CHOOSING BITUMENS AND POLYMERS WHEN WATERPROOFING WITH PREFABRICATED SHEETS

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A decade ago, the introduction of waterproofing roofing sheets made of bitumen-elastomer blends considerably increased roofing system performance, at a time when new constraints (extension of thermal insulation, lightening of building structures) required the improvement of roofing sheet elastic properties and thermal resistance at high and low temperatures. The achievement and maintenance of optimal quality over time are only possible with a selective choice of components and proportions.

Elastomeric bitumens are manufactured by incorporating into the bitumen an SBS-type trisequenced thermoplastic elastomer, then adding a filler and, sometimes, other ingredients in smaller quantities. The aim of the present study is to make this choice easier by trying to find a correlation between physical and mechanical propertis of filled elastomer binders and base product characteristics.

DESCRIPTION OF THE STUDY

Thirteen bitumens have been used, each one composed of three polymers and several fillers.

SELECTION OF THE COMPONENTS

Bitumen Characterization

The penetration of bitumens ranges from 100 to 200 ⅒ millimeters at 25C. Bitumens were chosen from different origins and manufacturing routes. Their chemical composition was determined by:

- a precipitation of asphaltenes (AS) with n-heptane;
- then, a liquid/solid chromatography on silica and alumina of the complementary fraction called "maltenes" (M), with elution by solvents having an increasing polarity. Some saturate (SAT), aromatic (AR) and resin (R) fractions can thus be collected;
- this analysis is accompanied by the measurement of apparent average molecular weights of malthenes (MMM) and asphaltenes (MMA), by means of tonometry.

The method described here is peculiar to SHELL Company. The analyses wre carried out by SHELL Research Laboratory (SRSA) in Grand-Couronne (France). The following table indicates the field studied:

FRACTIONS		MINI	MAXI
Saturates (SAT)	%w	7.7	24.7
Aromatics (AR)	%w	30.6	62.3
Resins (R)	%w	16.8	38.4
Asphaltenes (AS)	%w	5.7	17.8
MMM		439	887
MMA*		1059	2880

*The polarity of the solvent employed justifies the fact that MMA values are low.

Note that bitumens having the highest asphaltene contents are not very compatible with polymers.

Selection of polymers

Three SBS-type polymers, having the same polystyrene content, have been tested at different rates in order to obtain products with close viscosities at high temperature.

Polymer	Type	Corrected molecular weight (Mw)	Rate (%w)	Polydispersity
1	Linear	110,000	13.0	1.10
2	Star shaped	240,000	11.0	1.20
3	Star shaped	230,000	11.5	1.35

Selection of fillers

Four fillers (A, B, C, D) have been selected. They have different chemical natures, particle size distributions and crystalline structures. They were added to the previous mixtures at the rate of 30 percent weight.

Filler	A	B	C	D
Chemical nature	Fly Ashes	Chalk	Slate Powder	Talc
Particle size distribution				
<10 μm, % w	8.5	75	10	15
<49 μm, % w	93	100	97	15
50 57 w, μm	21	7	15	25
Blaine value cm²/g	7699	9497	7169	6512

Study of mixtures

The major concern was to comply with the UEATC (Union Europeean pour l'Agrement Technique de la Construction) recommendations, which aim at ensuring a longevity of at least 20 years. This led principally to a development of accelerated aging tests. The one UEATC recommends involves placing 2-millimeter-thick roofing and binder samples in an oven at a temperature of 70C and an air flow equal to 10 times its volume per hour, for a six-month period.

A deep concern for quality optimization has led to a definition of acceptability thresholds (see the following table) and development of complementary tests on binders in order to pinpoint the compatibility problems among components. The *storage stability* test of the non-filled binder involves storing the binder for five days at a temperature of 10C. The softening temperature variation between top and bottom of the test tube is then measured.

In the *aluminum sliding* test, a 2-millimeter thick filled binder is laid on an aluminum sheet and the sheet is held at 100-degree slope in an oven with a temperature of 90C. The sliding is measured after 24 hours.

In the *deposit rate on aluminum* test, two identical samples of a filled binder are laid on an aluminum sheet. The first one is peeled off after cooling; the second is maintained at a temperature of 70C for 48 hours, then undergoes the same test. The difference between deposited weights is measured. These measurements are sometimes accompanied by a study on the evolution of the polymer state throughout the aging tests, using gel permeation chromatography. The molecular weights of the residual polymer, averaged in weight ($\overline{M}w$) and number ($\overline{M}n$), are measured and the polydispersity is calculated $(D = \frac{\overline{M}w}{\overline{M}n})$

Result analysis

It appeared very early that some fillers had a particular behavior. The study was then divided into two parts: 1) study of the filler influence; 2) study of the relations between bitumen chemical components and properties of binders which were made with several polymers but with only one filler.

Properties		Method	Values Mini	 Maxi
Softening temperature T_{RB}F	C	AFNOR	115	
Penetration at 25C	1/10 mm	AFNOR		45
Storage stability (Delta T_{RB})	C	Internal		15
Cold bending (flexibility)	C	UEATC		−20
Flow	mm	DIN		10
Sliding on aluminum	mm	Internal		50
Deposit speed on aluminum	g	Internal		2
Viscosity at 170C	P	Internal		80
Viscosity at 190C	P	Internal		45
Evolution during aging		UEATC		
—T_{RB} Variation within 30 days	C			3
—T_{RB} Variation within 90 days	C			10
—Cold bending variation within 30 days	C			5

INFLUENCE OF FILLER ON INITIAL PROPERTIES AND DURING AGING

Fillers play two different roles: 1) in manufacturing, they adjust the rheological behavior of the binder to manufacturing requirements for a roofing sheet (*Figure 1* gives viscosity curves of an elastomeric-filled bitumen with three fillers of different chemical natures); (*Figure 1 and 2*) on site, they lead to tougher binders and to an easier setting.

On the other hand, some fillers have a very negative effect on binder evolution throughout aging tests. Table 1 shows the results provided by several types of binders, which were obtained with three bitumens blended with only one polymer but with four types of mineral compounds (A to D).

The destructive effect of the A-type filler on the polymer is obvious. The average molecular weight of the polymer decreases quickly, revealing some oxidation and polybutadiene chain-breaking phenomena which lead to the progressive disappearance of polymer molecules having a high molecular weight (*Figures 2A and B*).

This has a particular effect upon the ring and ball temperature of the binder, in a way which depends on the bitumen nature. With a very compatible bitumen, the time required by the polymer for changing is shorter than that needed for creating asphaltenes-asphaltenes interactions with bitumen aging. With a non-compatible bitumen, these interactions are prevailing and occur faster with this filler.

Cold bending does not seem to be closely bound to polymer deterioration, i.e. molecules with low molecular weights issued from SBS act as a binder plasticizer. The binder elasticity does not appear in the table, but some previous tests showed that there was a correlation between the polymer state, the elastic limit of the binder, and the elongation at break (*Figure 3*).

Consequently the need to maintain the polymer initial properties seems fundamental. Some fillers are clearly less destructive than others. Identical results have been obtained with star polymers (Table 1). B Filler has been selected for the continuation of the study.

Relationship between chemical composition of bitumen and binder properties

The analysis was made independently for each polymer; it consisted of showing the relationship between the chemical composition of bitumens and the initial properties and aging resistance of the elastomeric binder. Correlation matrices were calculated for all dependent and independent variables, and these showed which factors have an impact on the various properties.

Table 3 provides the limit values observed for the studied properties, whereas Table 4 gives the results of the statistical analysis of available data. In the latter, the "+" sign indicates a direct relationship between dependent characteristics and independent variables, and the "−" sign indicates an opposite relationship. Three successive signs stand for a strong relationship; one sign stands for a weak relationship.

Some variables, whether dependent or independent, do not appear in Table 4. Penetration at 25C and cold bending do not seem to be clearly related to the bitumen composition in the considered field. Viscosities at 170 and 190C depend above all upon the content and type of polymer and filler.

Average molecular weights of malthenes and asphaltenes (MMM and MMA) do not seem to have a direct impact on the studied properties. Only the aging resistance (measured by the TRB variation within 90 days) seems to be influenced by a high value of MMM, quite feebly for polymers one and three but strongly for polymer two.

Chemical composition of bitumens has a clear impact on some of the binder properties. Impact intensity depends on the polymer considered. A high content of *saturates* improves some of the initial properties (ring and ball temperature of the filled product (TRBF), flow resistance), but it has a negative effect on binder stability (deposit rate on aluminum) and aging resistance for all polymers. Sliding on aluminum tends to increase with the linear polymer.

The influence of aromatics is generally opposed to that of the saturates ($T_{RB}F$, flow, T_{RB} variation within 90 days). An increase of the aromatic fraction slows down the elastomeric bitumen aging process.

Resins have an effect comparable to that of saturates, but at a different level: an increase of the resin content improves the $T_{RB}F$ (mainly with polymers one and two) but slightly deteriorates the aging resistance. Flow and sliding on aluminum are dependent upon this group of components only for polymer two; for both star polymers, a high content increases the deposit on aluminum.

A variation of the asphaltene content has a particular influence on mixtures containing the linear polymer (1). An increase of the asphaltene content implies a decrease in $T_{RB}F$ and instability (sliding and deposit rate on aluminum).

Consequently, it appears that the impact of saturates and resins on most properties of the elastomeric binders is contrary to that of aromatics and asphaltenes.

The study of each component type influence was accompanied by a study of any interactions likely to occur between these four groups. The ratios of these parameters have been considered in pairs: SAT/R, SAT/AR, SAT/AS, AS/R and AR/R.

Tables 4 and 5 show the results obtained through a statistical process using available data: some optimal or limit values, allowing for checks of the required specification and varying from one polymer to another, can then be defined for these reports. (The AS/AR is not displayed in Tables 4 and 5: its only negative effect is the reduction of cold flexibility during aging).

The linear polymer studied seems more sensitive to a variation in the chemical composition of bitumen than star polymers. Some properties require certain composition characteristics which may be opposed to each other (e.g., the flow and sliding on aluminum versus the saturate content). It remains possible, with each of the three polymers tested, to check the required specification by means of bitumen selection.

CONCLUSION

This study was meant to integrate all characteristics dealing with the manufacture, setting, and "in-situ" behavior of some elastomeric bitumen sheets, and to analyze the influence of three unreinforced components (bitumens, polymers, fillers) on the properties of their blends and their evolution with time. The variety of products used allows for several conclusions. Some fillers have a particularly negative effect on the durability of bituminous roofing sheets, by accelerating the deterioration process of the polymer and the bitumen. Other types of fillers have practically no effect on durability. Thus the choice of the filler appears particularly important to ensure product longevity. In the search for optimization, the point to be considered is which bitumen/polymer couple best meets the specification of the product to be manufactured. The elements and mechanisms provided by this study enable accurate prediction of the development problems of bitumen elastomer blends at a selected site, both from technical and financial points of view. Financial considerations include existing resources, availability of the products, and transport expenses.

	Chemical composition of bitumen and characteristics of bitumen filled at 30 % (linear SBS)			A-type filler				B-type filler				C-type filler				D-type filler			
				new	1 month	2 months	3 months	new	1 month	2 months	3 months	new	1 month	2 months	3 months	new	1 month	2 months	3 month
A-type bitumen "very compatible"	Asphaltenes 10.5 Resins 33.5 Aromatics 41.1 Saturates 14.9	T_{RB} (°C)		114	93	91	92	111	111	106	104	112	112	108	103	113	112	112	110
		Cold Bending (°C)		- 30	- 25	- 25	- 10	- 30	- 25	- 10	- 5					- 30	- 30	- 30	- 25
		M_w	POLYMER	127710	70170	58860	55860	129800	118710	101780	95890	134490	115860	101970	93880	149840	144340	110230	11057
		D		1,19	1,43	1,54	1,56	1,10	1,22	1,52	1,45	1,12	1,31	1,46	1,60	1,09	1,10	1,19	1,22
B-type bitumen "fairly compatible"	Asphaltenes 11.4 Resins 17.6 Aromatics 51.3 Saturates 19.7	T_{RB} (°C)		109	100	100	103	106	105	105	107	109	107	109	107				
		Cold Bending (°C)		- 25	- 25	- 25	- 25	- 25	- 10	- 5	0	-	-	-	-	-	-	-	-
		M_w	POLYMER	124750	74360	65110	59120	136680	121150	115320	98180	135520	114450	104060	90790	-	-	-	-
		D		1,22	1,44	1,54	1,67	1,11	1,19	1,28	1,47	1,13	1,26	1,38	1,52	-	-	-	-
C-type bitumen "non-compatible"	Asphaltenes 17.8 Resins 22.6 Aromatics 42.9 Saturates 16.7	T_{RB} (°C)		110	109	115	128	108	110	112	115	109	114	114	121	-	-	-	-
		Cold Bending (°C)		- 30	- 30	- 25	- 25	- 30	- 30	- 25	-	-	-	-	-	-	-	-	-
		M_w	POLYMER	121390	79370	66510	62870	132030	121640	114090	89050	137160	116960	103550	89560	-	-	-	-
		D		1,19	1,42	1,64	1,54	1,18	1,20	1,35	1,50	1,21	1,24	1,38	1,48	-	-	-	-

Table 1 Influence of the filler nature (linear polymer)

			C-TYPE FILLER				D-TYPE FILLER			
			New	1 month	2 months	3 months	New	1 month	2 months	3 months
Compatible type bitumen Asphaltenes 7,6 Resins .. 28,5 Aromatics 51,0 Saturates 12,9	TRB (°C)		131	132	128	122	130	132	129	125
	Cold Flexibility (°C)		- 25	- 25	- 25	- 20	- 25	- 25	- 25	- 25
	$\bar{M}_w$	POLYMER	209550	190750	170160	160120	219260	196590	177090	168590
	D		1,32	1,42	1,54	1,58	1,29	1,41	1,50	1,55

Table 1.2 Influence of the filler nature (star polymer)

OBSERVED VALUES		MINIMAL			MAXIMAL		
POLYMER		**1**	**2**	**3**	**1**	**2**	**3**
Softening temperature $T_{RB}F$	C	106	108	118	122	131	139
Storage stability Delta T_{RB}	C	1	0	0	39	44	17
Cold bending temperature	C	−35	−35	−35	−25	−20	−20
Flow	mm	2	2	0	65	23	5
Sliding on aluminum	mm	0	0	85	135	250	190
Deposit rate on aluminum	g	0	0,5	0,1	0,9	5,8	2,2
Aging:							
—T_{RB} Variation within 90 days	C	2	7	4	22	19	25
—Cold bending temperature variation within 30 days	C	0	0	0	20	10	25

Table 2 Extreme properties of the studied mixtures

	Polymer	Saturates	Aromatics	Resins	Asphaltenes
$T_{RB}F$	1	+	−	+ + +	− − −
	2	+ + +	− − −	+ + +	− − −
	3	+ + +	−	+	−
Δ T_{RB} (Storage stability)	1	+			
	2	+			
	3			+	
Δ T_{RB} within 90 days aging	1	+ + +	− − −	+	
	2	+ + +	− − −	+	
	3	+ + +	− − −	+	
Deposit on aluminum (variation within 2 days)	1	+ + +			− − −
	2	+ + +	−	+ + +	−
	3	+ + +	−	+ + +	−
Flow	1	−	+		
	2	−	+		
	3	+ + +	−		− − −
Sliding on aluminum	1	+ + +	−		− − −
	2			+	
	3				
Δ Cold bending within 30 days aging	1				
	2		−	+	
	3	+		+	

+ :direct relationship
− :opposite relationship

+ + + or − − − : strong relationship
+ or − : feeble relationship

Table 3 Influence of bitumen components on the properties of filled products

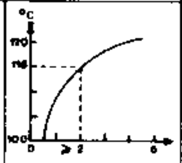
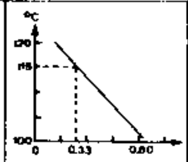
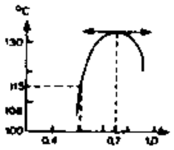
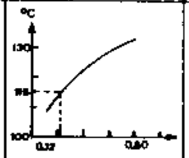
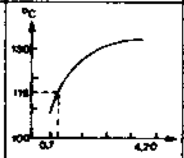
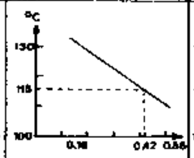
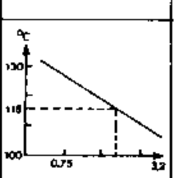
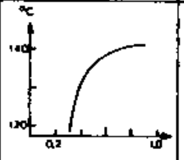
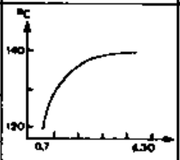
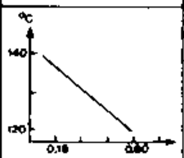
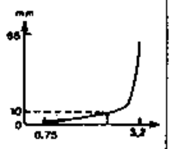
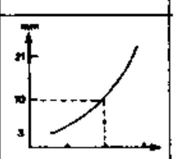
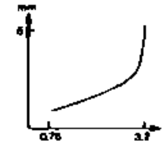
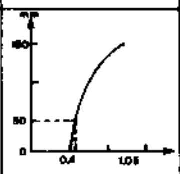
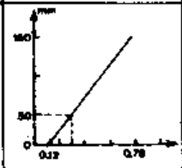
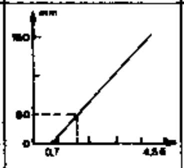
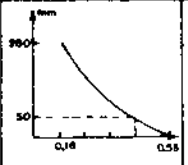
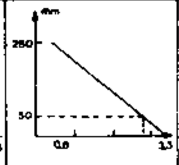
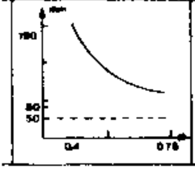
	POLYMERS	SATURATES / RESINS	SATURATES / AROMATICS	SATURATES / ASPHALTENES	ASPHALTENES / RESINS	AROMATICS / RESINS
TRB FILLED BLEND (°C)	1					
	2					
	3					
FLOW (mm)	1					
	2					
	3					
SLIDING ON ALUMINIUM (mm)	1					
	2					
	3					

Table 4 *Interactions between bitumen components*

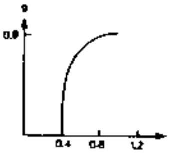
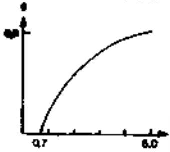
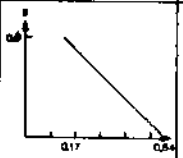
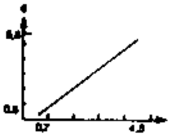
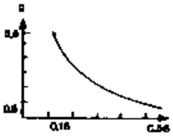
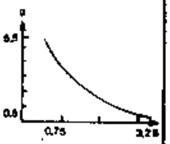
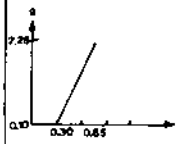
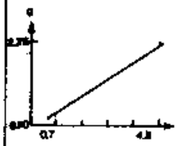
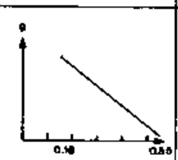
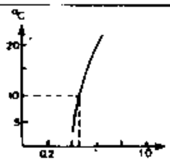
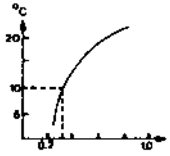
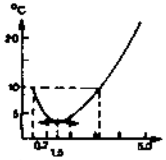
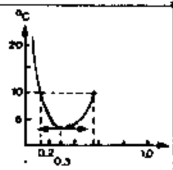
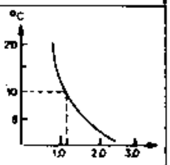
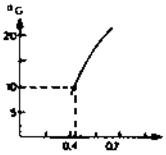
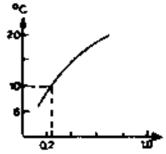
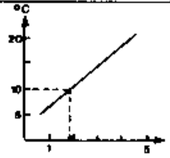
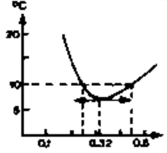
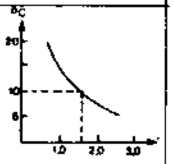
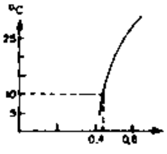
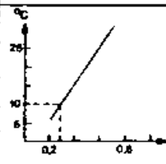
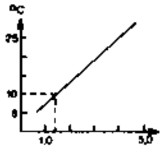
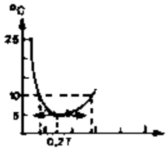
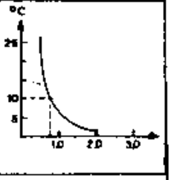
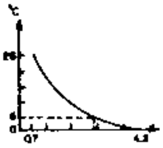
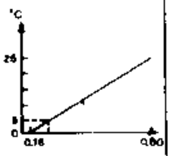
	POLYMERS	SATURATES / RESINS	SATURATES / AROMATICS	SATURATES / ASPHALTENES	ASPHALTENES / RESINS	AROMATICS / RESINS
DEPOSIT SPEED ON ALUMINIUM = $M_{2\ JOURS} - M_{(t\ =\ 0)}$ (g)	1					
	2					
	3					
Δ TRB WITHIN 90 DAYS (°C)	1					
	2					
	3					
Δ COLD BENDING TEMPERATURE WITHIN 30 DAYS (°C)	1					
	2					
	3					

Table 5 Interactions between bitumen components

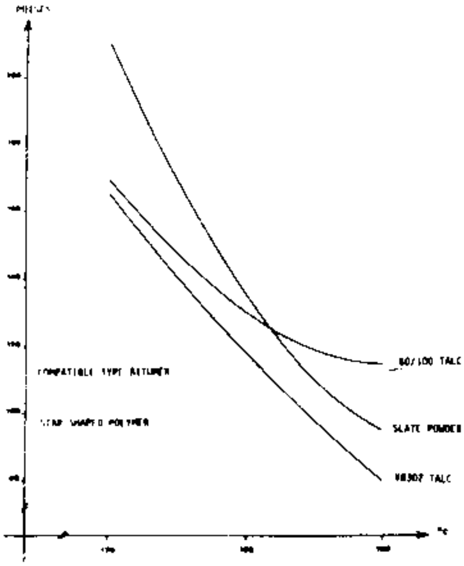


Figure 1　*Viscosity of filled blends as a function of temperature*

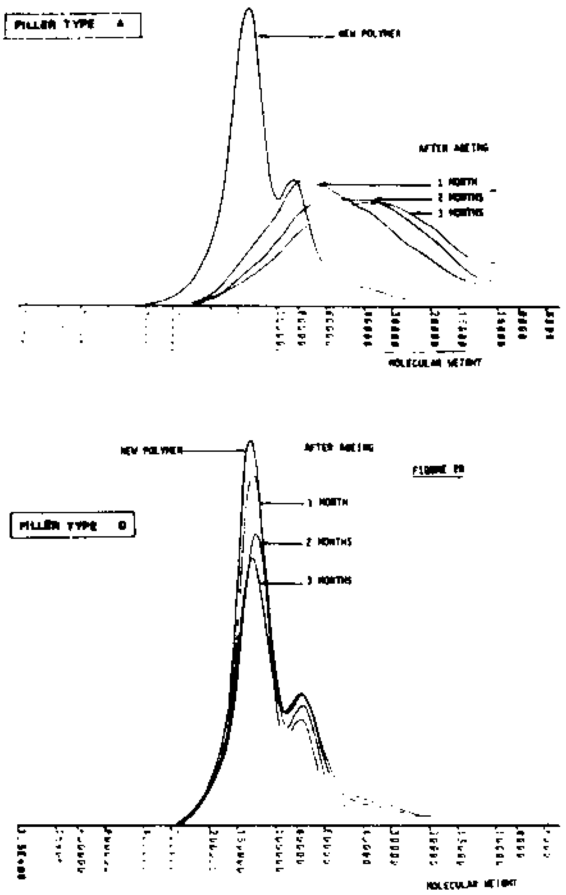


Figure 2　*Evolution of the polymer (linear polymer) "compatible bitumen"*

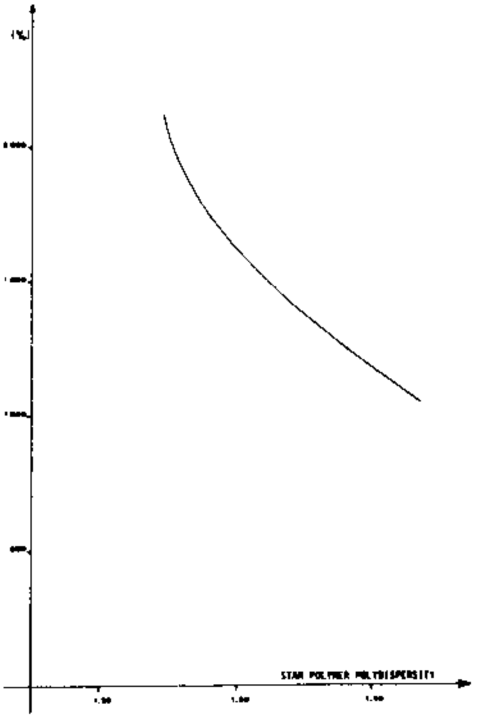


Figure 3　*Elongation at break of the filled bitumen elastomer blend as a function of polymer state*