Asphalt Nanocomposite Based on Calcium Carbonate

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Asphalt nanocomposites were prepared by mixing nanoparticles of calcium carbonate with a solution of bitumen in xylene in the presence of a solution of polymer in xylene. Calcium carbonate nanoparticles were obtained by wet milling and their characterization was performed by dynamic light scattering (DLS). The polymers used were either polyacrylate type and polystyrene homopolymers or copolymer of polyacrylate-polystyrene type synthesized by solution process. Asphalt nanocomposites prepared were characterized by dynamic mechanical analysis (DMA). The results indicate a close behaviour of nanocomposite based on polyacrylate and polystyrene homopolymers and polyacrylate-polystyrene copolymer.

Keywords: asphalt nanocomposites, calcium carbonate, dynamic mechanical analysis

Nanomaterials science has found application in the field of asphalt, mainly due to the special properties resulting from their nanoscale dimensions and increased ratio of surface area to volume. The influence of nanoclays on bitumen modified with linear and branched styrene-butadiene-styrene copolymers on physical, mechanical and rheological properties was studied. The results show that nanoclay improves physical properties, rheological behaviour and storage stability of polymer modified bitumen [1].

Use of organophilic nanoclay improve compatibility with monomers and polymers. Rheological studies of unmodified bitumen compared with nanoclay modified bitumen was conducted using Dynamic Shear Rheometer (DSR). It was measured also penetration, softening point, ductility and aging effect. It was noted that nanoclay change rheological characteristics of bitumen and increases stiffness, but decreases phase angle and improves aging resistances [2].

Dynamic Mechanical Analysis (DMA) was conducted over a wide range of temperature and frequency to study the thermo-rheological behaviour of polymer modified asphalt nanocomposites. Mechanical response was found to be closely related to nanocomposite changing and was identified a solid-like behaviour without Newtonian transition [3].

Mixtures of organophilic montmorillonite/SBS modified bitumen were prepared by melt mixing and compared before and after adding nanoclay in bitumen. The results indicate significantly improved storage stability without worsening other properties. X-ray diffraction has revealed an exfoliated nanoclay in nanocomposite structure [4].

Modifying road bitumens can be achieved with thermoplastic polymers like SBS, SEBS, EVA and EBA. Properties of the binder are significantly improved when the polymer forms a continuous phase at a concentration of 6%. Binder properties after aging depend on the type of polymer and bitumen, rheological changes beeing closely related to the oxidation of bitumen and polymer degradation [5].

By modifying the bitumen with plastomers its properties, like penetration, softening point, temperature susceptibility, are improved, being dependent on the type and concentration of the polymer and its solubility in bitumen. At low concentration of polymer is observed the existing dispersed polymer particles in the continuous phase of bitumen, while the high concentration of polymer lead to the existence of a continuous polymer phase [6-8]. Both synthesized and recovered polymers can be used in order to modify bitumen for road applications. The results on improving bitumen properties with virgin and waste polymers are similar [9].

As an alternative to modification of road bitumen was studied acrylic polymers. Copolymers styren acrylates show better weatherability and ozone resistance compared with styrene butadiene copolymers, since they have not double bonds. Monomers used for polymerization were ethyl acrylate and butyl acrylate. Rheological properties of modified bitumen were compared with the properties of road bitumens unmodified. Studying the rheological properties of the binders was shown that glass transition temperature of polyacrylates, rather than molecular weight, has a major influence of the properties in the field performance.

Experimental part

Raw materials

The raw materials used to prepare polymers were monomers ethylacrylate (Aldrich), styrene (Aldrich), solvent – p-xylene (Sigma-Aldrich) and initiator - benzoyl peroxide (Aldrich), used as received. For the preparation of asphalt nanocomposites has been used powder of calcium carbonate (Sigma-Aldrich) and a local bitumen D50/70 type. Bitumen characteristics D50/70 type used for asphaltic nanocomposite are presented in table 1.

The particle size of calcium carbonate was reduced using a planetary ball mill as described in [11]. A laboratory planetary mill - Fritsch Pulverisette 6 with 500 mL stainless steel grinding bowl and 10 stainless steel grinding balls (20 mm diameter, 30 g/ball) was used to reduce particles size of calcium carbonate. Milling conditions were: mass ratio balls:powder 1:3, for 60 min. at 500 rpm with 10 balls. Dynamic light scattering (DLS) - Nano ZS (Red badge-Malvern Instruments) was used to measure the milled particles size.

Polymer synthesis

Synthesis of polymers was performed in solution in a three necks flask equipped with stirring, heating oil bath

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Characteristic	Method	Value
Penetration at 25°C, 1/10 mm	SR-EN 1426	61
"Ring and ball" softening point, °C	SR-EN 1427	44
Ductility at 25°C, cm	SR 61-97	150
Fraass breaking point, °C	SR EN 12593-07	-18
Flash point, °C	STAS 5489-80	260
Density at 15°C, g/cm^3	SR ISO 3838-04	1.037

Table 1
BITUMEN CHARACTERISTICS D50/70 TYPE USED FOR ASPHALTIC NANOCOMPOSITE

Sample code	Filler	Bitum	Polymer
M0	Calcium carbonate	D50/70	-
N2	Calcium carbonate	D50/70	polyethylacrylate
N3	Calcium carbonate	D50/70	copolymer ethylacrylate-styrene
N4	Calcium carbonate	D50/70	polystyrene

Table 2
COMPOSITIONS OF ASPHALTIC NANOCOMPOSITES

Table 3
POLYSTYREN AND POLYETHYLACRYLATE SOLUTIONS VISCOSITIES

Polymer	Viscosity, cSt
PS	197
PAE	187
PAES	221

thermostat and inert gas blanket. After the introduction of solvent has added the initiator (benzoyl peroxide 0.5% molar) when temperature has reached (80°C), followed by the addition of monomer (mass ratio monomer / solvent: 1/1) in four equal portions during 40 min. The reaction mass was maintained at working temperature and stirred for 10 h. Using this mode were prepared polystyrene (PS), polyethylacrylate, (PAE) and copolymer styrene-ethyl acrylate (PAES - molar ratio styrene/ethyl acrylate=1/4).

The prepared polymers were characterized by determining their solutions viscosity, concentration 5% wt. at 30°C using an Ubbelohde viscometer. Polymers have been conditioned by removing the solvent from the polymer solution using a vacuum oven heated to 40°C for 48 h to perform thermal analysis. Thermogravimetric analyzes were performed with TA Q5000 IR (TGA) instrument with a heating rate of 10°C/min, in atmosphere of inert gas (nitrogen) flow 50 mL / min, in the temperature range up to 700°C starting from room temperature.

Nanocomposite materials were obtained by mixing the bitumen with polymer solution for 30 min, followed by the addition in three equal portions the inorganic material and continuing mixing for 60 min. The compositions of prepared samples are presented in table 2.

The obtained composition was poured in trays to allow solvent to evaporate. The samples were pressed in a hydraulic press into a mold at a temperature of 100°C for 5 min. at 160 kgf/cm^2 with 5 min. preheating. After removal from the mold, samples were cut to size needed for DMA. There were recorded DMA profiles for the studied samples: displacement, relaxation modulus, stiffness and strain as function of temperature.

Results and discusions

Polystyren and polyethylacrylate solutions show similar viscosities , while copolymer solution viscosity is approx. 10% higher (table 3).

The TGA and DTGA profiles of polystyrene, polyethylacrylate and copolymer eltylacrylate-styrene are shown in figures 1-3.

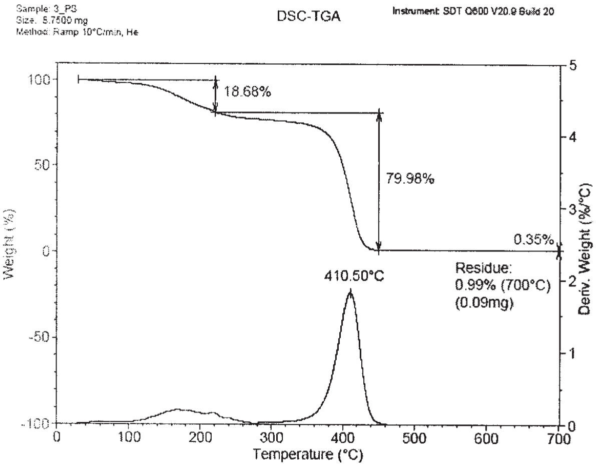

Fig. 1. TGA and DTGA for polystyrene

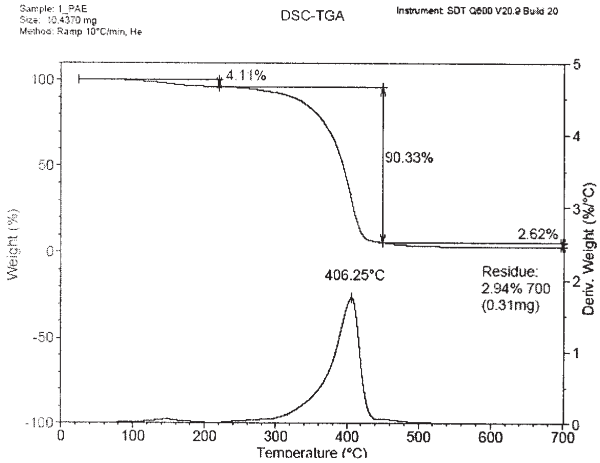

Fig. 2. TGA and DTGA for ethyl-polyacrylate

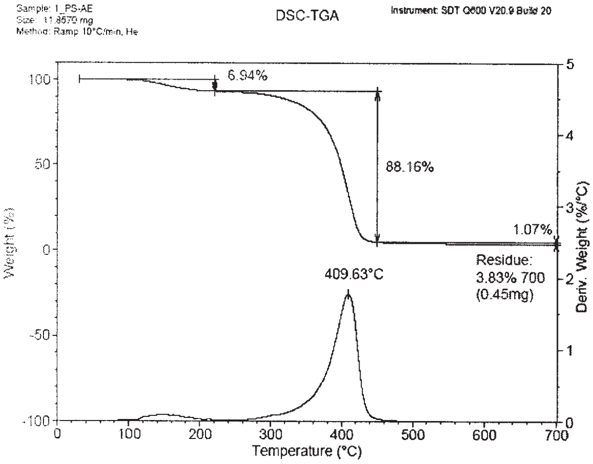

Fig. 3. TGA and DTGA for ethylacrylate- styrene copolymer

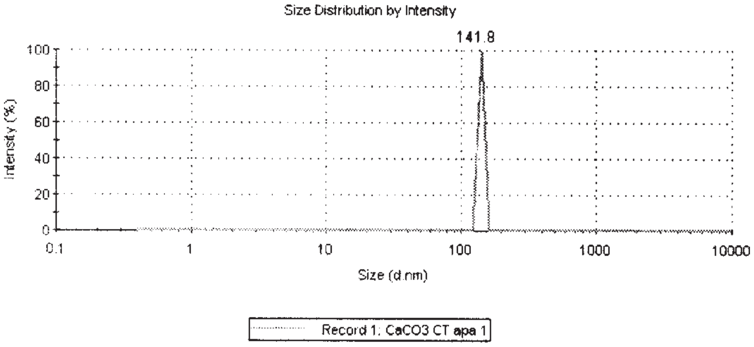

Fig. 4. DLS of calcium- carbonate

DTGA peak of copolymer ethylacrylate-styrene (409.63°C) is between the peak of polyethylacrylate (406.25°C) and polystyrene (410.50°C).

From DLS analysis (fig. 4) results that by grinding in the planetary mill were obtained calcium carbonate nanoparticles with narrow mono-modal particle size distribution and median particle size of 141.8 nm.

The DMA profiles of asphaltic nanocomposites samples are shown in figures 5…12. The sample without polymer (M0) exhibits the highest deformation with temperature increases The analysis of displacement-temperature chart (fig. 5) shows that nanocomposite containing polystyrene (N4) shows the lowest deformation with temperature increases.

Asphalt nanocomposite containing polystyrene (N4) has the highest stiffness and the most pronounced decrease in stiffness with increasing temperature (fig. 7). Sample containing ethyl acrylate-styrene copolymer (N3) shows improved rigidity, compared with the control sample (M0).

In figures 9 ... 12 are presented the DMA results for determinations at three applied forces 0.1N, 0.5N, 1N for each sample.

For the control sample (fig. 9) is noticed pronounced increase of displacement with increasing applied force at temperature increase. Nanocomposite stiffness becomes constant in the temperature range 70 ... 90°C.

Nanocomposite containing ethyl polyacrylate (fig. 10) shows low strain at small forces (0.1N) regardless of temperature and more pronounced strain with increasing forces at temperatures higher than 60°C.

Nanocomposite containing copolymer ethylacrylate-styrene (fig. 11) shows low variation strain at 0.1N in the temperature range studied. Applying forces for 0.5N to 1N result the same deformation until 50°C. At temperatures above 50°C is noticed a pronounced strain with increasing force.

From determinations achieved at three values of applied force is highlighted an increasing of deformation with increasing force, the strain depending on the components nature and concentration. Nanocomposite containing polystyrene showed a different behaviour (fig. 12); thus, with increasing of the force, deformation decreases and the stiffness of the composite increases.

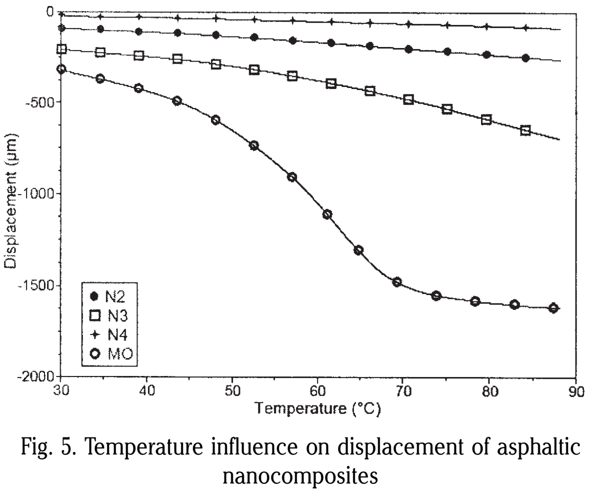

Fig. 5. Temperature influence on displacement of asphaltic nanocomposites

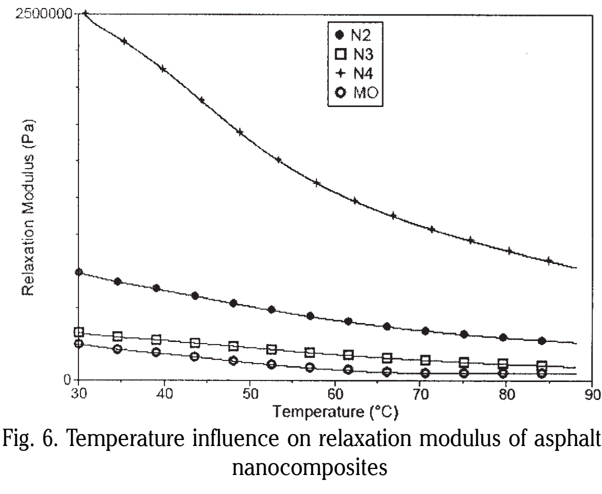

Fig. 6. Temperature influence on relaxation modulus of asphaltic nanocomposites

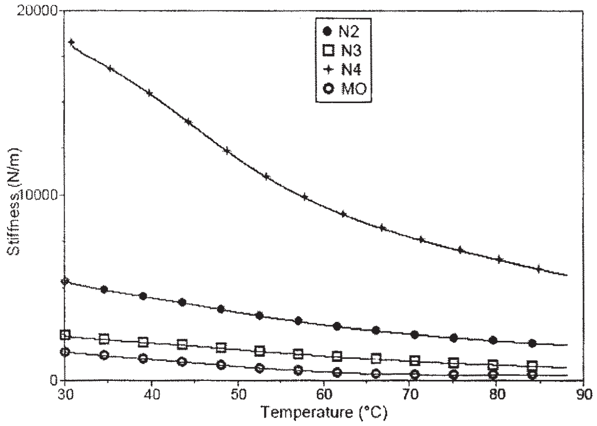

Fig. 7. Temperature influence on stiffness of asphaltic nanocomposites

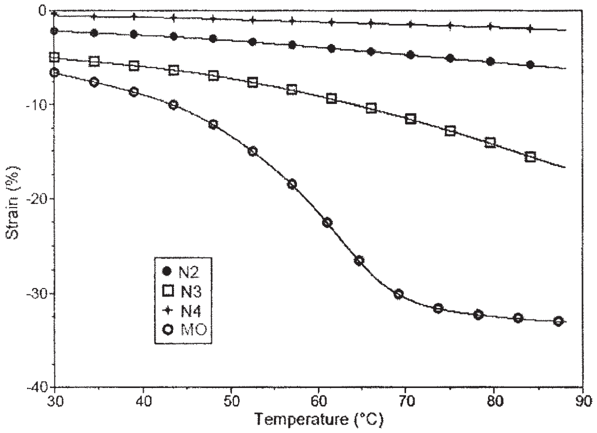

Fig. 8. Temperature influence on strain of asphaltic nanocomposites

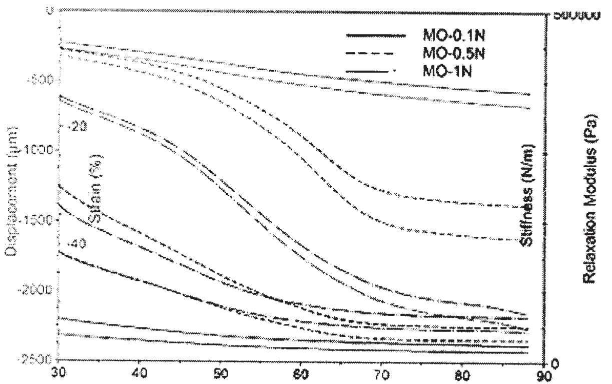

Fig. 9. DMA profiles of control sample at 0.1N, 0.5N, 1N

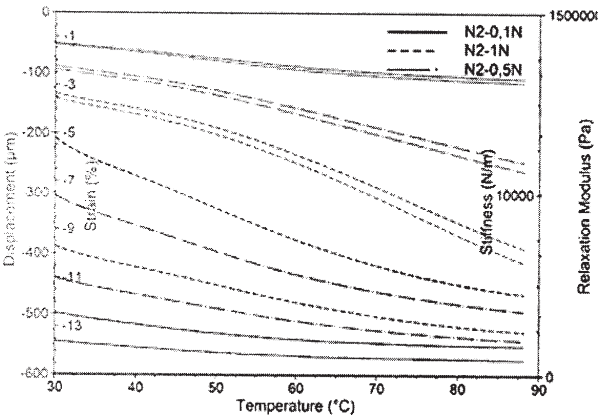

Fig. 10. DMA profiles of nanocomposite with polyethylacrylate at 0.1N, 0.5N, 1N

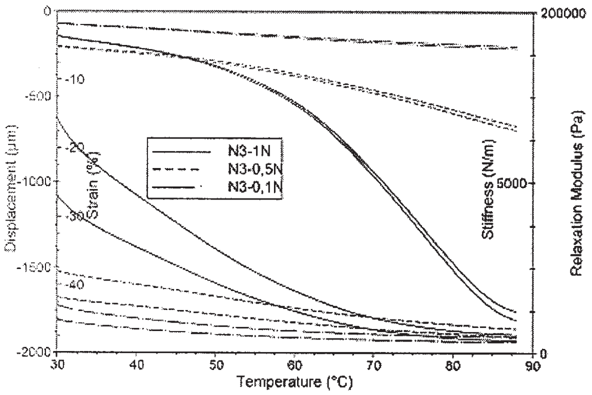

Fig. 11. DMA profiles of nanocomposite with copolymer ethylacrylate styrene at 0.1N, 0.5N, 1N

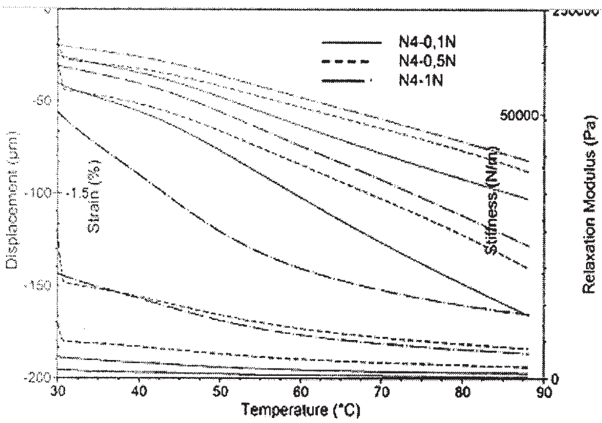

Fig. 12. DMA profiles of nanocomposite with polystyrene at 0.1N, 0.5N, 1N

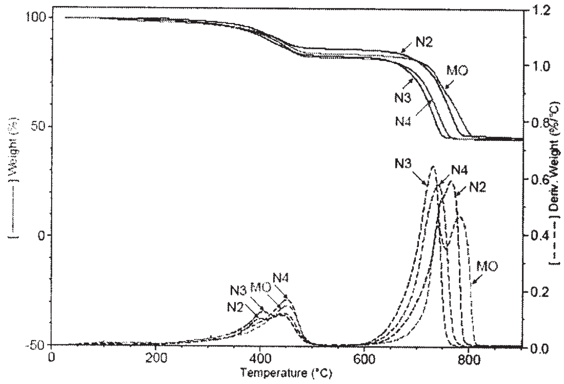

Fig. 13. TGA and DTGA curves for asphalt nanocomposites prepared

Thermogravimetric profiles for asphalt nanocomposites are shown in figure 13.

From thermogravimetric analysis results that N2... N4 asphalt nanocomposites prepared are thermally stable up to a temperature of 200°C. Decomposition of organic components occurs at 480°C, and partial decomposition of inorganic nanocomposites at 760°C.

Conclusions

In this paper was presented a processing technique to make asphalt matrix nanocomposites and focused on comparing the characteristics of materials prepared according to the type and concentration of components used.

Asphalt nanocomposite containing polystyrene has the highest stiffness and the most pronounced decrease in stiffness with increasing temperature. Sample containing ethyl acrylate-styrene copolymer shows improved rigidity, compared with the control sample.

From determinations achieved at three values of force is highlighted increasing deformation with increasing force, the strain depends of the nature and concentration of the components. Nanocomposite containing polystyrene showed a different behaviour, the deformation decreases with increasing force and increases the stiffness of the composite.

Characteristics obtained from tests performed with DMA did not reveal significant differences between polymer nanocomposites.

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