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Physical and Rheological Properties of Asphalts Modified with Polyethylene-co-methylacrylate and Acids

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Abstract

Polymer-modified asphalts are prepared by mixing various amounts of polyethylene-co-methylacrylate (2-8 wt%) and polyphosphoric acid (1-3 wt%) in asphalt (60/70 penetration grade) at 170ₒC for 2 h. The Physical and rheological properties were investigated and compared with the reference asphalt, modified with 4 wt% SBS, styrene butadiene styrene polymer (elastomer). The strength and compatibility of the modified asphalts were increased, demonstrated by the increase of softening point and the decrease in penetration value. The temperature susceptibility was decreased and storage stability was improved. The elastic recovery and complex modulus were increased, indicating the resistance in deformation. The asphalt mixtures containing 4% copolymer and 1% polyphosphoric acid were found to have a the good performance, showing a 12% increase in strength and a 28% increase in compatibility, compared to the reference asphalt. The effects of type (polyphosphoric acid, phosphoric acid or citric acid.) and concentration (1-3 wt%) of acid were studied with asphalt containing 4 wt% polyethylene-co-methylacrylate. The efficiency of acid in improving asphalt's properties are: polyphosphoric acid > phosphoric acid > citric acid.

Keywords: modified asphalts; polyethylene-co-methylacrylate; phosphoric acid; polyphosphoric acid; citric acid

Introduction

Asphalts are widely used in road paving because of their good adhesion to mineral aggregates and their viscoelastic properties. Alathough its true nature is not completely known, it is commonly accepted that asphalt is a colloidal system where asphaltene micelles are peptized by resins in an oily medium (maltenes). With the increased traffic volumes and vehicles loads combined with extreme weather temperatures, which drastically reduce the lifetime of pavements, there is a need to improve conventional asphalt properties, particularly the resistance to rutting (permanent deformation of the pavement in the form of ruts or corrugations) and thermal cracking (fracture of the pavement due to the lack of flexibility at low temperatures). Therefore, asphalt has been developed by adding fillers, fibres, rubber and polymers. Some aspects need to be taken into account, when selecting a polymer as a modifying agent: chemical compatibility with the asphalt, mixing times and temperatures, workability of the final mixture and cost. Polymer-modified asphalts (PMA) have reduced thermal susceptibility and permanent deformation and have enhanced resistance to low-temperature cracking. The properties of PMA depend on the concentration and the type of polymer used. The polymer portion ranges from 2 to 10wt%, mostly 5wt%. Polymers can be grouped into three main categories: thermoplastic elastomers (e.g.SBS copolymers)(1-2) which confer good elastic properties, plastomers (e.g. polypropylene (PP), ethylene vinyl acetate (EVA) and ethylene butyl acrylate (EBA) random copolymers)(3-4) and reactive polymers with maleic anhydride or epoxide functional groups(5-6) which are added to improve rigidity and reduce deformations under load.

The thermo-mechanical characterization of asphalt is based on various empirical tests: penetration, softening point, etc. In 1987, the Strategic Highway Research Program (SHRP) proposed new tests for measuring the physical properties of asphalts that can be related to field performance(7) Asphalt is a Newtonian fluid when mixed with mineral aggregates at high temperatures. The linear viscoelastic region describes the resistance to traffic loading (rutting and cracking due to fatigue). As a result, understanding asphalt rheology is necessary. It was observed that the acid-treated asphalts gave products having better physical and rheological properties and a much better ageing resistance(8) One of the most critical aspects of asphalt modification is storage stability. For reactive polymer modified asphalt, the formation of a chemical bond between polymer and asphalt helps to prevent phase separation.

Ageing is a very complex process in asphalt, it was characterized by measuring physical/rheological properties (e.g. penetration, softening point and viscosity) before and after ageing in the laboratory. As some fillers: fiber, rubber and most polymers occur to be insoluble in the asphalt matrix, resulting in phase separation. Polyethylenes require high energy to disperse. The increase in viscosity make them incompatible with the conventional techniques for making use of these compositions.

This research aimed to study the physical and rheological properties of the asphalt modified with polyethylene-co-methylacrylate (EMA copolymer). This copolymer is thermoplastic, it has a higher heat resistance than EVAs and other polar copolymers whose lower thermal tolerance is often a major handicap when they serve as impact modifiers or as carrier resins for masterbatches. EVA, for example, starts to degrade around 220°C, whereas the EMAs remain stable up to 350°C in air. Morever, it is highly cost effective.

The addition of small quantities of phosphoric acid was reported to improve the ageing resistance of straight run asphalts by reacting with the destabilizing components formed during thermal processes(9) In addition, some dicarboxylic acids were found to have an affect on the rheological properties of straight run asphalts modified with maleic anhydride by forming networks with asphalt by dipole-dipole interaction(8) Therefore, in this work phosphoric acid, polyphosphoric acid and citric acid which is monocarboxylic acid were chosen for investigating the effects of acid.

Experiment

Materials

Asphalt (60/70 penetration grade) was supplied from the Thai Petrochemical Industrial Co., Ltd, styrene butadiene styrene (SBS) polymer from Shell Co., Ltd, polyethylene-co-methylacrylate from DuPont. Polyphosphoric acid (5%), orthophosphoric acid (85 wt%) and citric acid were supplied from Merck and used without further purification.

Preparation of asphalt mixture

Polymer modified asphalts were prepared using a low shear mixer Silverson lab mill, at 170°C and a speed of 1200 rpm. In preparation, 500 g of asphalt was heated to fluid conditions and a preweighed amount of polyethylene-co-methylacrylate(2, 4, 6 or 8 WT% of asphalt) was added gradually. Mixing was then continued at 170°C for 2 h. For acid modified samples, polyphosphoric acid was added (1-3 wt% of asphalt). The stirring was continued for a further 2 h at 170°C. At the end of the mixing, the mixture was transferred to an oven at 170°C. It was poured into molds for rheological testing. The physical properties of the asphalt mixture were investigated by measuring penetration, softening point, elastic recovery, viscosity, storage stability, thin film oven test and dynamic shear rheology. At least two replicates of each test were done.

For other acids (phosphoric acid or citric acid, in 1-3 wt%), the same procedure was performed.

Characterization

The asphalts were characterized according to the standard ASTM procedures. Penetration tests were carried out at 25°C according to ASTM D5-73 using a Stanhope Seta penetrometer. The penetration of a standard needle under a standard load (50 g) was measured during 5 s and reported in tenths of a millimeter. The Softening point temperature (ring and ball test) of asphalts was measured according to ASTM D36-76. In this test, two disks of sample were cast into a shouldered ring, then they were heated at a constant rate (5°C/min) in a water bath using a special apparatus. The Thin Film Oven Test was determined according to ASTM D1754 using Blue M for the age hardening occurring during mixing. Elastic recovery was carried out according to ASTM D5892, (6.2). The viscosity was measured by a Brookfield Thermosel Viscometer model DV-II+, according to ASTM D4402 at elevated temperatures at 135, 145, 155 and 165°C. The shear rate was applied at about 18.6 s, spindle no.21. A factor is applied to the torque dial reading to yield the viscosity of the asphalt in centipoises (cP).

The SHRP test was performed by measuring rheological curves with a Methrom Dynamic shear rheolometer (DSR) according to AASHTO TP5 Standard Test Method. The DSR measures the complex shear modulus (G*) and phase angle (δ) of asphalt mixture at the desired temperature and frequency of loading. Complex shear modulus (G*) can be considered as the total resistance of the mixture to deformation when repeatedly sheared. G* consists of two components: (a) storage modulus G' or the elastic part, and (b) loss modulus W or the viscous part. The parameter phase angle (δ) is used as a measure of the relative elasticity of the asphalt. The testing temperature is 76°C. A small sample of asphalt is placed between two round plates with a 1 mm gap at a frequency of 10 rad/s. The strain and torque were measured and inputted into a computer for calculating complex modulus and phase angle.

Storage stability (toothpaste tube test) was determined according to ASTM D5892, (6.1). The sample was placed in a tube and put into an oven at 163±5°C oven for 48 h. The tube was then cooled to room temperature and stored in a freezer. It was cut into three equal parts. The upper and lower parts were then melted and poured into the rings for the ring and ball softening point test. The difference in °C between the softening point of respective top and bottom samples was reported.

Infrared spectra were recorded using the Fourier-transform infrared spectrometer. Thin films of asphalt samples were prepared by melting 15 mg of sample on a NaCl plate. Another plate was used to distribute the sample to obtain a smooth, even film.

Results and Discussion

Table 1 shows a comparison between the properties of the original asphalt and those of asphalts modified with EMA (4 wt% SBS asphalt was used as a reference).

Table 1. The properties of asphalt and asphalts modified with EMA-A

Properties	A	4% SBS- A	2% EMA-A	4% EMA-A	6% EMA-A	8% EMA-A
Penetration (0.10mm)	65	53	52	51	44	40
Softening point (°C)	49	63	50	55	68	80
Penetration index	0.2	2.5	-1.1	0.0	2.3	3.9
Elastic recovery (%)	ND	85	46	63	80	84
Variation of softening point (°C)	ND	5	5	5	7	8
Retained penetration (%)	76	74	77	73	70	68
Stability ΔT (K)	ND	22	25	25	26	27
Viscosity 135°C	356	878	483	598	987	1685
145°C	248	575	308	390	753	1135
155°C	185	387	215	270	513	808
165$_{o}$C	137	257	163	190	425	583
Dynamic shear modulus (G*/sinδ) (KPa)	ND	4.6	2.6	3.3	5.0	7.3

A = asphalt, SBS= styrene butadiene styrene polymer,
EMA = polyethylene-co-methylacrylate
ND = not determined

Polymer modification of asphalt is dependent on polymer content. As indicated in Table 1, asphalts which were added with polymer (4, 6 and 8 wt%) show comparable properties to the SBS-modified asphalt (which was used as a reference). But at a low polymer content (2-4 wt%), the viscosity of the modified asphalt is too low. The SBS, thermoplastic elastomer gives the flexibility or stretchiness of the asphalt, shown by the higher value of elastic recovery compared to the EMA, plastomer. It is usually found that plastomers will generally stiffen the asphalt to increase its high-temperature performance(1) For surface mixtures, this results in greater resistance to rutting and deformation.

Asphalts can be evaluated with respect to relative temperature susceptibility by using the penetration index which was calculated(8) = $20U-300V/U+30V$, where $U = (\log 4)(TRB-TP)$, $V = (\log 800- \log PT)$, TRB = the value of softening point ($_o$C), TP = the temperature of penetration test ($_o$C), PT = the value of penetration at temperature of penetration test. Penetration index lower than zero indicates high temperature susceptibility.

In order to further improve the properties of the asphalts, the polyphosphoric acid addition was investigated. It was found that some properties were affected, the results are displayed below.

Penetration test and penetration index

The results of the penetration test are shown in Figure 1, the penetration value curves of the asphalts modified with polyphosphoric acid (PPA) and EMA. The values of asphalts modified with EMA decrease with increasing PPA concentration. This indicates an increase in the consistency of asphalt which might be due to two factors. One is the maltene penetrated into EMA and it swells and disperses thoroughly in the asphalt phase. Another factor is the interaction between PPA and polar molecules of asphaltene which makes the molecules of asphaltene larger with a higher molecular weight(1) A lower penetration value means high resistance to deformation in the road pavement.

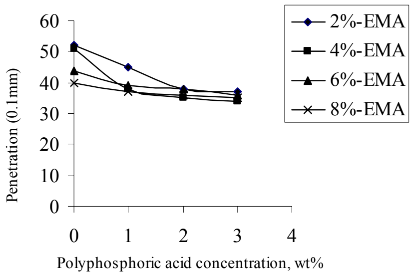


Fig. 1 Effect of EMA and PPA concentration on penetration

In Figure 2, the penetration index of the asphalts modified with EMA and PPA was increased. The greater penetration index, the less temperature sensitive the sample and more rubbery elastic behavior(10) For asphalts with 8 wt% EMA, the value was constant regardless of the acid amount added.

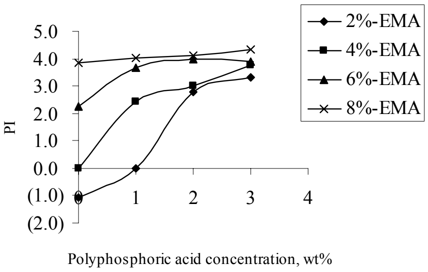


Fig. 2 Effect of EMA and PPA concentration on penetration index

The percentage of retained penetration indicates ageing of the asphalt. It is measured by penetration before and after the thin film oven test: % retained penetration = penetration after TFOT (100)/ penetration before TFOT. It is seen that retained penetration decreases when the concentration of EMA and PPA was increased. For general road pavement aging performance, low percentage of the retained penetration gives a good rutting resistance and also increasing stiffness.

Ring and Ball test

The Ring and Ball test estimates the resistance of asphalt to rutting (permanent deformation). It also shows increases in the softening point of the asphalt after incorporation of polymer. The softening point (shown in Figure 3) increases with increasing EMA and acid contents. This means the modified asphalt has a high temperature susceptibility which can be due to the dispersion of polymer in the asphalt phase and interaction of acid and asphaltene.

In summary, the polyphosphoric acid treatment was responsible for higher softening points and lower penetration values, with an increase in the penetration index of all asphalt samples. These results are consistent with the results reported, that the reaction of phosphorus compounds with asphalts produces a decrease of penetration and an increase of softening point(9)

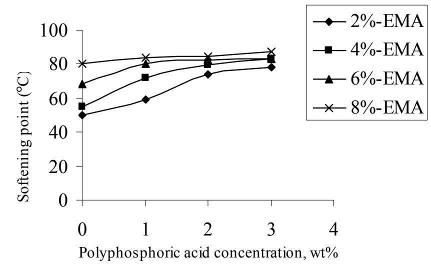


Fig. 3 Effect of EMA and PPA concentration on softening point

Compatibility test

The difference of softening point value before and after performing the Thin Film Oven Test can be used to indicate the compatibility of modified asphalt materials. The variation of softening point values of EMA modified asphalt is shown in Figure 4. The value slightly increases with increasing of EMA concentration. When increasing PPA concentration it dramatically decreases. Since crosslinking between PPA and polymer occurs, the polymer becomes completely networked in asphalt before aging in the Thin Film Oven Test. The variation of softening point of all modified asphalts meet the Thai industrial standard (a range of -4 to +6).

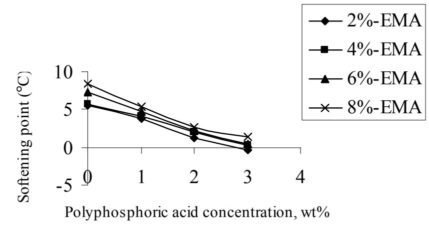


Fig. 4 Effect of EMA and PPA concentration on variation of softening point

Elastic recovery

Figure 5 shows the curve of elastic recovery, it is seen that the elastic recovery values of the modified asphalts increase when increasing EMA and PPA. For a high polymer concentration, it is hard to disperse thoroughly into the asphalt phase due to the limitation of the maltene phase. The increased elasticity of the modified asphalts indicate intermolecular association within the material. The acid groups are able to hydrogen bond to polar groups on asphalt molecules, giving rise to the observed changes in physical properties. The result of this work is similar to the reported result that the elasticity of the modified asphalts with polypropylene and polyphosphoric acid is increased(3) The added acid enhanced the elasticity of the treated samples, suggesting a shift from sol to gel structure(14).

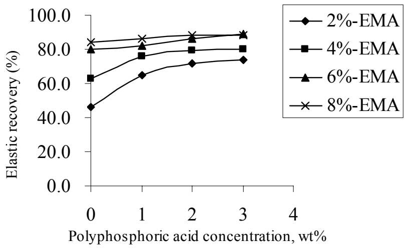


Fig. 5 Effect of EMA and PPA concentration on elastic recovery

Viscosity

The viscosity of asphalt depends on several factors such as amounts of asphaltenes, saturates and resins (and possibly aromatics) and the strength of the interactions between the asphaltenes and resins. Among these variables, the contribution of asphaltenes has been reported to be of greater importance.(11) The viscosity is used to evaluate the proper mixing conditions on hot mixed applications. General specification proper viscosity should not be over 300 cP at mixing temperature.

Figures 6-9 show the Brookfield viscosity of modified asphalts. For the same proportion of asphalt mixture it was found that the temperature increase results, as expected, in a decrease in viscosity. When increasing the EMA concentrations, the curves show an increase in viscosity. During mixing at high temperature, hot asphalt penetrates the polymer particles and the polymer becomes solvated and/or swollen. High viscoelastic properties in the high temperature region are needed for enhanced rutting resistance of binders. The addition of polyphosphoric acid can increase the viscosity due to the interaction between polar molecules of asphalt and acid. It was demonstrated that the reaction of polyphosphoric acid with asphalts can be considered as a chemical oxidation in which the increase in asphaltenes and viscosity are similar to those for blown samples. This involves a change towards a gel structure of the colloidal system.(12) It was reported that an increase in polarity of asphalt due to ester formation was excluded from the 31P NMR spectroscopy result.(9) Instead, in that work, the presence of charge-transfer complexes between phosphorus and the aromatic structures of the asphaltenes was shown, which increased the average molecular weight of the asphaltenes.

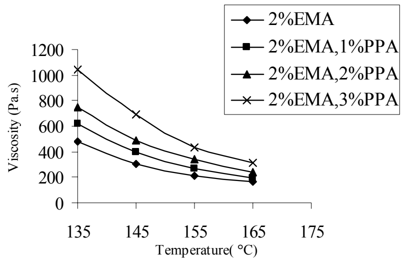


Fig. 6 Effect of EMA and PPA concentration on viscosity, 1

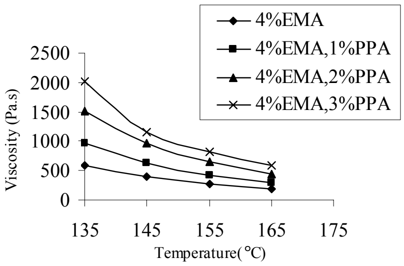
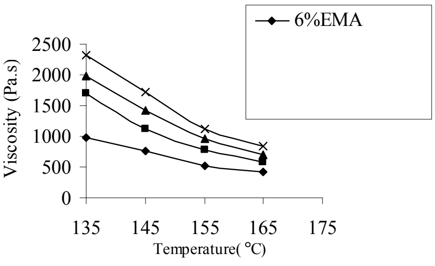


Fig. 7 Effect of EMA and PPA concentration on viscosity, 2



over traditional viscosity and penetration measurements, is that it allows measurement of physical properties at low strains and short loading times (frequencies), close to those likely to be experienced in the field due to traffic. The small deformations involved allow characterization of the material without destruction of internal structure. The parameter, G*/sinδ is for grading asphalt according to their resistance to rutting at high temperatures. The asphalt with the higher value should have more rutting resistance.

Figure 11 shows the dynamic shear modulus (G*/sinδ) of the modified asphalts. When increasing the quantity of acid, the dynamic shear modulus was increased. The performance temperature of asphalt modified with a high amount of polymer (8% EMA) changes dramatically. It behaves more elastically and has a higher stiffness. AChange in size and chemical composition of the asphaltenes could explain the modification of flow properties of the modified asphalts. It was reported that a conversion of aromatics to resins and of resins to asphaltenes occurred. The action of phosphorus compounds on asphalt could be linked to mild oxidation, giving rise to a shift to gel structure.(14) The increase in penetration index also confirms this behavior.

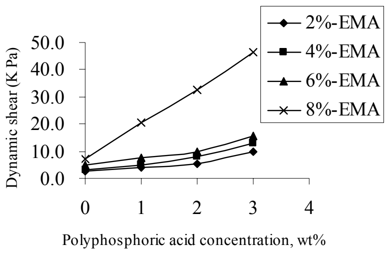


Fig. 11 Effect of EMA and PPA concentration on dynamic shear modulus

From the above investigation of EMA- and acid-modified asphalts, it can be concluded that the EMA and PPA improve some physical properties of the modified asphalt, the resistance to deformation, the consistency, the temperature susceptibility, the elasticity properties, viscosity and storage stability. By adding PPA into the asphalt, the amount of copolymer can be lowered.

Asphalts modified with phosphoric acid or citric acid

Table 2 summarizes the properties of EMA-modified asphalts added with different acids (phosphoric acid, PA and citric acid, CA), compared with one added with polyphosphoric acid (PPA). The results obtained indicate that the asphalt modified with PPA display better rheological properties than the asphalts modified with phosphoric acid and citric acid. It was previously supposed that dicarboxylic acid might link asphalt molecules through hydrogen bonding or dipole-dipole interactions, however, the result obtained using citric acid shows poorer properties compared to the polyphosphoric acid or phosphoric acid, this might be due to the too small molecule size of the citric acid. In the previous report, it was shown that dicarboxylic acids with a long chain length increased the rheological properties of asphalt.(8)

For the effect of acid concentration, it can be seen that the trend of each value measured was similar for each acid, that is, when increasing acid concentration, penetration value, retained penetration and variation of softening point decreased whereas softening point, penetration index, elastic recovery, viscosity, dynamic shear modulus increased. Storage stability was improved. However, it was less noticeable less noticeable degree was resulted for PA and much lesser for CA.

Table 2 Properties of EMA-modified asphalts added with different acids

Properties	%EMA-%PPA			%EMA-%PA			%EMA-%CA		
	4-1	4-2	4-3	4-1	4-2	4-3	4-1	4-2	4-3
Penetration (0.10 mm)	38	35	34	42	36	34	49	47	42
Softening point (°C)	71	79	83	69	76	81	57	60	64
Penetration index	2.4	3.0	3.8	2.4	3.0	3.5	0.4	0.9	1.5
Elastic recovery (%)	76	79	80	63	67	71	61	65	67
Retained penetration	71	71	68	76	75	74	64	66	68
Variation of softening point (°C)	4	2	0	6	5	3	12	12	9
Stability ΔT (K)	20	3	1	21	4	2	23	12	7
Viscosity 135°C	963	1515	2025	673	818	1022	583	593	708
145°C	633	975	1158	423	598	797	395	400	460
155°C	420	650	813	305	413	642	268	273	308
165°C	290	445	598	248	318	467	190	193	213
Dynamic shear modulus (G*/sinδ) (KPa)	5.1	8.1	12.7	5.1	8.7	10.2	3.9	4.0	4.3

FTIR spectra of EMA-modified asphalts added with different acids were shown in Figure 12. and summarized in Table 3.

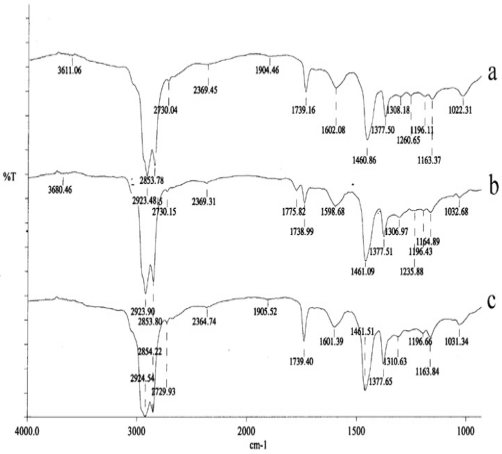


Figure 12 FTIR spectra of EMA-modified asphalts added with different acids (a) PPA, polyphosphoric acid (b) CA, citric acid (c) PA, phosphoric acid

Table 3 IR absorbances of the EMA-modified asphalts added with different acids

vibration	EMA-PPA	EMA-CA	EMA-PA
C-H	2853	2854	2853
C=O	1739	1739	1739
C=C	1602	1599	1601
S=O	1030	1032	1031

The C-H stretching vibrations appear around 2850 cm-1 and C-H deformation vibrations around 1460 cm-1 indicate the presence of alkanes. Peaks at 1739 and 1600 cm-1 show carbonyl (C=O) and C=C stretching vibrations. The peak at 1030 cm-1 is due to sulphoxide formed from the oxidation of sulfide groups, this peak has reduced intensity compared to the unmodified asphalt.(15)

Conclusion

Asphalts modified with polyethylene-co-methylacrylate and acid showed different properties compared to the untreated asphalt. By adding 6 wt% of EMA polymer, a product with the similar characteristics of SBS modified asphalt reference is obtained. Furthermore, the acceptable properties can be obtained by using a smaller amount of EMA polymer (4 wt%) with added acid (1-2%).The softening point and temperature susceptibility of penetration are also improved for practical applications by addition of acid. In terms of the ageing resistance, the treated asphalts were more stable. By adding polyphosphoric acid, the asphalt structure was changed from sol to gel. A greater effect on the rheological properties and on the stability of the treated asphalts was obtained by increasing the quantity of the added acid. Besides the improved properties, the advantage of this treatment is the lower cost. The EMA polymer has a lower cost and better resistance to ageing than SBS.

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