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Evaluation Of Ageing Properties Of Polymer Modified Bitumen

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Polymers are the most common modifiers currently being used to improve bitumen, BIT, viscoelastic properties. The polymers increase the temperature range over which a binder resists both rutting and thermal cracking as well as lengthening the time before fatigue failure. In this paper SBS block copolymer is used as the polymer modifier. The ageing properties of polymer modified bitumen, PMB, have the main role in quality of PMB dispersions and solid PMB. In road applications, BIT and PMB dispersions are exposed to thermooxidative ageing in production of PMB dispersions, during their storage, mixing and transporting. The thermooxidative processes in PMB dispersions affect the quality and ageing processes of solid PMB in their service life. For this reason, it is very important to determine the intensity of thermooxidative degradation of pure component as well as PMB dispersions. In this paper the bitumen and BIT/SBS blends are aged by means of the Rolling Thin Film Oven Test, RTFOT, at a temperature of 163 ^{o}C in the presence of oxygen. The chemical and rheological evaluation of ageing properties of PMB is investigated. The oxidative degradations of BIT, SBS and PMB are followed by IR spectras. Thermooxidative stability of PMB is evaluated on the base of viscosity changes of PMB dispersions by rotational viscosimeter. The ageing of solid PMB is evaluated through the changes of viscoelastic behaviour, relaxation spectras, which are obtained by Dynamic Mechanical Analyzer, DMA. The results obtained indicated that the changes in rheological properties, chemical and morphologycal structures, of aged PMB depend on a combined effect of SBS and bitumen oxidation and degradation processes. The phase content and morphological characteristic in PMBs changes in a much more complicated fashion than in neat block copolymers. The rheograms' shear viscosity, ˜, vs. shear rate, ˜, of aged BIT and PMB indicated the rise of the viscosity as well as the changes of flow type. The curves of storage modulus, E´, loss modulus, E´´, and loss tangent, tg˜, vs. temperature of aged BIT and PMB indicated the changes of the swollen polybutadyene, PB, and polystyrene, PS, phases in bitumen phase and results with destroying the swelling polymer network. Thermooxidative degradation occurs in BIT and in middle unsaturated PB block in SBS block copolymer. Oxidative structures result. The effect varies with bitumen source/grade. Besides the conventional test for evaluation of ageing properties of PMB dispersions and solids, both chemical and rheological methods are required.

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References

1. *Dimone M, Dana B, Cinueu C, Staicu D (1998) Revue Roomaine de Chimie 1: 45*
2. *Newman K J (1998) Elasto Plast 30:245.*
3. *Deffor F F (1992) Fine Research, Hamburg*
4. *Whiteoak C D (1991) Shell Symposium, Bucharest, Romania*
5. *Lu X H, Isacsson U (1998) Fuel 77 9-10: 961*
6. *Wloczysiak P, Vidal A, Papirer E, Gauvin P (1997) J Appl Sci 65:595*
7. *Lu X H, Isacsson U (2000) J Appl Poly Sci 76 12:1811*
8. *Lu X H, Isacsson U (2002) Construction and Building Materials 16:15*
9. *Rek V, Barjaktarovi´10. M Z (2002) Mat Res Innov 6 2:39*
11. *Rek V, Barjaktarovi´12. M Z, Holjevac Grguri´13. T (2004) The rheological properties of aged polymer bitumen. In: Reichert T, eds. (2004) Natural and Artifical Ageing of Polymers. Gesellschaft fq´rUmweltsimulatione eV GUS, Pfinztal*
14. *Rek V, Barjaktarovi´15. M Z, Vranješ N (2004) Dynamic mechanical properties of polymer modified bitumens. In: Grilec K, eds. (2004) International conference Materials Tribology Processing Matrib. Croatian Society for Materials and Tribology, Zagreb, p 44*
16. *Rek V, Špehar Z (1986) The properties of bitumen/styrene-butadiene-styrene blends. In:Filetin T, eds. (1996) 1st International conference Development Testing and Application of Materials MATEH. Croatian Society for Materials and Tribology, Zagreb, p 315*
17. *Casson N (1959) Rheology of Disperse Systems, Pergamon Press, New York*
18. *Ferguson J, Kembkowski Z (1991) Applied fluid rheology, Elsvier Applied Science, London- New York*
19. *Bahia H U, Anderson D A (1993) J Assoc Asphalt Paving Technol 62: 93*
20. *Murayama T (1978) Mechanical Analysis of Polymeric Material, Elsevier Science Publi New York*
21. *Eisele V (1990) Introduction to Polymer Physics, Springer-Verlag, Berlin*
22. *Bocci M, Montepara A (1995) Bitumen 2000-International Conference. World Road Association, Balatonszeplak*
23. Holjevac Grguri´24. T, Rek V, Jel´25. i´26. } (1999) Polym Eng Sci 39 8: 1394

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The polymer modified bitumens, PMBs, are very important as binders in road service [1]. To achieve desired rheological properties, the polymers are used as bitumen modifiers [1-3]. One of the most important modifiers is styrene-butadiene-styrene block copolymer, SBS [4]. SBS widens the temperature region of BIT application. It is due to the low glass transition, T_g, of soft polybutadiene, PB, phase, as a middle block in SBS, and high T_g of hard polystyrene, PS, phase. Beside this, SBS enhances the viscoelastic behaviour of bitumen [2-9]. In road applications, BIT and PMB are exposed to ageing processes during storage, mixing, transport and laying, as well as in their service life. Oxidative ageing of BIT and PMB cause hardening of BIT and consequently may make a contribution to the deterioation of asphalt pavements [1] The complex process of ageing has been studied by several authors[5, 6, 8, 10, 11]. It has been established that the complexity increases when the polymer is present. In phases of PMB dispersions processing as well as in phases in use, the rheological properties of PMB are very important [4-9, 12]. So for the evaluation of ageing properties of PMB, the conventional test of the viscosity of PMB dispersion before and after ageing and the PMB resistance to deformation must be evaluated. The purpose of our work is to present the artificial thermooxidative ageing of PMBs dispersions and solids. The key objective is to observe how thermooxidative ageing influences the rheological properties, chemical structure of BITs and PMBs as well as morphological structure, and to interpret the results in terms of phase content end morphological characteristics of investigated systems. The evaluation of ageing properties of PMBs is studied through changes in chemical structures, rheograms and relaxation spectras.

Experimental

Materials

Two BITs denoted BIT 1 and BIT 2 are used in this study. The source of BIT 1 and BIT 2 is INA Rafinery, Croatia, Rijeka. The content of asphaltene in BIT 1 is 10.2% weight and in BIT 2 it is 17.3% weight. Linear styrene/butadiene/styrene, SBS-L, block coopolymer commercial grade Kraton 1101, Shell Co., Germany is used as polymer modifier, with content of polystyrene, PS 29% weight. The content of SBS in PMB is 4% weight.

Specimens preparation
The blends were prepared by using a Silverson L4R mixer at a frequency of 1500 min^{-1}. SBS was added into bitumen at 185 ^oC over a two h period. The specimens for dynamic mechanical analysis, DMA, were obtained by molding at 25 ^oC. The dimensions of investigated specimens are 18x13x5 mm.

Ageing procedure
Accelerated thermooxidative ageing of BITs and PMBs were performed using the Rolling Thin Film Oven Test, RTFOT, according to ASTM D 2872. The RTFOT test simulates the conditions during production and mixing as well as laying of asphalt mixes. The sample holders are kept in an oven at 160 ^0C for 15 min and than aged at 163 ^oC for 75 min.

Measurements
The rheological properties of BITs and PMBs dispersions were measured by rotational viscosimeter Brookfield, Programmable DV-//+Viscometer, before and after ageing. The rheological parameters shear stress, τ, and shear viscosity, η, were measured varying shear rate, γ. The rheograms of shear stress, τ, and shear viscosity, η, vs. shear rate γ were constructed. Using the Ostwald-de Waele model: $\tau = k \cdot \gamma^n$ the flow index, n, was evaluated [13, 14]. The rheological properties were also followed by DMA, using the Dynamic Mechanical Analyser 983, TA Instruments. The storage modulus E', loss modulus E'' and the loss tangent tan δ of BITs and PMBs were obtained before and after ageing. The conditions were as follows: the rate of heating 5 ^oC/min, traffic frequency 5 Hz and amplitude 0.3 mm. A fluorescent microscope Olympus BX51M was used to investigate the morphology of PMBs.

FTIR spectras
FTIR spectras before and after thermooxidative degradation were performed on Fourier Transform Infrared Spectroscopy, FTIR, Nicolet 5 DX-FTIR.

Results And Discussion
Rheological behaviour of BIT and PMB dispersions

From the rheograms of shear stress, τ, and shear viscosity, η, vs. shear rate, γ, obtained for BITs before and after ageing, it is evident that rheological curves are shifted in the region of higher share stress and higher share viscosity values, for the same shear rates, after the RTFOT test (See Fig. 1). BIT has dilatant behaviour, which becomes more pronounced in aged BIT. It is evident from the flow index, n, in the Ostwald-de Waele model (Table 1) [10].

The addition of SBS shifts the rheological curves in rheograms of shear stress, τ, and shear viscosity, η, vs. shear rate, γ, to the higher shear stress and viscosity regions for the same share rates values (Figs. 2, 3.). Investigated PMBs have pseudoplastic behaviour (Table 1). After ageing under the conditions of the RTFOT test, the following changes are visible: the increase of shear stress and viscosity values in the curves of shear stress, τ, and shear viscosity, η, vs. shear rate, γ, and more pronounced pseudoplastic behaviour (Figs. 2, 3. and Table 1).

These changes are faster in aged PMB 2 than in PMB 1. The changes in rheological behaviour of aged BITs may be the consequences of physical hardening and may be attributed to the reorganization of bitumen molecules [15]. The higher viscosity of PMBs in comparison with the BIT, indicated the interaction of PB and PS phases with BIT and their swelling in BIT phase. It leads to the formation of a continuous elastic network [5-9], which is evident from the microphotograph (Fig.4a).

Rheological behaviour of BITs and PMBs under the traffic frequencies

From the DMA spectras of BITs (Figs.5 and 6), it is evident that both BITs have one glass transitions temperatures , T_{gs}, at very low temperatures and at the BITs T_{gs} an abrupt change of the slope of the curves storage modulus, E', vs. temperature occurs. BIT 1 has lower E' values than BIT 2.

After artificial ageing under the RTFOT test conditions, the curves storage modulus, E', vs. temperature in DMA spectras of BIT 1 is shifted to lower values of E' while in RTFOT aged BIT 2, the shift is the opposite (Figs. 7, 8.).

The glass transitions temperatures, T_{gs} values are changed, too (Table 2). With the introduction of SBS in BIT 1 and BIT 2, the rubbery plateaus are visible on the curves storage modulus, E', vs. temperature in DMA spectras and new T_{gs} at negative temperatures on the curves loss modulus, E′′ vs. temperature which correspond to the swollen PB phase (Figs. 9, 10. and Table 2) [4-6, 9].

The T_{gs} which are at positive temperature are associated with the bitumen phase which did not take part in SBS swelling [4-6, 9]. These DMA spectras of PMB 1 and PMB 2 indicate better rheological behaviour in the conditions of physical ageing caused by traffic frequency due to the formation of the continuous polymer network in the BIT continuous phase (Fig. 4a). As a consequence of this, PMBs have better viscoelastic bahaviour and better resistance to temparature, as well as higher viscosity than BITs [16, 17]. After ageing, the rheological behaviour of PMBs change (Figs. 11, 12.).

In aged PMB 1 the curve storage modulus, E', vs. temperature has a rubbery plateau, but it is shifted to lower E' values. The rubbery plateau in the PMB 2 curve storage modulus, E', vs. temperature disappears after ageing. The changes in E' and the changes of T_{gs} are connected with changes of the polymer swelling network. T_{gs} are not distinctly separated as before ageing. It indicates that the continuous network is affected (Fig. 4b). The authors who examined the content of phases in BIT after ageing found that the content of asphaltene increased, while the maltene content decreased after ageing [18]. FTIR spectras of aged BIT and PMB investigated systems indicated the increase of carbonyl groups with a simultaneous decrease of diene sequencies (Table 3.).

It indicated BIT oxidative degradation as well as oxidation of unsaturated middle block in SBS [10, 19]. It is in agreement with the changes of the rheological properties under the conditions of ageing in the RTFOT test and changes in microphotographs.

Conclusions

Ageing in RTFOT conditions influences bitumens and polymer bitumen chemistry and rheology. As a consequence of this, the rheological properties of BITs and PMBs dispersions are changed and their share viscosity increases. The changes of rheological properties of aged BITs and PMBs under the traffic loading conditions are connected with destroying the swelling polymer network. Thermooxidative degradation occures in BIT and polymer and oxidative structures result. The effect varies with the bitumen source/grade. For evaluation of ageing properties of PMB both chemical and rheological methods are required.

Acknowledgments
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References

1. Dimone M, Dana B, Cinueu C, Staicu D (1998) Revue Roomaine de Chimie 1: 45
2. Newman K J (1998) Elasto Plast 30:245.
3. Deffor F F (1992) Fine Research, Hamburg
4. Whiteoak C D (1991) Shell Symposium, Bucharest, Romania
5. Lu X H, Isacsson U (1998) Fuel 77 9-10: 961
6. Wloczysiak P, Vidal A, Papirer E, Gauvin P (1997) J Appl Sci 65:595
7. Lu X H, Isacsson U (2000) J Appl Poly Sci 76 12:1811
8. Lu X H, Isacsson U (2002) Construction and Building Materials 16:15
9. Rek V, Barjaktarović M Z (2002) Mat Res Innov 6 2:39
10. Rek V, Barjaktarović M Z, Holjevac Grgurić T (2004) The rheological properties of aged polymer bitumen. In: Reichert T, eds. (2004) Natural and Artifical Ageing of Polymers. Gesellschaft fűrUmweltsimulatione eV GUS, Pfinztal
11. Rek V, Barjaktarović M Z, Vranješ N (2004) Dynamic mechanical properties of polymer modified bitumens. In: Grilec K, eds. (2004) International conference Materials Tribology Processing Matrib. Croatian Society for Materials and Tribology, Zagreb, p 44
12. Rek V, Špehar Z (1986) The properties of bitumen/styrene-butadiene-styrene blends. In:Filetin T, eds. (1996) 1st International conference Development Testing and Application of Materials MATEH. Croatian Society for Materials and Tribology, Zagreb, p 315
13. Casson N (1959) Rheology of Disperse Systems, Pergamon Press, New York
14. Ferguson J, Kembkowski Z (1991) Applied fluid rheology, Elsvier Applied Science, London- New York
15. Bahia H U, Anderson D A (1993) J Assoc Asphalt Paving Technol 62: 93
16. Murayama T (1978) Mechanical Analysis of Polymeric Material, Elsevier Science Publi New York
17. Eisele V (1990) Introduction to Polymer Physics, Springer-Verlag, Berlin
18. Bocci M, Montepara A (1995) Bitumen 2000-International Conference. World Road Association, Balatonszeplak
19. Holjevac Grgurić T, Rek V, Jelčić Ž (1999) Polym Eng Sci 39 8: 1394

Table 1 Flow index values, n

SAMPLE	Flow index values, n	
	Before ageing	After ageing
BIT 1	1,0532	1,3423
BIT 2	1,2930	1,4735
PMB 1	0,9880	0,9774
PMB 2	0,9997	0,9821

Table 2 Glass Transitions Temperatures, T_g of BITs and PMBs

SAMPLE	T_g PB phase, S °C		T_g phase BIT, °C	
	E´´		E´´	
	Before ageing	After ageing	Before ageing	After ageing
BIT 1	-	-	11,3	25,3
BIT 2	-	-	26,87	35,61
PMB 1	-19,05	-63,51	34,98	49,98
PMB 2	-61,59	-51,25	43,13	43,70

S – swollen phase

Table 3 Flow index values, n

SAMPLE	BEFORE AGEING		AFTER AGEING	
	$1705cm^{-1}$	$965cm^{-1}$	$1705cm^{-1}$	$965cm^{-1}$
PMB 1	3,98	2,47	5,44	2,30
PMB 2	3,69	4,19	8,01	3,76

Fig. 1 Rheograms for BIT 2 (▲) before ageing, (●) after ageing: a) τ/γ, b) η/γ

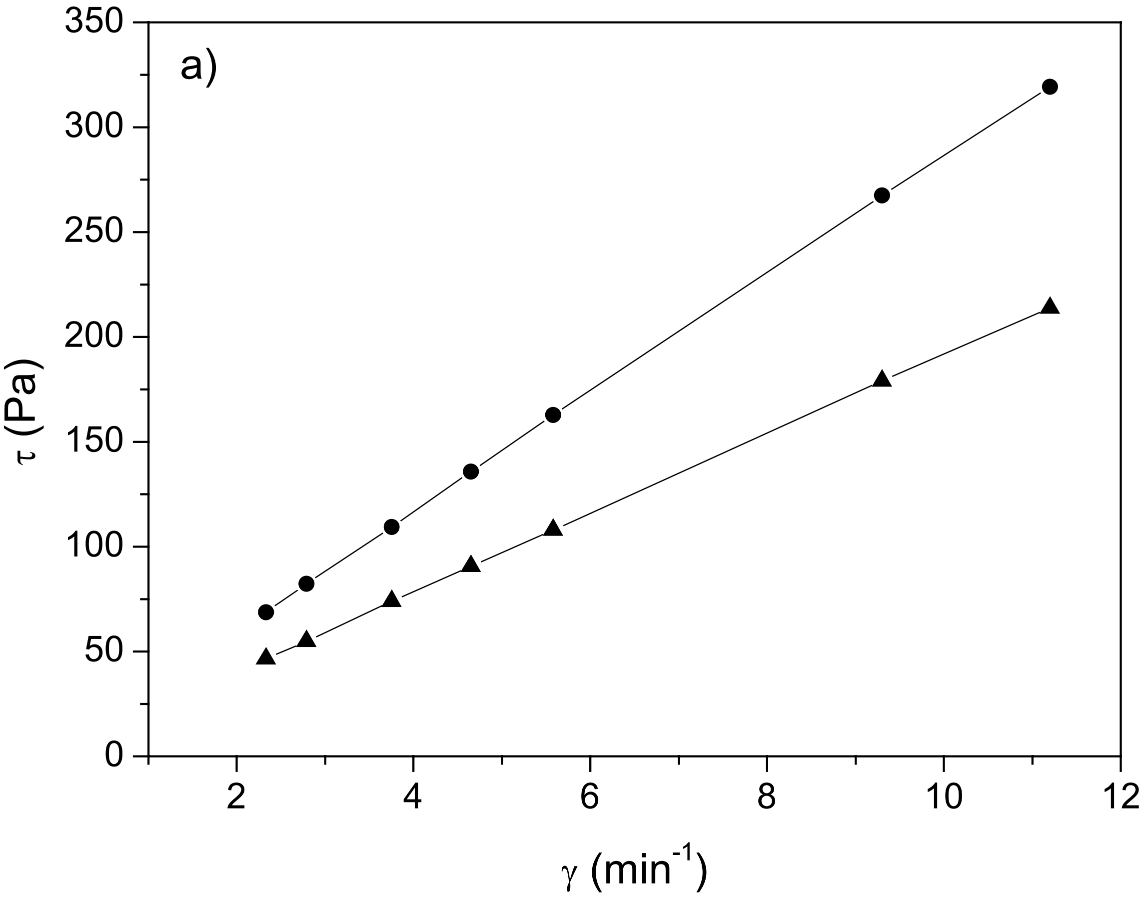

Fig. 1 Continued

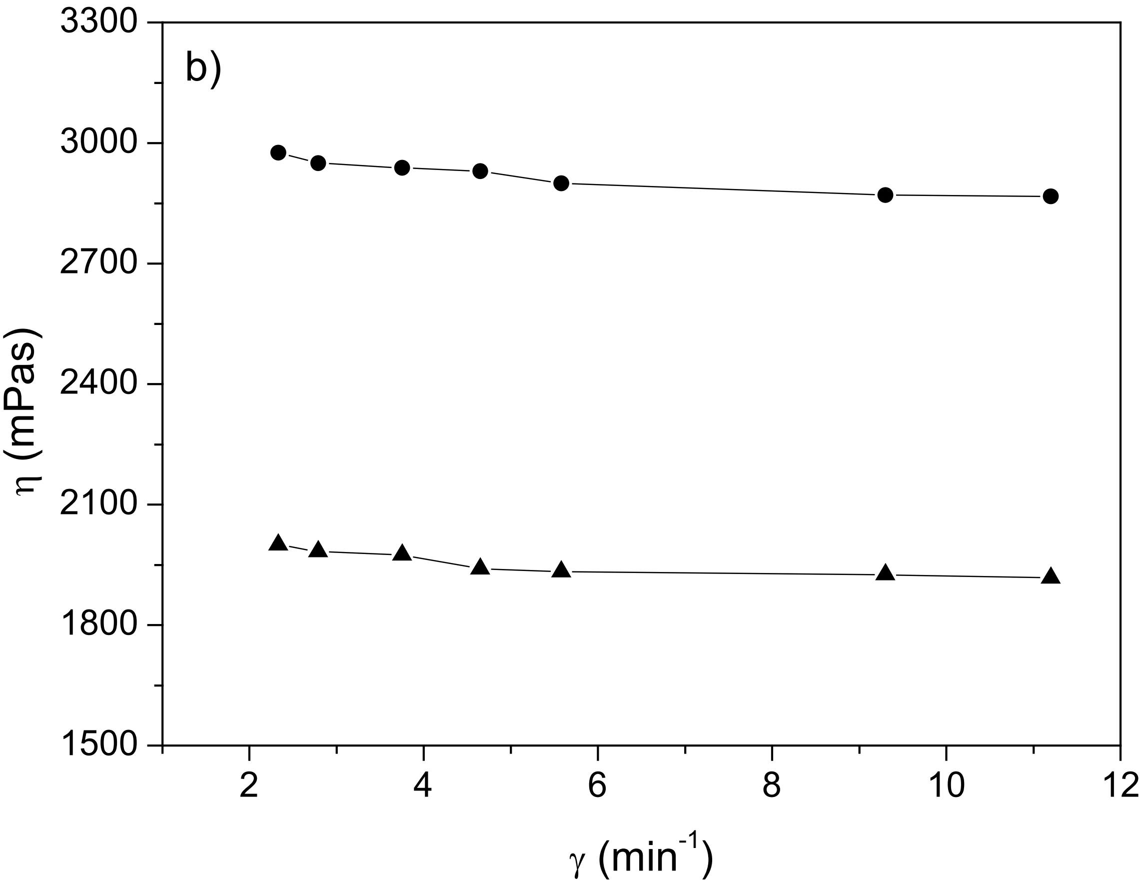

Fig. 2 Rheograms for PMB 1 dispersion (▲) before ageing, (●) after ageing: a) τ/γ, b) η/γ

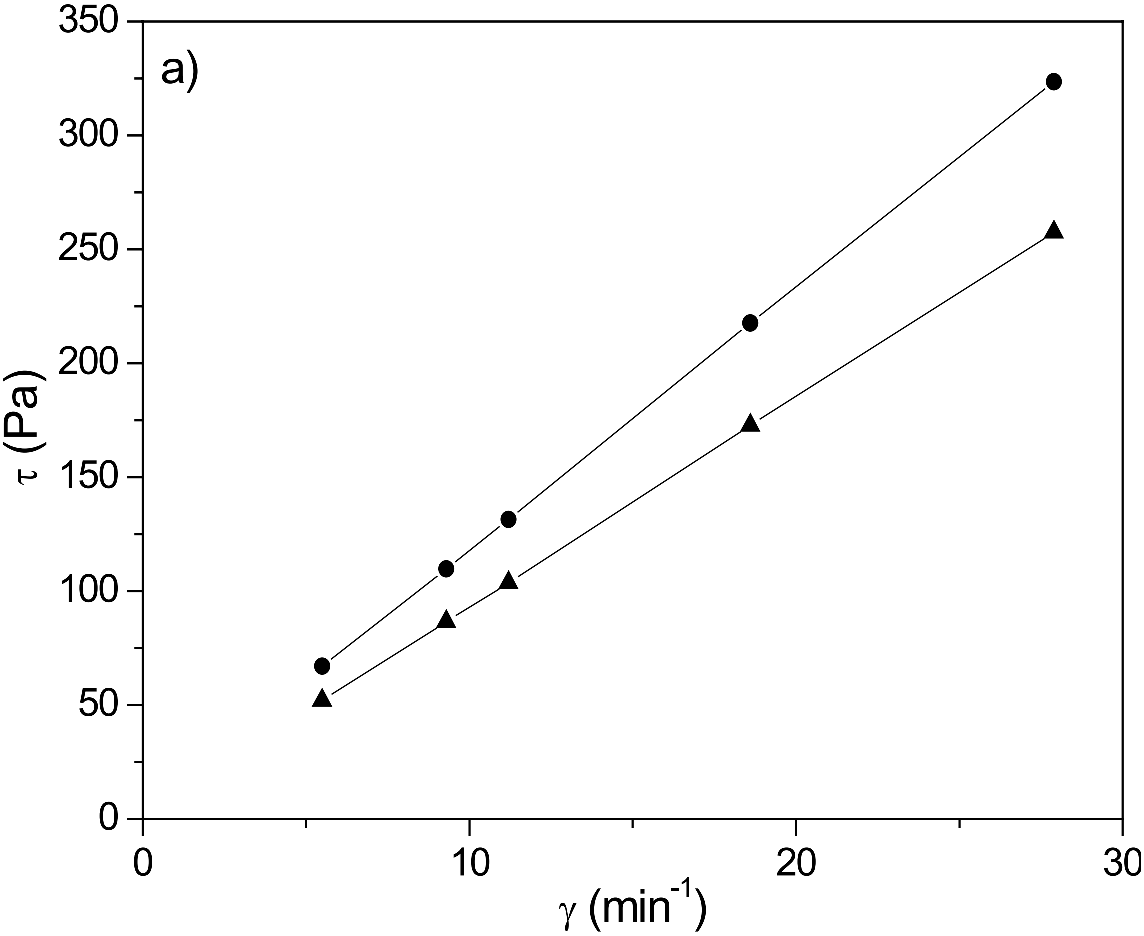

Fig. 2 Continued

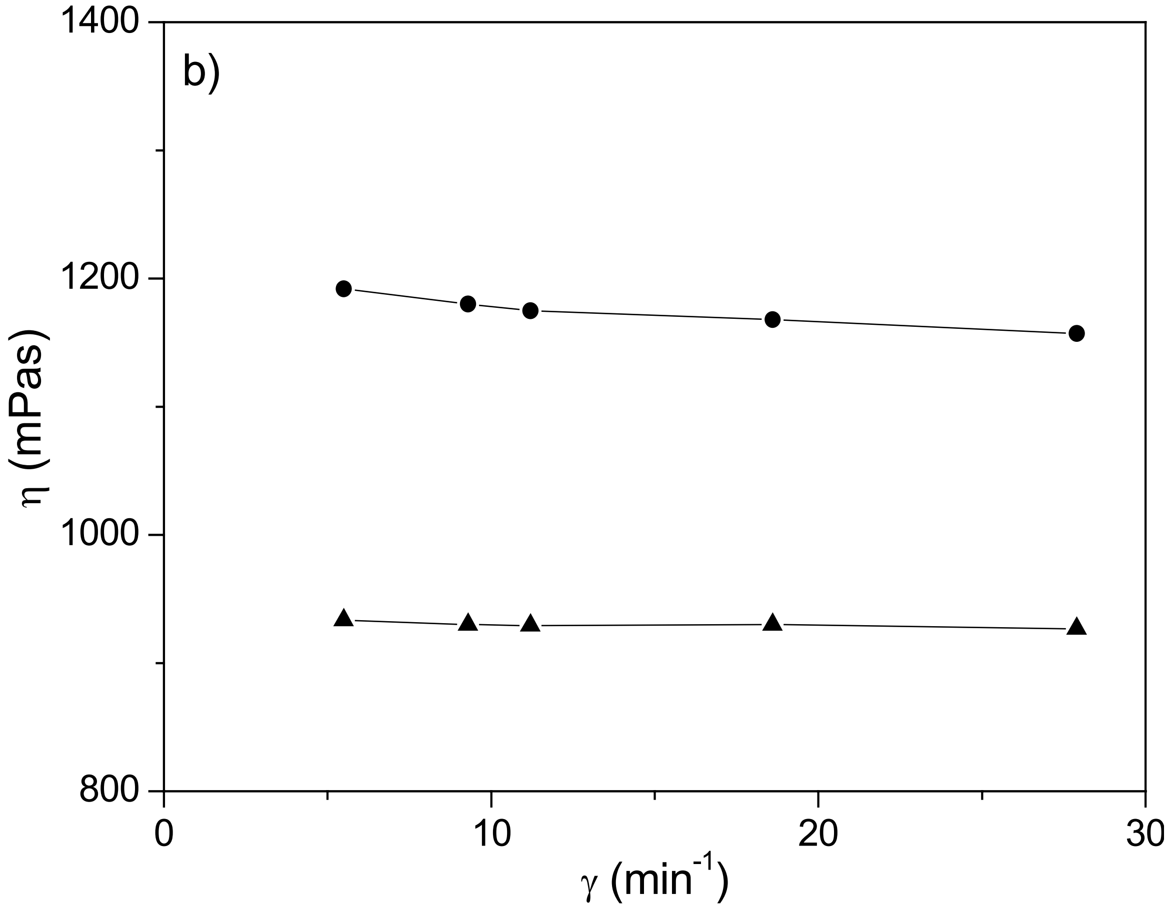

Fig. 3 Rheograms for PMB 2 dispersion (▲) before ageing, (●) after ageing: a) τ/γ, b) η/γ

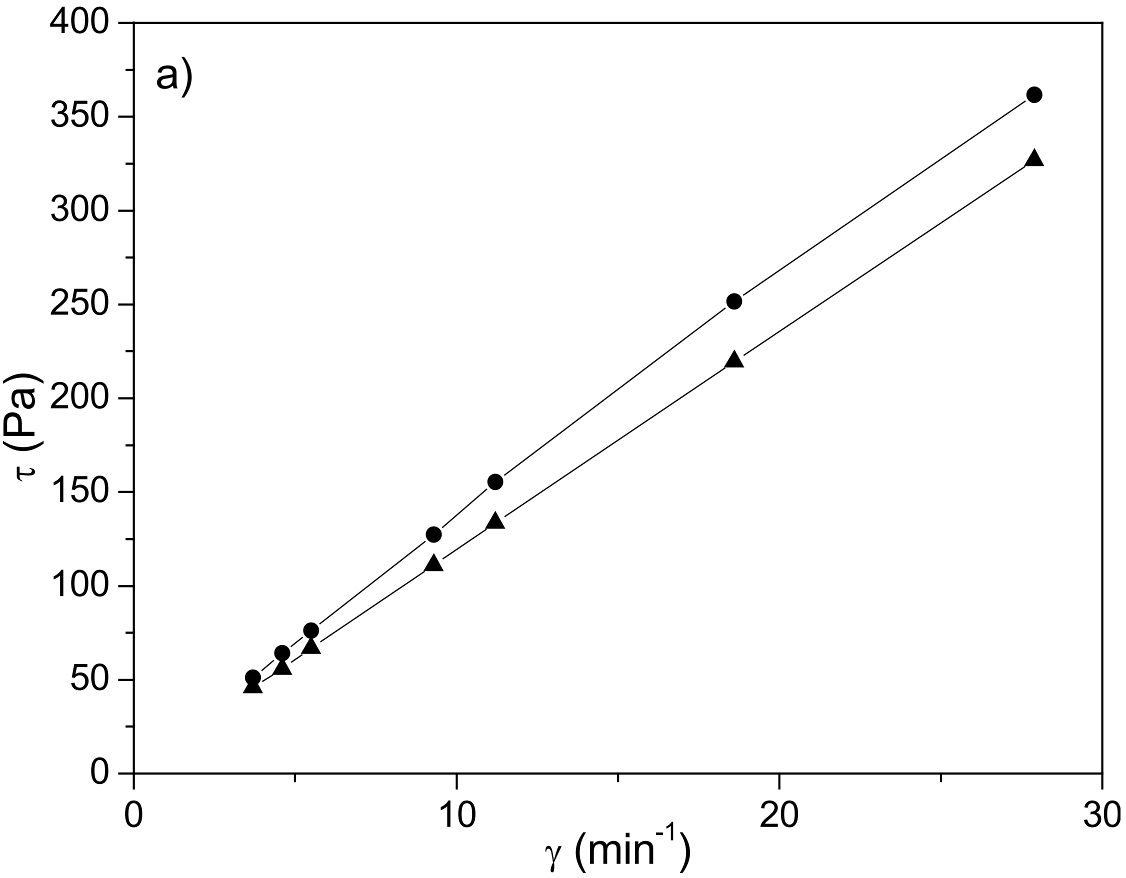

Fig. 3 Continued

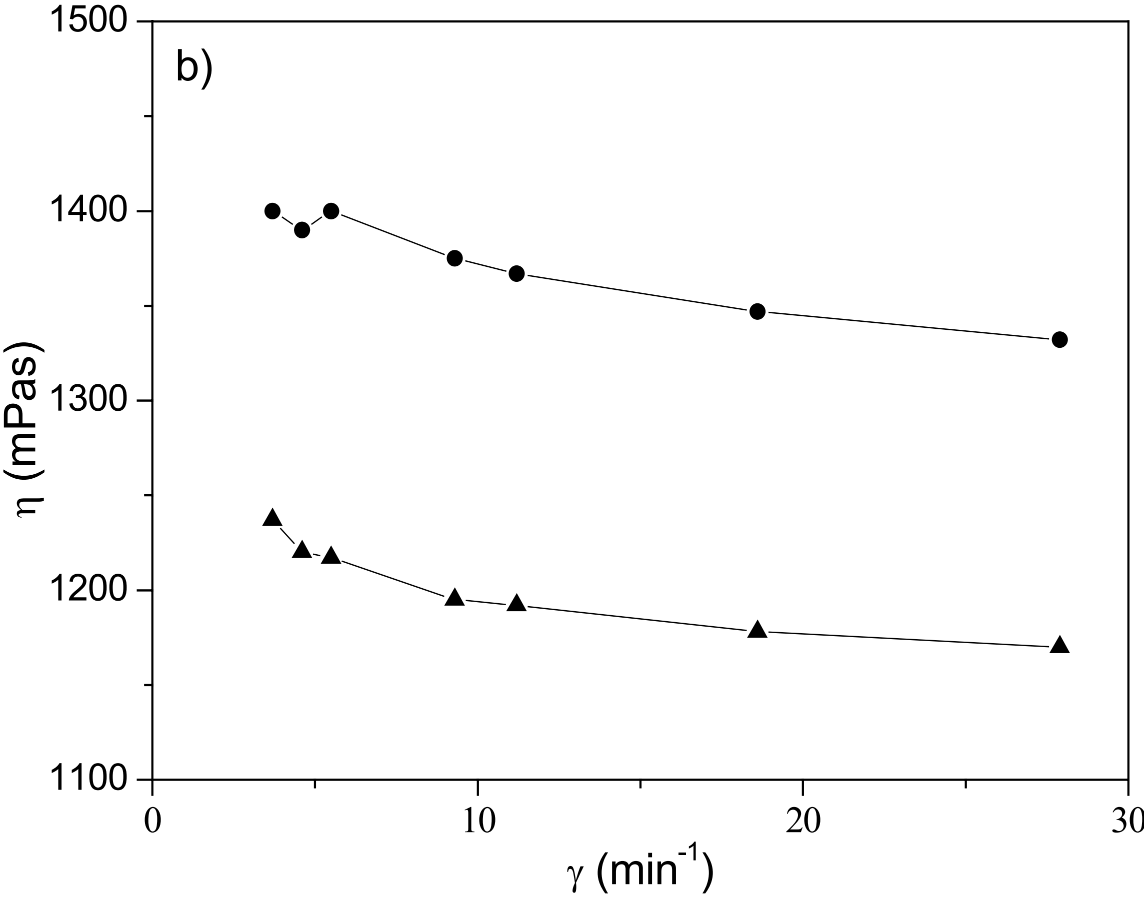

Fig. 4 Microphotographs of swollen SBS in BIT: a) before ageing, b) after ageing

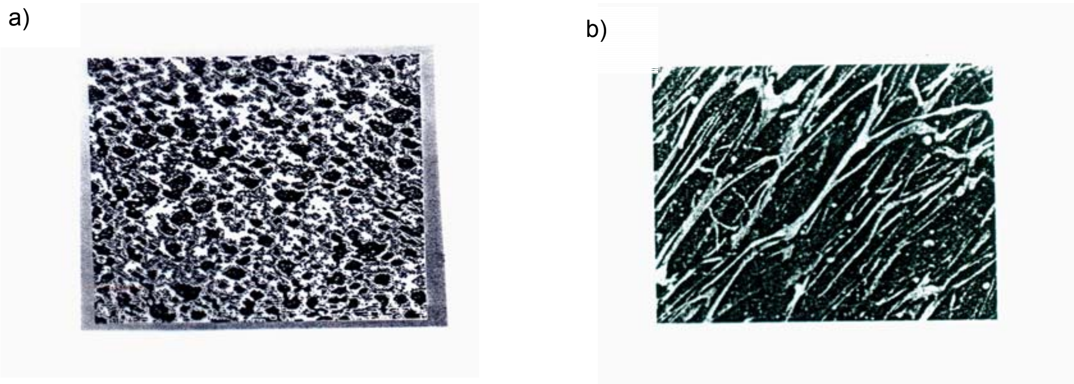

Fig. 5 DMA spectra for BIT 1

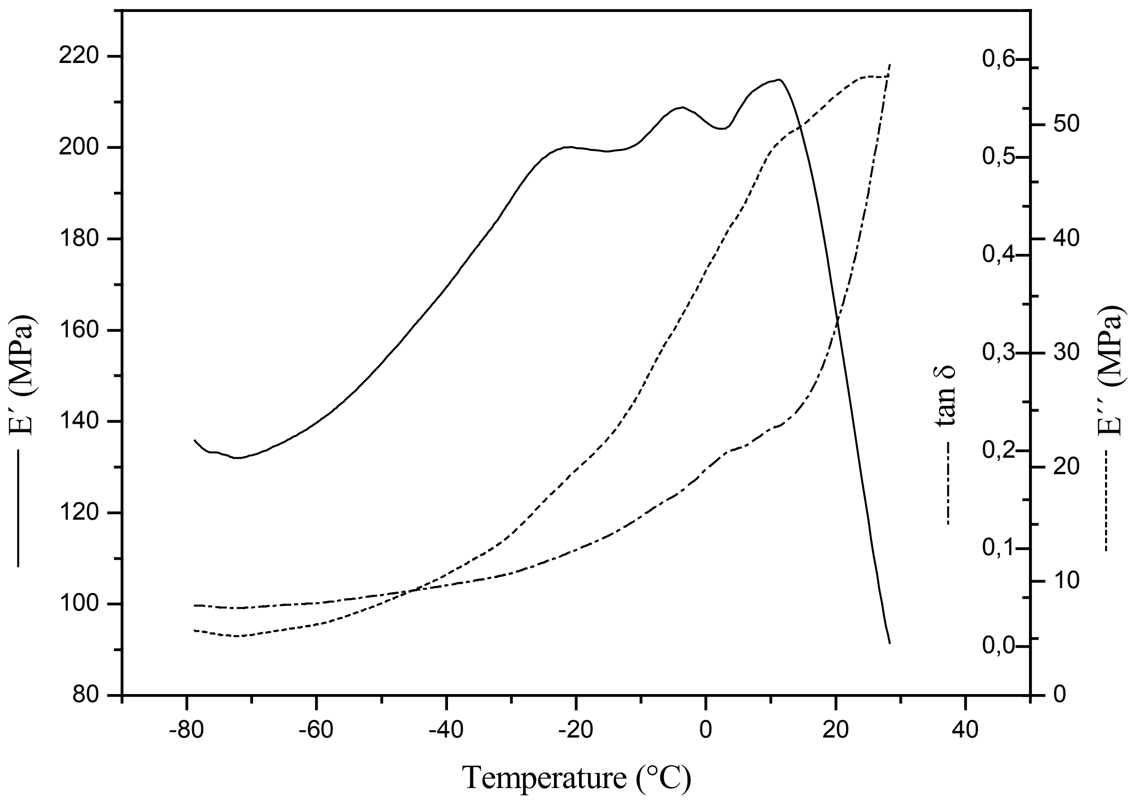

Fig. 6 DMA spectra for BIT 2

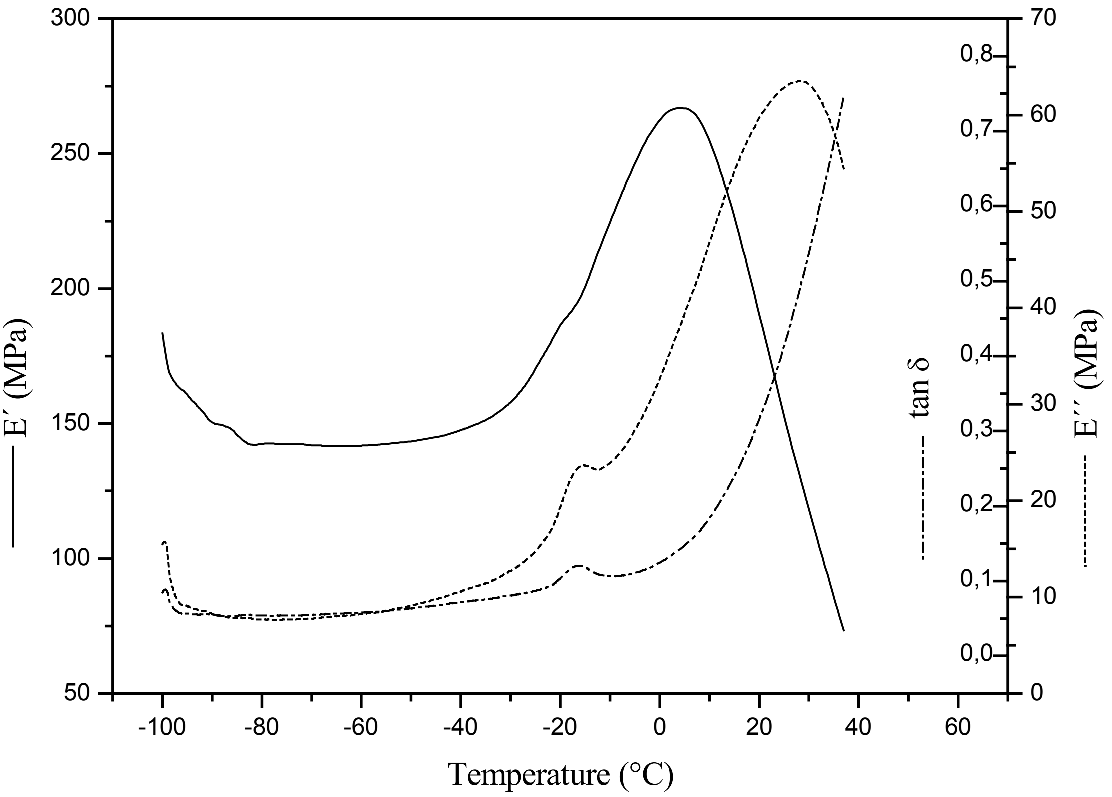

Fig. 7 DMA spectra for BIT 1 after ageing

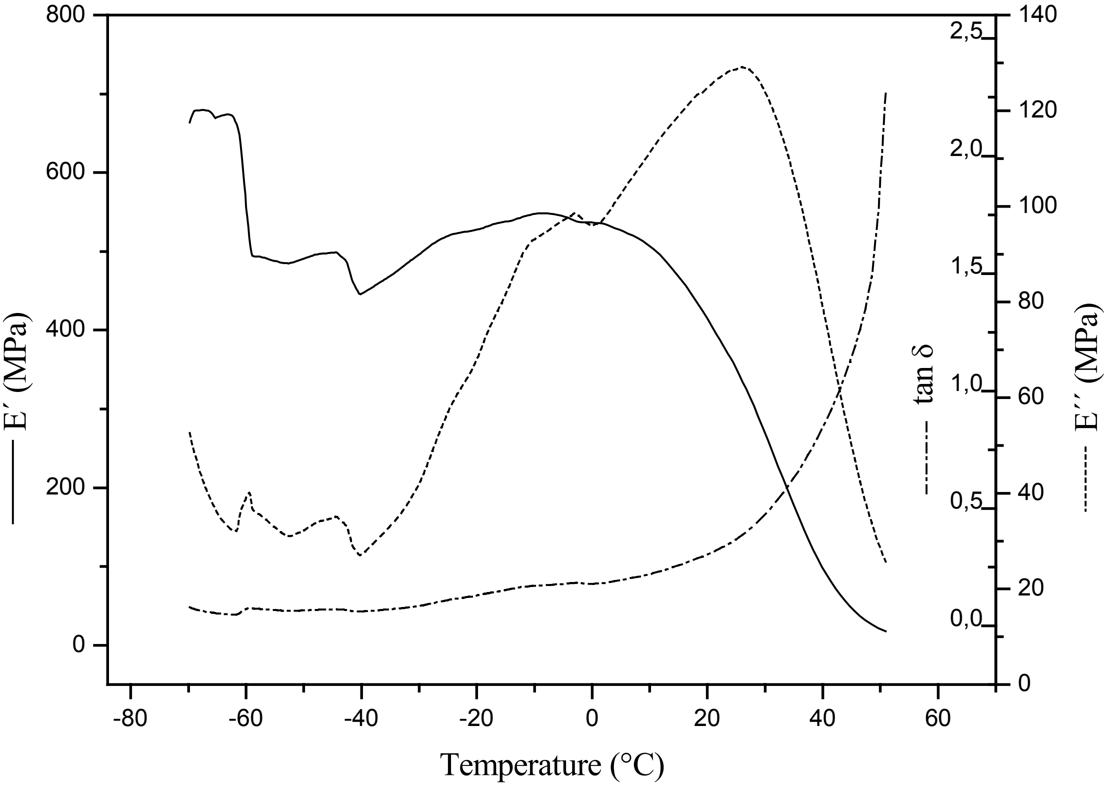

Fig. 8 DMA spectra for BIT 2 after ageing

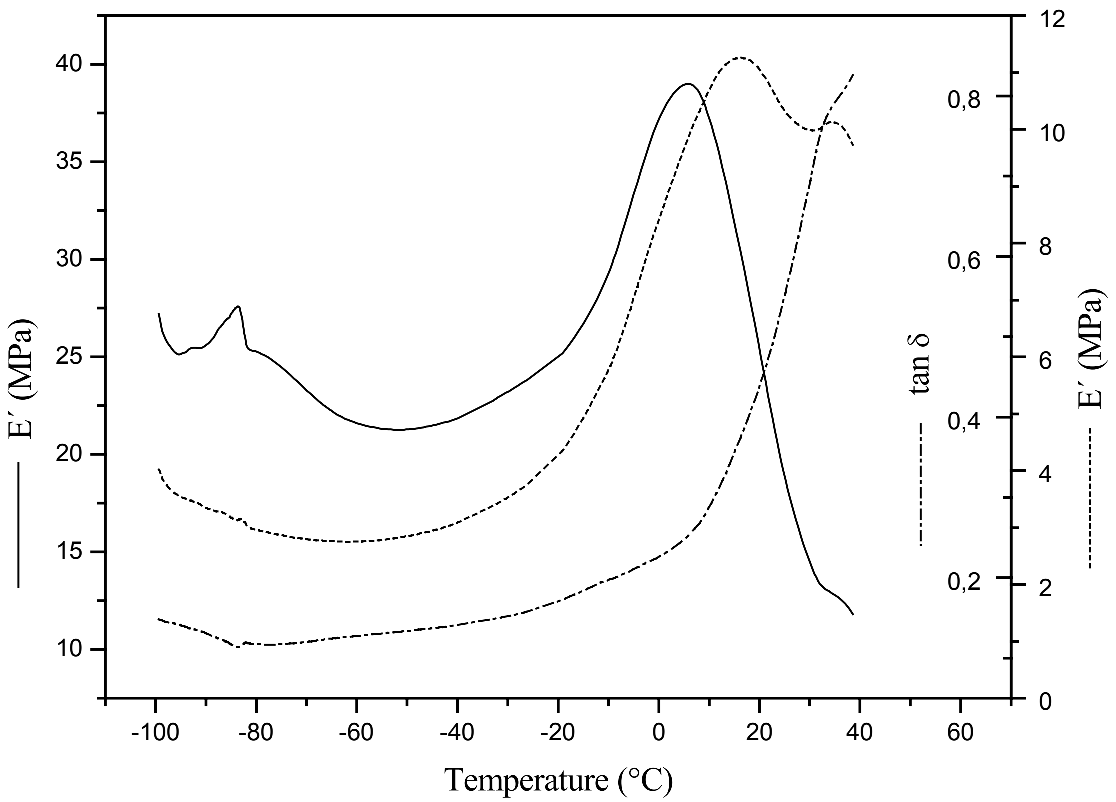

Fig. 9 DMA spectra for PMB 1

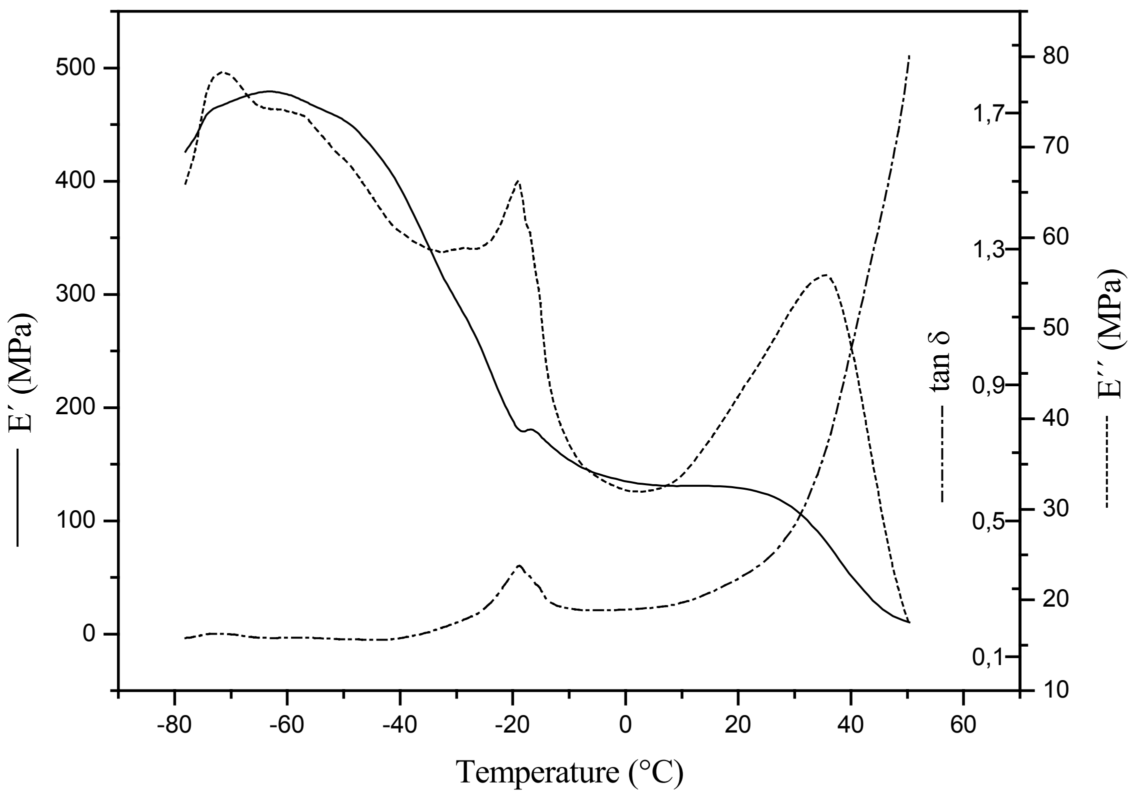

Fig. 10 DMA spectra for PMB 2

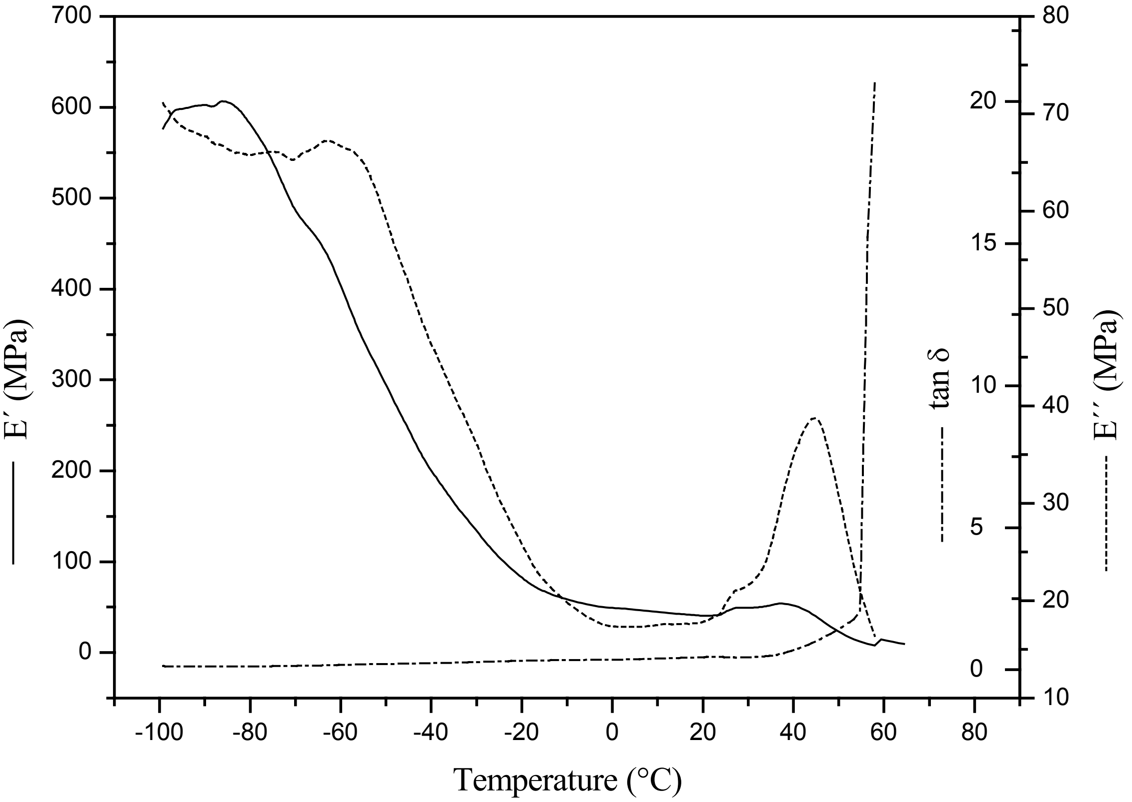

Fig. 11 DMA spectra for PMB 1 after ageing

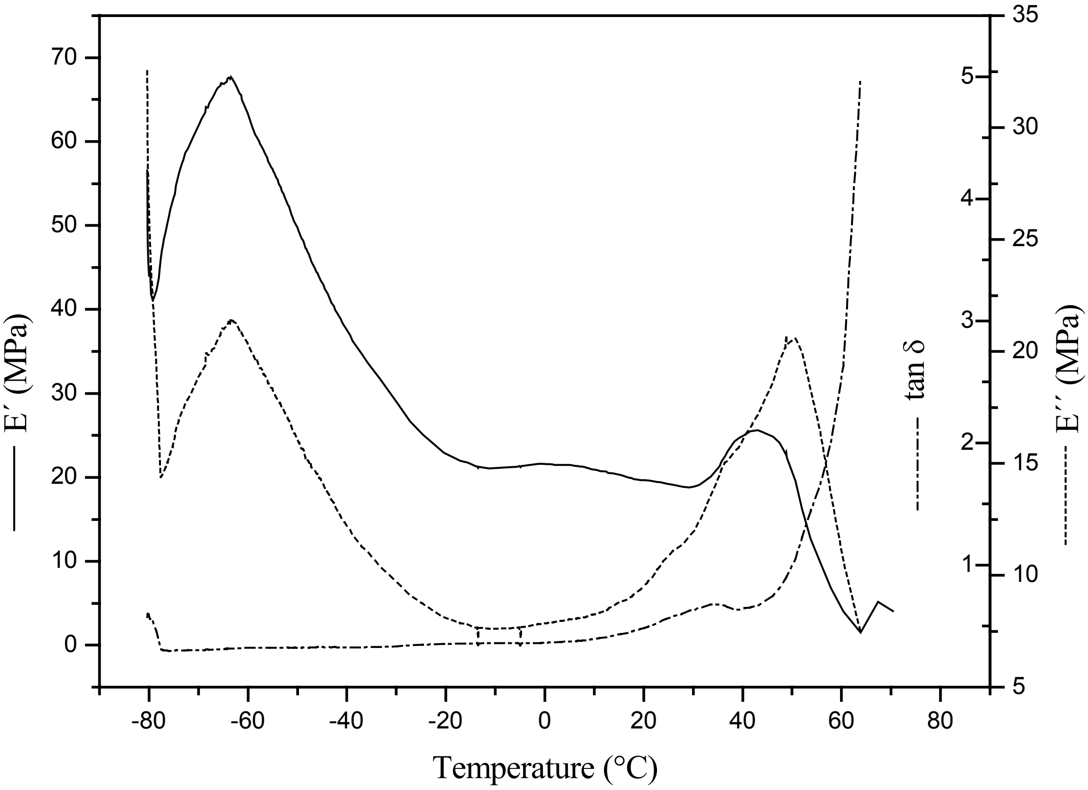

Fig. 12 DMA spectra for PMB 2 after ageing