POLYMER MODIFICATIONS IN ASPHALT ROOFING

Qian Qin[1], Denis Tibah[1], Logan Wilks[2], Zhanping You[3]
[1] GAF Materials, Ennis, TX 75119
[2] Cockrell School of Engineering, University of Texas at Austin, Austin, TX 78712
[3]Department of Civil and Environmental Engineering, Michigan Tech University, Houghton, MI 49931

Abstract

Polymers have been widely used in asphalt roofing industries in order to reduce premature failure and improve final performance such as cracking and impact resistance, which is difficult to be achieved by asphalts alone. This work focuses on styrene-butadiene-styrene block copolymer (SBS), styrene-ethylene/butylene-styrene copolymer (SEBS), and Elvaloy modifications on asphalt roof coatings. The thermal susceptibility, low temperature cracking propensity were investigated and compared with unmodified version to present the advantages and challenges of polymer modifications. From the perspective of manufactures, the possibility to double stack roof pallets were estimated based on blocking resistance evaluation via an axial rheological method.

Introduction

Asphalts have been widely used for roofing, road pavement and sealing applications due to its good waterproofing and binding properties. In residential roofing industry, asphalts generally need air blowing process to achieve appropriate softening point and penetration. In addition to softening point and penetration specifications, durable asphalts are desirable in order to produce top quality shingles which can last for a couple of decades under harsh environment. Low quality of raw materials might lead to various distresses or premature failure during shingles' service life. For instance, thermal cracking, aging hardening, temperature susceptibility of shingles can be attributed to asphalt properties. On the other hand, characteristics of asphalts depend on the crude oil sources and refinery processes, which put great limitation for further improvement in their properties. Therefore, an increasing number of modifications have been extensively applied for various purposes [1-4].

Among all kinds of modifiers such as rejuvenators used for recycled roofs [5-6], re-refined engine oil bottoms, polymers have become a major asphalt modification in asphalt residential roofing industry. Polymers that have been used include styrene-butadiene-styrene block copolymers (SBS) [7], styrene – ethylene/butylene-styrene block copolymer (SEBS), Elvaloy, poly (ethylene-co-vinyl acetate) (EVA) [8], polyethylene [9], reclaimed tire rubber. By incorporating appropriate polymer modifiers, improvement of shingle performance can be achieved, which includes but not limited to enhanced impact resistance, aging resistance, less scuffing propensity and less thermal cracking propensity.

In this work, SBS, SEBS and Elvaloy modified asphalt roofing coatings were investigated in terms of thermal stability and low temperature cracking properties. Besides advantages of polymer modifications, the challenge for storing polymer modified shingles is also covered. A rheological tool to evaluate its potential blocking resistance under pallet storage is proposed from the respective of raw material formulation.

Methodology

Materials

A base asphalt with performance grade of PG 70-10 was used as matrix for SBS modifications without air blowing process.

Kraton D1191 SBS triblock copolymer was used to modify the above base asphalt at 5.5% and 8% by weight. The mechanical blending was performed by high shear mixing at temperature not greater than 385 °F for 1 hour until the homogeneous morphology was achieved upon observation via fluorescence microscopy.

Similar blending procedure was applied for Elvaloy and SEBS modifications, which consist 1.5% DuPont Elvaloy AM and 4.5% Kraton G1650 SEBS respectively. It needs to mention that except SBS modifications, all the modifications use different asphalt matrix.

Non-isothermal TGA Measurement

Thermal decomposition of modified materials was evaluated by non-isothermal Thermogravimetric Analysis (TGA) under a nitrogen flow during heating scan from 35 to 600 °C. The heating rate of 20 K/min is used to evaluate thermal stability of those modified materials.

Additionally, decomposition kinetics was performed via TGA at various heating rate of 5, 10, 20, 50 K/min. The iso-conversion method from Ozawa [10, 11] was applied to obtain apparent activation energy of decomposition.

Fourier Transform InfraRed Spectroscopy (FTIR)

FTIR spectra were collected on Thermo Fisher Scientific Nicolet 6700 spectrometer equipped with diamond smart orbit Attenuated total reflectance (ATR). Absorbance spectra were recorded from 4000 to 600 cm^{-1} with an average of 64 scans at 4 cm^{-1} resolution.

Low Temperature Cracking Measurement

Cracking potential of virgin asphalt and modified asphalts were measured by Asphalt Binder Cracking Device under a constant cooling rate according to AASHTO TP 92. The measuring device consists of an environmental chamber, a metal ring of Invar with a very low coefficient of thermal expansion (1.4×10^{-6} /°C) and a silicone mold with a disk-shaped cavity [13]. An electrical strain gauge and a resistive temperature detector (RTD) were glued to the inside of the ring to closely monitor strain and the specimen temperature during cooling. Sample was confined between metal ring and cavity of silicone mold.

The dissimilarity of thermal expansion coefficients of Invar ring and asphalts will cause development of thermal stress in asphalts. Static equilibrium requires that load induced by thermal contraction of the asphalt should be equal in asphalt and metal ring. Based on force balance, the fracture stress can be calculated and used as average tensile strength of asphalt at failure.

Once specimen cracks, the accumulated thermal stress is relieved and the cracking temperature can be determined from strain-temperature curve where a sudden drop of strain occurs.

Rheological Measurement

The axial rheological test with parallel plates of 8 mm diameter was conducted to evaluate blocking resistance of materials. The disk sample with thickness of 2 mm was loaded and kept equilibrium at 50 °C for at least 10min. It is followed by application of contact force of 1 N for 10 seconds before the upper plate is pulled away at a defined speed. The blocking resistance is characterized by the work needed to completely separate sample from itself.

Results and Discussion

Thermal susceptibility

Oxidation hardening has been extensively studied for asphalt materials, which is believed to partially contribute to shingle premature failure under natural weathering condition. Few work was focused on thermal stability in the literature. For thermal susceptible asphalt materials, the loss of volatile molecules would lead to shingle shrinkage and embrittlement, which will exert a negative effect on roof aging process. From the respective of manufacturing and transportation point, the thermal stability needs to be considered to maintain raw materials' quality.

Figure 1 shows the non-isothermal TGA and DTG curves of base materials, SBS triblock polymer and polymer modifications. It was found that thermal susceptibility of SBS modification was slightly affected when compared with base asphalt. Great improvement can be found in Elvaloy modification as suggested by much higher onset decomposition temperature and smaller weight loss than base material. Since manufacturing and raw materials storage temperature are generally kept below 300 °C, the weight loss at that temperature was calculated. Both base asphalt and SBS modifications show about 4.9-5.5% weight loss while Elvaloy modification has negligible decomposition. The excellent thermal stability was presumably due to the stable backbone structure of Elvaloy and possible chemical association between asphalt and Elvaloy. The latter can be suggested by FTIR spectra illustrated in Figure 2.

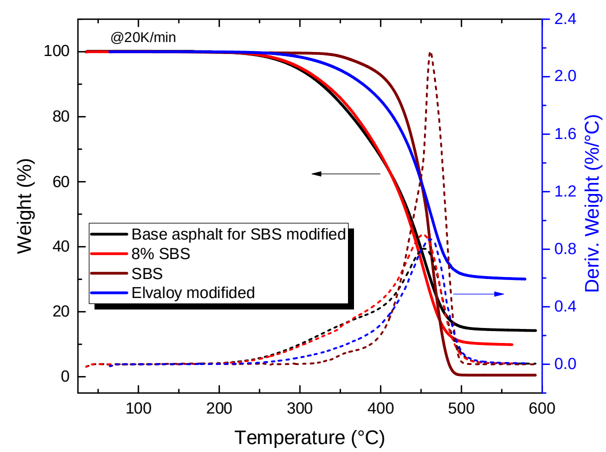

Fig.1. TGA curves and its derivative curves at 20K/min under nitrogen of SBS, base asphalt, SBS modification and Elvaloy modification.

Elvaloy is in ethylene-co-glycidyl methacrylate (GMA)-co-n-butyl acrylate (nBA) terpolymer with characteristic IR absorbance at 1160 cm^{-1}, 840 cm^{-1} and weak shoulder at 911 cm^{-1}. High intensity absorbance at 1160 cm^{-1} is assigned to ether stretching. The latter two peaks are characteristic of epoxy group of glycidyl methacrylate, representing the reactive functionality of Elvaloy. Upon incorporating Elvaloy into asphalt, absence of epoxy IR absorbance suggests ring opening reaction occurs, and thus the possible association or reaction with asphalt, giving rise to enhanced thermal stability of modified material.

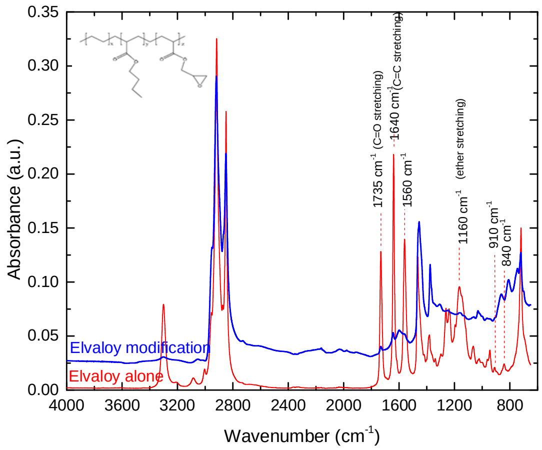

Fig.2 FTIR-ATR spectra of Elvaloy itself and Elvaloy modified asphalt.

The initial thermal decomposition of base asphalt and SBS modification appears very similar, their decomposition kinetics were further studied according to Flynn-Wall-Ozawa method [10, 11] in order to obtain apparent activation energy. The results are tabulated in Table 1. They suggest SBS modified asphalt is more susceptible to thermal decomposition than base asphalt. Distinct difference of activation energy between those two materials can be found at the early stage of decomposition, implying the less thermal stability of SBS modification.

Table 1. Apparent activation energy of thermal decomposition under N_2.

Mass	**Activation Energy of thermal decomposition (KJ/mol)**	
	Base asphalt	**8% SBS**
95%	135.8	107.9
90%	130.2	111.8
85%	129.7	114.9
80%	130.2	118.4
70%	130.5	125.9
60%	138.5	136.5
50%	149.6	148.8
40%	158.6	157.6

Cracking susceptibility at low temperatures

Low temperature thermal cracking is one of the major distresses for shingle roofing at locations where experience cold climates or large rate of temperature drop. Thermal cracking potential is both asphalt and climatic dependence. Under cold climates, thermal contraction occurs in combination with asphalt embrittlement. When thermally induced stress goes beyond the tensile stress of the shingle composite, it is most likely to form cracks. The conventional way to measure low temperature property of asphalts is the determination of creep stiffness or relaxation rate without sample cracking. The method used in this work provides a direct measurement of thermal cracking of asphalt under controlled cooling. The results for different polymer modifications are shown in Figure 3 and Table 2.

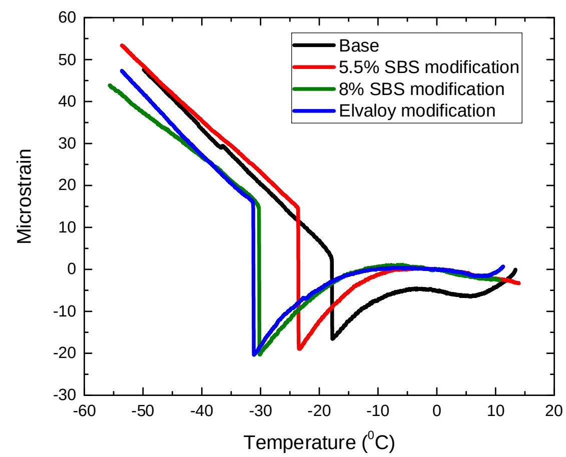

Fig. 3. Strain change with temperature during cooling for base asphalt and SBS, Elvaloy modifications (4 runs for each sample were tested and one of them is randomly selected here)

Table 2. Cracking properties of asphalt, SBS modifications and Elvaloy modification.

Samples	Cracking Temp. (°C)	Fracture stress (MPa)
Base	-18.1±0.5	2.7±0.7
5.5% SBS modification	-23.7±1.3	3.8±2.2
8% SBS modification	-31.3±1.5	4.8±2.3
Elvaloy modification	-30.1±1.4	4.0±1.5

The results suggest either SBS or Elvaloy modifications can offer greatly enhanced low temperature properties than unmodified asphalt. By incorporating those polymers, improved cracking temperature can be achieved in spite of relatively large variability in fracture stress. The presence of rubbery mid-block butadiene and flexible side chain of Elvaloy provide good flexibility to the asphalt matrix, leading to the enhanced cracking resistance.

Blocking potential during storage

Due to the limited space to store inventory shingles for roofing manufactures, double-stacking of pallets is preferred for non-impact resistant grade products. It requires good blocking or fusion resistance in order to avoid being stick to itself or to adjacent shingles. No apparent blocking issue has been found for shingles made from unmodified asphalt coatings. However, polymer modified coatings are likely to have poor blocking resistance, which prevents from being double stacked. Therefore, for non-impact resistant polymer modified shingles, it is necessary to estimate blocking potential of coatings during formulation stage.

In this work, axial probe test described in Methodology session is used to predict blocking potential for different modifications. The results are presented in Figure 4 & 5.

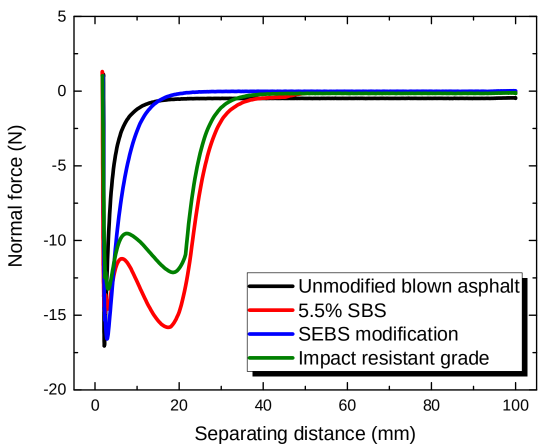

Fig. 4 Normal force vs. separating distance after 1N contact force for 10 s at 50 °C.

In order to ease comparison, unmodified asphalt and SBS modified impact resistant grade material are included. As mentioned above, impact resistance grade shingles are generally stored in single pallet form. The reason to include unmodified material is to provide a reference for double stacking. Therefore, those two samples can be used as the baseline regarding the suitability of new formulations for double-stacking or not.

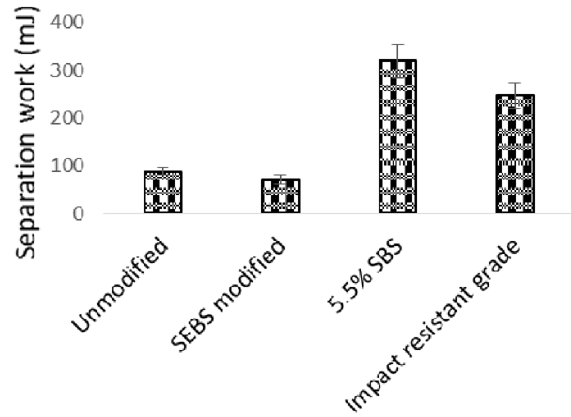

Fig.5. Total work or energy required for sample separation.

Figure 4 suggest the difference of anti-blocking response of SBS modification from unmodified and SEBS modified asphalts. For the latter materials, there is only one maximum in normal force during separating profile whereas two maximums are found for SBS modifications. It might associated with different anti-blocking mechanisms which need further investigation.

Although the maximum force to overcome adhesion for unmodified and SEBS modified materials are slightly greater than that for SBS modification, unmodified and SEBS modified asphalt coatings require much less energy to resist adhesion as indicated in Figure 5. This finding suggests less blocking resistant for SBS modification. In addition, the 5.5% SBS modification formulation appears to need larger separation energy than impact resistance sample, implying it is not suitable for double-stacking. Further formulation modification is needed to avoid this issue. It is worth mentioning the low temperature cracking property and blocking resistance have to be compromised with each other in order to achieve optimum overall performance.

Conclusions

During in-service life, asphalt roofs are submitted to both thermal and thermal oxidation processes. The thermal susceptibility of SBS, Elvaloy modified asphalts were evaluated by non-isothermal TGA. Elvaloy modifications exhibit excellent thermal stability when compared with SBS modifications and base asphalt. It was attributed to its stable backbone structure and potential chemical association between asphalt and epoxy functional group in glycidyl methacrylate block of Elvaloy as implied by FTIR. SBS modifications show similar thermal decomposition behavior as base asphalt. However, after TGA kinetic analysis, smaller apparent activation energy at early stage was found for SBS modification, suggesting slightly more thermal susceptible of SBS modification.

Low temperature cracking propensity has been a great concern and an important performance consideration for asphalt roofs. This work employs a direct cracking measurement instead of taking the traditional non-crack stiffness or relaxation rate method. Results indicate a dramatic improvement for asphalts upon incorporating either SBS or Elvaloy due to the flexible rubbery block or side chains. In order to avoid the self-sticking of asphalt shingles at storage condition, the blocking resistance of asphalt coatings are evaluated in order to seek the possibility of double stacking of shingle pallets. It was found SEBS is suitable for double stacking, however, SBS modification studied in this work is not recommended for double stacking because of poor blocking resistance of raw materials.

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