Binder performance and testing

Properties and performances of polyurethane modified bitumen

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Abstract

Bitumen materials are widely used for waterproofing and road pavement applications. Since more than 40 years, these ones are modified with polymers in order to increase their thermo-mechanical properties over a wide range of temperatures. Polymers commonly used to modify bitumen are thermoplastic elastomers such as poly(styrene-b-butadiene-b-styrene) block copolymers (SBS) due to their good compatibility with bitumen and specific interactions with the different chemical species Nevertheless, SBS polymers display poor resistance to UV and therefore give poor aging resistance to the polymer-modified bitumen materials. To overcome these drawbacks, thermoplastic polyurethanes (TPU) are considered in the present study due to their improved durability and rheological behaviour compared to SBS. Furthermore, the architecture and microphase-separated morphology of the thermoplastic polyurethanes which controlled the miscibility and interactions with the bitumen can be easily tuned from the polymerization step by a proper copolymerization of the nature of the soft and hard segments. The aim of this work is to study the relationships between the TPU mixes design and the bitumen fractions, multi-scale microstructures, and thermo mechanical properties in thermoplastic polyurethane modified bitumen (PmB) blends. Thus, several polyurethane modified bitumen blends were prepared in order to evaluate TPU components impact (isocyanate, alcohol, extender and hard blocks ratios) on the thermo mechanical PmB performances in comparison with high SBS content modified bitumen. Both empirical and rheological characteristics like viscosity, Fraass breaking point, elastic recovery, RTFOT, complex shear modulus, fatigue resistance, were investigated in laboratory. Furthermore, Tension/compression complex modulus, fatigue resistance, and thermal stress-restrained specimen tests were performed on semi-coarse asphalt concrete, containing five different polyurethane modified bitumen binders. The results indicate that the proposed innovative polyurethane modified bitumen binders may be from now as a relevant solution for sustainable long-life and high performances overlays.

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4 - INTRODUCTION

The use of synthetic polymers to modify the bitumen performances that date back to the early 1970s; in order to decrease thermal sensitivity, increase cohesion and modified rheological characteristics.
The Styrene-Butadiene-Styrene (SBS) is the most widely used elastomer. It gives binders elastic properties but also a good resistance to rutting for polymer rates of around 5%. However, this polymer is sensitive to oxidation and more particularly to ultraviolet rays (UV). In the long term, binder's performances are therefore increased.

The study deals with the modification of bitumen with a new polymer: thermoplastic polyurethanes (TPU). Its objective is to obtain a binder / polymer combinig resistance and durability. The TPU presents a great industrial interest for pavement applications and roofing due to its thermo mechanical properties and its aging resistance for long-lasting overlays and pavements.

Thus, five polyurethane modified bitumen blends (BTPU) were prepared in order to evaluate TPU components impact (isocyanate, alcohol, extender and rigid segments ratios) on the thermo mechanical TPU-bitumen blends performances in comparison with high SBS content modified bitumen (PmB). Both empirical and rheological characteristics like viscosity, Fraass breaking point, elastic recovery, complex shear modulus, and compatibility parameters were investigated in the laboratory.

5 – EXPERIMENTAL STUDY

5-1 Materials

5-1-1 Bitumen

The bitumen used during this study is a French 50/70 pure bitumen pen grade. Its composition (SARA fractions) was determined by chromatography using an Iatroscan device. The main characteristics are shown in Table 1.

Composition (% w)			Characteristics	
Asphaltenes	10,9		Needle penetration @ 25°C	57 1/10° mm
Saturates	11,9		Softening point	49,4°C
Aromatics	59,5		Fraass breaking point	-13°C
Resins	17,6			

Table 1. SARA composition and properties of the pure bitumen used in the study.

5-1-2 Polyurethane Modified Bitumen (PmB) blends

TPU chemistry is similar to the classical thermosetting polyurethanes [1]. They are produced by reaction between an isocyanate and a multifunctional alcohol. A short diol used as a chain extender is often added as shown in Figure 1 [2].

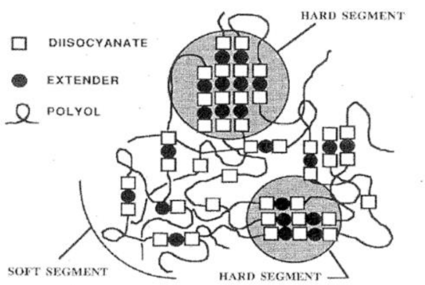


Figure 1. Structure of a basic thermoplastic polyurethane.

The previous laboratory had conducted to design 27 TPU polymers synthetized by reactive extrusion (Figure 2). Five of them have been identified and selected. All the TPU formulae contain the same isocyanate and alcohol chains.

Isocyanate,

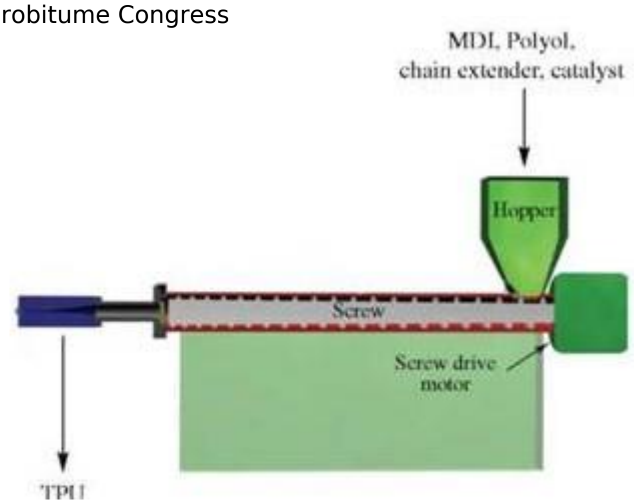


Figure 2. Reactive extrusion principle of a thermoplastic polyurethane.

The TPUs selected for the study are shown in Table 2.

N°	Extender	Extender structure	Rigid Segments (%)	Melting Flow Index (MFI)
TPU1	B	Linear	17	86
TPU2	C	Cyclic	17	143
TPU3	C	Cyclic	25	68
TPU4	C	Cyclic	20	99
TPU5	H	Linear	17	214

Table 2. TPUs used in the study

The TPUs aforementioned have been mixed with the 50/70 pure bitumen following the same procedure:

- Slow addition of 11% TPU into bitumen : stirring speed = 500 rpm / bitumen temperature = 170°C
- Stirring maintained between 20 to 45 minutes (depending of TPU melting flow index)

The TPU optimum content into bitumen (~11%) has been chosen because of the performances and the morphology of the blends by fluorescence microscopic analysis and more particularly with the appearance of a TPU-rich continuous phase (table 3) [3]. These observations are a reliable indication of the miscibility and interactions of the TPU polymers with the different chemical species of bitumen.

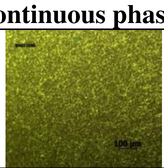
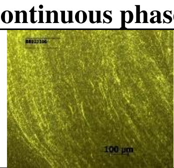
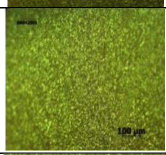
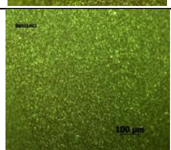
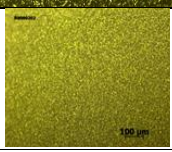
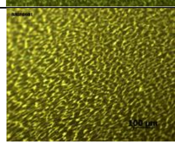
N°	TPU rate = 9% (bitumen-rich continuous phase)	TPU rate = 11% (Polymer-rich continuous phase)
BTPU1		
BTPU2		
BTPU3		
BTPU4		
BTPU5		

Table 3. Morphology of TPU-Bitumen blends according to the TPU contents.

The fluorescence microscopic analysis confirms that for both TPU-bitumen blends the polymer phase inversion is obtained for a minimum rate of 11% TPU into bitumen. Taking into account these observations, we have manufactured the TPU-Bitumen at this ratio.

The five blends manufactured are shown in Table 4.

N°	Extender	Rigid segments ratio in TPU (%)	% TPU in bitumen
BTPU1	B	17	
BTPU2	C	17	
BTPU3	C	25	11
BTPU4	C	20	
BTPU5	H	17	

Table 4. TPUs used in the study

In order to properly evaluate the TPU-bitumen blends performances, we have compare the 5 TPU-bitumen blends with a high performances PmB (SBS-based) as shown in Table 4.

Composition	Needle penetration	Softening point	Elastic recovery	Fraass Breaking Point
PmB 50/70 pen grade + 5% SBS (linear vinyl modified) + cross-linking agent	39-50 1/10° mm	≥ 80-87 °C	≥ 88-97%	-15 / -19 °C

Table 4. Typical characteristics of the SBS-based PmB.

5-2 Methods

The different TPU-bitumen blends were evaluated and graded with the following tests:

- Needle penetration @ 25°C (EN 1426) [4]
- Softening point – Ring and Ball method (EN 1427) [5]
- Fraass breaking point (EN 12 593) [6]
- Elastic recovery @ 20°C (EN 13 588) [7]
- Brookfield viscosity (internal method) [8]
- Complex modulus with Dynamic Shear Rheometer (EN 14 770) [9]

5-2-1 Conventional tests

The results of the conventional tests performed on the five TPU-Bitumen blends are shown in Table 5.

	BTPU1	BTPU2	BTPU3	BTPU4	BTPU5	PmB (SBS-based)	50/70 Pen grade
Needle penetration @ 25°C - EN 1426 (1/10° mm)	26	41	30	34	35	39-47	57
Softening point - EN 1427 (°C)	122,0	110,0	101,5	105,5	105.5	88-97	49,4
Fraass breaking point - EN 12 593 (°C)	-17	-18	-16	-17	-17	-15/-19	-13
Elastic recovery @ 20°C - EN 13 588 (%)	Rupture	53	Rupture	62%	Rupture	88-97	-
Brookfield viscosity (P)	4,5	4,4	4,3	4,2	4,2	5,3	-

Table 5. Typical characteristics of the PmB (SBS-based and TPU-based) used in the lab study.

As expected, the TPU polymer modifies significantly the characteristics of pure bitumen.
In addition, we can observe a substantial decrease of the needle penetration, corresponding to a well-known phenomenon where a thermoplastic polymer is added to bitumen [10] [11]. However, we have notice a significant increase of the blends softening point values, from 100°C and above the SBS-modified bitumen. This may result from the following factors:

- A higher modifying power.
- A good polymer-bitumen compatibility embodied by a high swelling of the TPU soft segments in the bitumen aromatics components.
- A lower thermal susceptibility of the TPU than SBS polymers.

TPU-bitumen blends and PmB (SBS-based) present similar low temperature brittleness due to the repeatability of the test (3°C).
Considering elastic recovery as a high deformations indicator, we can notice that TPU-bitumen blends show a lower tensile strength than PmB (SBS-based) probably impacted because of the brittleness at the test temperature.

The Brookfield viscosity results indicate that the TPU-bitumen blends are less viscous than PmB (SBS-based) despite a high rate of polymer. It's a significant advantage in an industrial context for the pumping and the use of TPU-bitumen blends.

5-2-2 Rheological test - Complex modulus

Complex modulus tests were performed at EIFFAGE Infrastructures Research Center (France) using a Dynamic Shear Rheometer DSR (Physica 501 Anton Paar) over a frequency range from 1 to 100 Hz and a temperature range from -30°C to 70°C.

Thus complex modulus, master curves and Black diagram are presented in Figures 3 and 4 [12].

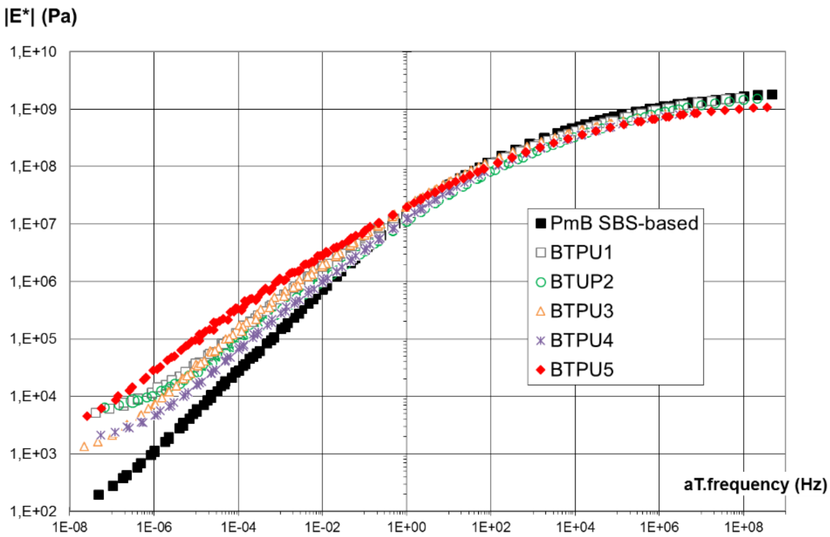


Figure 3. Results of the modulus tests – master curves at T_{ref} = 15°C

The complex modulus is mainly influenced by the modulus of the polymer in the high-temperature and low-frequency domains.
Regarding the master curves in Figure 3, we can notice that TPU-bitumen blends present a higher stiffness for aT.frequency < 1 hz (flow, creep area) and lower stiffness for aT.frequency > 1hz (transition area) than PmB (SBS-based) due to the lower thermal susceptibility of TPU polymers compared to SBS. This is particularly significant for the all the BTPU and particularly for the BTPU5.
Thus, the particular rheological properties of TPUs allow to consider better performances than SBS at high temperatures and low frequencies (creep resistance/rutting) but also at low temperatures and high frequencies (thermal cracking resistance) [13] [14].
Rely on the master curves, and more particularly on the "flow or creep area", it is possible to establish a ranking of the different blends. BTPU1, BTPU2 and BTPU5 are the most efficient with a very high creep resistance, while PmB (SBS-based) is more thermal sensitive [15].

The effect of polymer modification on the rheological parameters could be explored through "Black Space Diagrams" as shown in figure 4. The morphology, and therefore the rheological characteristics of the polymer modified bitumen depend on the nature, the content and the compatibility between polymer and bitumen.

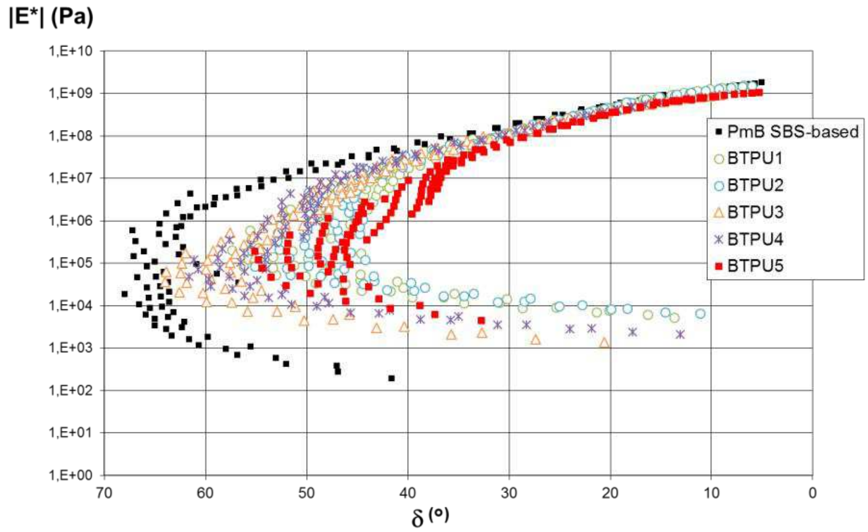


Figure 4. Results of the modulus tests – Black diagrams.

Due to the high TPU contents, the polymer network in the bitumen leads to a lower phase angle decrease than PmB (SBS-based). The decrease of phase angle is correlated with lower thermal dissipation and a better elastic response in small strains domain.

Also, BTPU1, BTPU4 and BTU5 have a lower phase angles than BTPU2 and BTPU3. However, BTU5 shows a significant discontinuous curve related to the non-compliance of the time-temperature superposition principle. This effect is directly linked to the polymer microstructure/morphology and more particularly with the TPU extender nature (H).

Furthermore, BTPU1 and BTPU2 have a very close rheological behavior and seem to be more influenced by the rigid segments ratio (17%) than the nature of the extender.

Regarding the rheological graphs and the conventional test results, we can observe that for the same rigid segment content (17%), the TPU extender nature impact directly thermal susceptibility and elastic recovery. BTPU2 presents the more effective elastic recovery whereas BTPU5 presents a lower thermal susceptibility and a higher stiffness.

5-2-3 Solubility parameters and compatibility

TPU polymers have a semi-crystalline structure that allows selective swelling with the different components of bitumen that can impact TPU-bitumen blend performances.
In order to compare the compatibility and the interactions between TPU polymers and the 50/70 pen grade bitumen, we have calculated the Hansen solubility parameters (HSP) by taking into account 3 types of interactions: dispersive (δ_D), polar (δ_P), hydrogen (δ_H) and calculating a global solubility parameter $\delta_{TOT}^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$.
Thus, using the HSPiP sotftware, we have studied the TPU phases solubility and compatibility in the bitumen. The results are shown in figure 5.

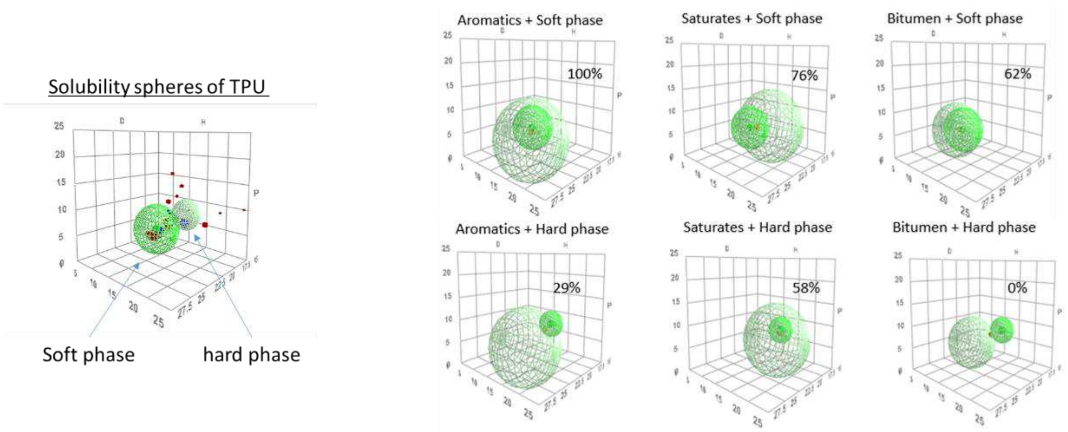


Figure 5. Solubility parameters of TPU1 into 50/70 pen grade bitumen.

We can observe that the TPU's soft phase is compatible with the bitumen fractions (aromatics and saturates) which ~~is not the~~ case for the rigid phase. Thus, these parameters are directly correlated to the polymer swelling rate into bitumen considered as a compatibility indicator.

On this basis, we have compared the TPUs swelling rate in bitumen for both polymers with a 17% rigid segments content. The results are shown in table 6.

N°	Extender	Rigid segments ratio in TPU (%)	Swelling rate
TPU1	B	17	1,80
TPU2	C	17	1,75
TPU5	H	17	1,90

Table 6. TPUs swelling rate in 50/70 pen grade bitumen.

The three TPU polymers present a low swelling rate due to their poor rigid phase compatibility with saturates and aromatics bitumen fractions. The TPU5 shows a slightly higher swelling rate regarding TPU1 and TPU2.
At this stage of the study and regarding the rheological performances and properties of BTPU1, BTPU2, and BTPU5, it is hazardous to correlate the swelling rate and the rheological behavior of the blends.

6 – CONCLUSIONS

Five TPU-bitumen blends and a SBS-based polymer bitumen were produced using a pure 50/70 pen grade bitumen. Performances of all materials were investigated by performing conventional trials, DSR complex modulus tests at different temperatures and frequencies. The compatibility between TPU polymers and bitumen was also investigated in order to understand the extender effect on TPU-bitumen rheological performances.
Due to their higher stiffness and the specific polymer microstructure, TPU-bitumen blends present a lower thermal susceptibility and a lower viscous dissipation than PmB at high temperatures and low frequencies.
Considering the elastic recovery test, and TPU polymers with a rigid segments rate below 20%, BTPU2 and BTPU3 designed with the extender B present the higher elastic behavior (in a large strains domain) However, BTPU 2 and BTPU3 values are still below PmB results. But, if we consider a small deformation domain (black space diagram), we observe an opposite result; BTPU blends are more efficient.
Future work will focus on further optimization of the TPU content in order to identify an optimum rate. We also continue to explore the interactions between TPU polymers microstructure and bitumen and carry on several tests with comparatives bituminous mixtures.

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