	24.5	55	44.6	71
−10	0	36.9	100	13.4	100	41.5	100	59.0	100
	7	26.0	70	5.7	42	31.9	77	48.5	82
	28	14.1	38	5.3	39	30.8	74	48.9	83
	84	17.8	48	10.5	78	28.3	68	44.2	75
	168	14.0	38	7.4	55	21.9	53	26.1	44
−20	0	7.5	100	26.3	100	28.5	100	57.5	100
	7	6.0	80	24.5	93	19.9	70	40.6	71
	28	6.4	86	20.7	79	23.2	82	27.3	47
	84	7.2	96	25.2	96	17.8	63	6.5	11
	168	14.4	191	21.1	80	17.3	61	13.7	24
−30	0	27.1	100	23.1	100	13.3	100	6.4	100
	7	20.4	75	20.1	87	15.3	115	5.1	79
	28	23.4	86	22.8	99	14.6	110	8.9	139
	84	19.5	72	26.8	116	16.0	120	17.6	275
	168	19.6	72	22.4	97	21.7	163	21.4	334

Table 4 Glass transition temperatures of bituminous membranes heat-aged at 80°C

Ageing (days)	T_g (°C)			
	A1	A2	B1	B2
0	−25.39	−24.50	−39.21	−33.05
7	−25.61	−24.13	−35.34	−34.11
28	−26.36	−25.31	−35.54	−33.51
84	−25.54	−25.31	−34.70	−33.39
168	−26.61	−24.41	−30.26	−29.18

(−25.39 and −24.50°C) than samples B1 and B2 (−39.21 and −33.05°C, respectively). After ageing, the glass transition temperature for A1 slightly decreases by 1.22°C. For A2 it remains fairly constant. The response for samples B1 and B2 is quite different. After 168 days of ageing, the glass transition temperature for B1 decreases by 8.95°C and by 3.87°C for B2. However, after ageing, the glass transition temperatures for B1 and B2 are lower than those for A1 and A2. As the glass transition temperature has an influence on the performance of a membrane in cold weather applications, lower values of T_g indicate lower temperatures at which a membrane can perform suitably. According to the results obtained, membranes made with SBS are more suited to cold weather applications than membranes made with APP. On the other hand, heat-ageing has a greater negative effect on membranes made with SBS than on those made with APP.

Bitumen has a glass transition temperature around −30°C [7], but the glass transition temperature of the membranes will depend also on the glass transition temperature of the modifier polymers. There are several factors that affect the transition temperature of polymers, such as chemical structure, molecular weight, stereochemical features, intermolecular interactions, flexibility, etc. Although the influence of chemical structure on the glass transition is not understood in full detail, the general rule is that any structure that increases flexibility will decrease the value of T_g. The substituent groups in the polystyrene blocks of SBS lead to an increase in structural rigidity in comparison with APP polymers, but the presence of polybutadiene blocks in SBS leads to an

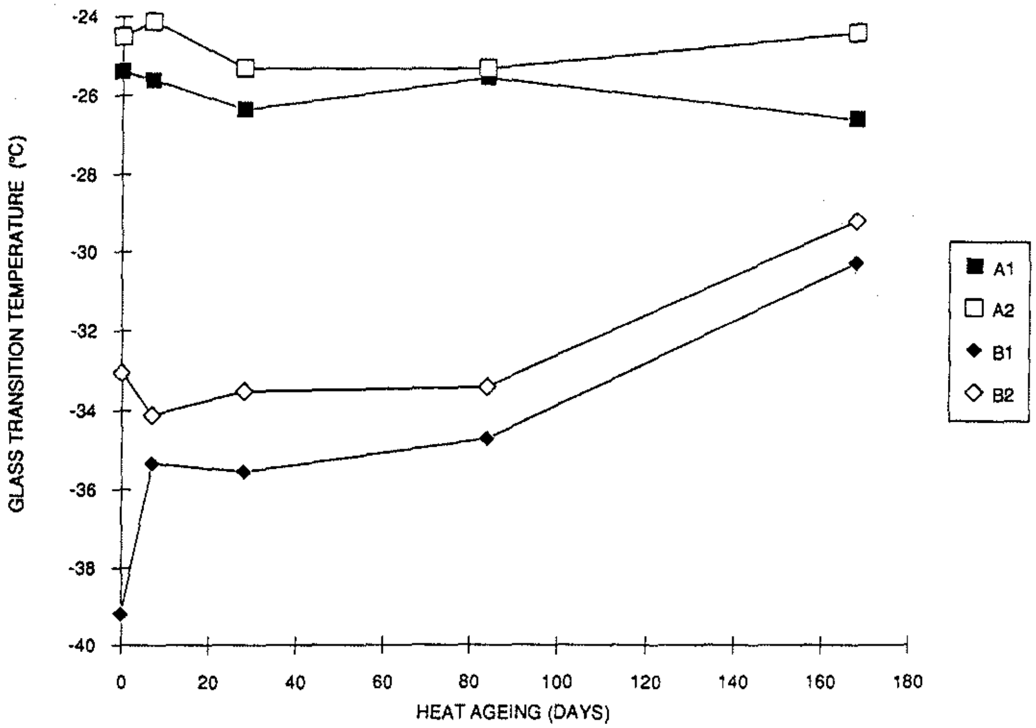

Fig. 3 Glass transition temperature–heat-ageing.

increase in structural flexibility, resulting in a copolymer with a lower glass transition temperature [8]. Therefore membranes made with SBS will exhibit lower values of T_g than those made with APP.

3.3 Relationship between mechanical and thermal properties

The variation in mechanical properties can be partially explained by taking into account the behaviour of polymers and the influence of glass transition temperatures. These are discussed below.

SBS behaves as a rubber because of its elastomeric nature. The polystyrene blocks fit together to give a totally reversible reticulation, while the polybutadiene blocks swell with bitumen-compatible oils. This mixing of the two constituents leads to a phase reversal and a bitumen blend with elastic characteristics, as shown by the higher values obtained for elongation. On the other hand, it is believed that APP does not chemically react with bitumen, but it will organize itself at the molecular level so as to create a network capable of locking in place the bitumen's molecular structure. APP stiffens the bitumen and elongation values are lower.

Glass transition temperatures can be connected with variations of mechanical properties. For example, there is a drop in elongation values at around −20°C for sample A1 (Fig. 2). The glass transition temperature for this sample is −25°C. For sample A2, the drop of elongation values occurs at −10°C. For this sample the glass transition temperature is −24°C. For membranes B1 and B2, the drop in elongation values starts at −30°C and the glass transition temperatures for these samples are −39.21 and −33.05°C, respectively. After ageing the minimum of the elongation values keeps quite constant for membranes A1 and A2. For membranes B1 and B2, there is a shift of the minimum towards higher temperatures (−20°C) and the glass transition temperature also increases.

The tensile strength has its maximum at −10°C for membranes made with APP and around −20°C for membranes made with SBS. Although these temperatures do not exactly match the values of the glass transition temperature obtained by DMA, the variations of the mechanical properties always occur at higher temperatures for membranes made with APP than for membranes made with SBS. Glass transition temperatures of membranes made with SBS are lower than glass transition temperatures of membranes made with APP.

4. CONCLUSIONS

1. The polymer modifiers influence the performance properties of bituminous membranes through their inherent behaviour and their respective T_g values. For example, the rubber-like SBS increases elongation in comparison with APP. Tensile strength values are controlled by the weight of the reinforcement used for manufacture of the bituminous sheets.

2. T_g values influence the low-temperature mechanical properties. This accounts for the variation in mechanical properties at low temperatures.

3. After heat-ageing, the values of T_g and tensile properties indicate that both membranes can be applied under adverse environmental conditions. Membranes

made with SBS are more suited to cool-weather applications and membranes made with APP withstand strongly the effect of heat-ageing.

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RESUME

Influence du vieillissement par la chaleur sur les propriétés thermiques et mécaniques de membranes d'étanchéité traitées par APP et SBS

On a étudié l'influence du vieillissement par la chaleur sur quatre membranes d'étanchéité, deux d'entre elles étant traitées par APP (polypropylène atactique) et deux par SBS (styrène de styrène butadiène), à l'aide de l'essai en traction et de l'analyse thermique mécanique (DMA). Les échantillons ont été chauffés à 80°C pendant 7, 28, 84 et 168 jours et essayés en traction à 23, 0, −10, −20 et −30°C. Chaque échantillon vieilli par la chaleur a été également soumis à un essai thermomécanique pour identifier sa température de passage à l'état vitreux T_g.

Les résultats montrent des différences importantes dans l'influence de la chaleur sur la résistance en traction et l'allongement des membranes. Les valeurs de T_g *diffèrent selon les traitements et les autres composants des membranes, et sont affectées par le vieillissement par la chaleur. L'influence de la zone de passage à l'état vitreux mesurée par l'analyse thermique mécanique se traduit aussi dans les résultats de l'essai en traction.*