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Study of Rheological and Mechanical Properties of Bitumen Blended with Two Alpha Phases of Polyamide

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Abstract: The effect of α phase polyamide (PA6)on the rheological properties, Young Modulus and the thermal expansion coefficient of two blends groups (bitumen-polyamide) were tested. The first group was for bitumen-PA6 blends and the second group for bitumen blended with polymer resulted from the crystallization of PA6-formic acid solution in water(PAFW).The obtained results proved that adding both types of polyamide has led to a rise in toughness and softening point temperature while the penetration Index approached -3 after adding the polyamide. So, all these changes make bitumen-polyamide blends more suitable for use in hot climate regions. The blends properties were explained according to the reaction that takes place between the polyamide and the epoxy present in the bitumen at temperatures exceeding 200 ° C. However, these changes were more pronounced for mixtures that contained PAFW due to their porous morphological structure, which increased the reaction and made the blends more miscibility even when the addition ratio reached to4%. In the case of PA6, when its ratio in bitumen increased by more than 1%, the unreacted portion of this polymer with epoxy would be mere filler in the mixtures and it did not appear to have a pronounced effect on the properties of bitumen.
Key words: polyamide, bitumen, young modulus, Penetration index.

INTRODUCTION

Bitumen is a complex compound consisting of several polymers of different molecular weights, in addition to a small percentage of fatty oils and solid compounds [1, 2]. The polymer, which makes up the largest part of the bitumen, is generally composed of polarized resin particles called (maltenes) which are responsible for the adhesive strength of the bitumen. The other part is asphalten, which has a high molecular weight and is responsible for the rheological and mechanical properties of bitumen[3].

Previous research has contributed to improving the performance of asphalt mixtures in order to be more appropriate to working conditions in traffic roads or in construction applications. These modifications and improvements in the properties of the bitumen depende on their nature, the chemistry of the constituent polymers, the additive ratio in the mixture, the chemical compatibility, the molecular weight, the size of the particles, as well as the mixing conditions that play an important role in determining the modified asphalt[4,5].The addition of thermoplastic polymers in bitumen such as polystyrene, polyisobutylene, polyethylene , polypropylene has given acceptable results of viscus behavior at certain temperatures, as this was reflected positively on the amount of rutting resistance as well as on the permanent deformation resulting from the high loads on asphalt but these additives have weakened the crack resistance of asphalt at low temperatures [6,7].However, there are many saturated aliphatic polymers that are insoluble in bitumen even at high temperatures, so the mixture will be of two heterogeneous phases, so it will not have a positive effect on the properties of bitumen, especially when they are added in low concentrations[8, 9].

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The ratio of the added polymers depends on their ability to swell with the maltene phase in the bitumen while the unreacted polymer will act as a filler to make the bitumen a heterogeneous system with no significant effect on the rheological properties. In other words، the minimum quantitative of polymer to ensure the formation of continuous bitumen phase depends on the ability of polymer to swell with maltene [10].Therefore, the added polymeric portion will play the major role in enhancing the mechanical and rheological properties of the mixture [6, 11].

In this work, the effect of blending two types of α phase polyamide with bitumen on the rheological, mechanical properties and the thermal expansion coefficient was evaluated.

EXPERIMENTAL WORK

Two blends groups of polyamide - bitumen (grid 40-50 from Al-Nasiriyah liquidator, Iraq) samples were prepared, the first group were prepared by adding neat Polyamide (PA6) of viscosity-average molecular weight of 50 kDa(Alyaf Company), and the second, by adding the polyamide obtained from its crystallization process of solution polyamide - formic acid with water (PAFW). The (PAFW) was prepared by dissolved 6 gm of PA6 in 50 mL Formic acid in glass flask at 40 C°, then mixed at 200 cycle/ min by electric stirrer for 10 minutes.After the solution was cooleddown to the laboratory temperature, quietly poured into a glass flask with 200 ml of distilled water, then a white and swollen polymer quickly formed.This polymeric sample was separated from the water by filter paper and then dried in the oven at 40 ° C for 4 hours. After drying, the solid and brittle polymer been ground by a hand mill to obtain 50-100 micrometer of polymer powder. The polymer-bitumen mixtures were prepared by adding PA6 to the first group and PAFW to the second group with ratio (0,1,2,3,4,5)% of polyamide in bitumen.The blended samples was prepared by heating the mixtures at 120 C° by hot plate and then poured in aluminum flasksand mixed by electric stirrer with 400 cycle/min speed at 205 C° for 15 minutes. The samples were left at the laboratory temperature for 72 hours to ensure their stability before testing.

Differential scanning calorimetry (DSC) of samples was performed by DSC-60 system Shimadzu company- Japan. Thermal expansion coefficients results was obtained by Thermo-mechanical Analysis (TMA), model PT1000, European. The rheological tests were carried out by using the ring- ball apparatus and Penetrometer, UTEST, Turkey.

RESULTS AND DISCUSSION

The thermal behavior of the polyamide samples by Differential scanning calorimetry tests (DSC) showes a clear variation in the glass temperature transformation Tg as well as in the form of the melting peaks, Fig.1. The value of T_g for neat polyamide(PA6) increased from 63 °C to 75 °C of the polyamide obtained from the reaction of the polyamide solution in the formic acid with water (PAFW),this change confirms that PAFW has a higher crystallization degree, because the presence of the amorphous phase reduces the free energy needed for the glass transition. The two endothermic peaks at 204 °C and 206 °C are the melting temperatures of a α phase for both PAFW and PA6, respectively[12,13], while the two peaks of PA6, at 187 and 194°C were results of the thermal re-crystallization of γ in mesophase to more stable α phase , this, usually occurs due to the tendency of the crystal system to remove the internal residual stress which results by the cooling or the casting during the polymers manufacture process [14] .

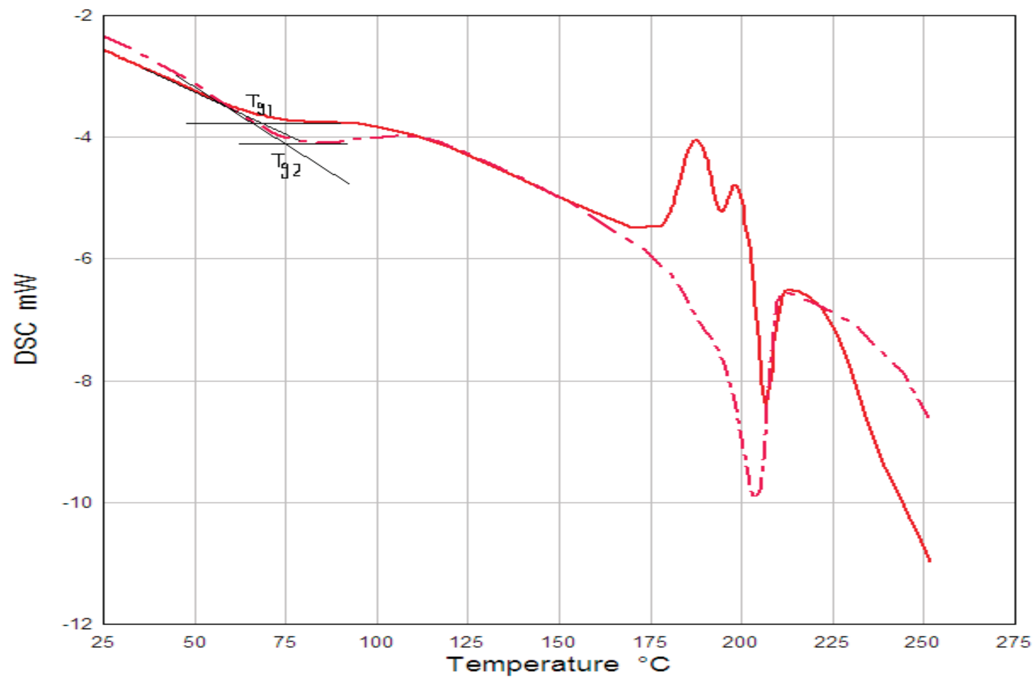

FIGURE 1. DCS curves of PA6 contentious line and PAFW dashed line.

Bitumen is a viscous material, therefore, its thermal expansion coefficient and mechanical properties cannot be directly measured by the thermo-mechanical analysis (TMA) technique. To use this technique for this purpose, so, a crucible of Pyrex was made in the form of a cylinder with an inner diameter of 5 mm and an outer diameter of 8 mm and opened from the one side and the other side was closed by epoxy with a thickness of 1.37 mm as in theFig.2 below.

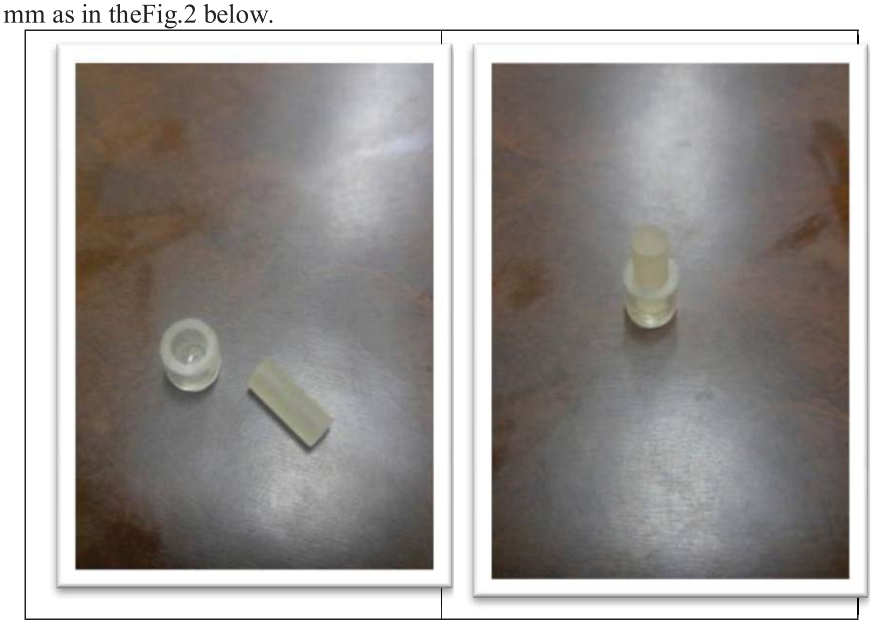

FIGURE 2. The crucible made of Pyrex and the epoxy rod, for thermal expansion coefficients measurements of bitumen samples.

The pressure on the sample during the test was by a rod made of epoxy, 15 mm in length and 4.9 mm in diameter to ensure its vertical movement inside the crucible. A sample without bitumen was first examined, i.e., the thermal expansion coefficient values of this rod and the epoxy base subtracted from the results of the tests obtained when presence of bitumen samples in the crucible.

The samples were melted to 100 ° C, then carefully inserted into the crucibles using small sticks of wood to avoid any air bubbles in the samples, and then the thickness of the samples was calculated before the test.

The effect of polyamide on the thermal expansion coefficients (α) in its blends with bitumen was evident, Fig. 3. It was clearly observed thatα values decrease from 143 to less than 125 / °C with an increase in the ratio of both PA6 and PAFW in bitumen, but this effect was lower when the ratio was less than 1%.

Young Modulus (E') values were also affected with the addition of the polymer to bitumen Fig.4. The relationship curves between E' and the temperature showed that there is a noticeable increase in its values, as this modulus rose to almost three times when adding the PA6 as well as to the twice for PAFW at 25° C. The rapid slope that occurred in these modulus with a rise in temperature is expected because the bitumen loses many of its mechanical properties as the temperature approaches the softening point due to the weakening of the bonding forces between the molecules as well as a loss in the modulus which happens of elasticity for polyamide between the 0-50° C, which they leads to less its toughness and rise the ductility, when exposed to external forces [15]. It is worth noting that the values of this coefficient become negative after the temperature becomes higher than 45 , 40° and 46° C for each 1% and 4% of PA6 and 4% PAFW, respectively, While its values remain positive and higher than the neat bitumen when adding 1% of PAFW.

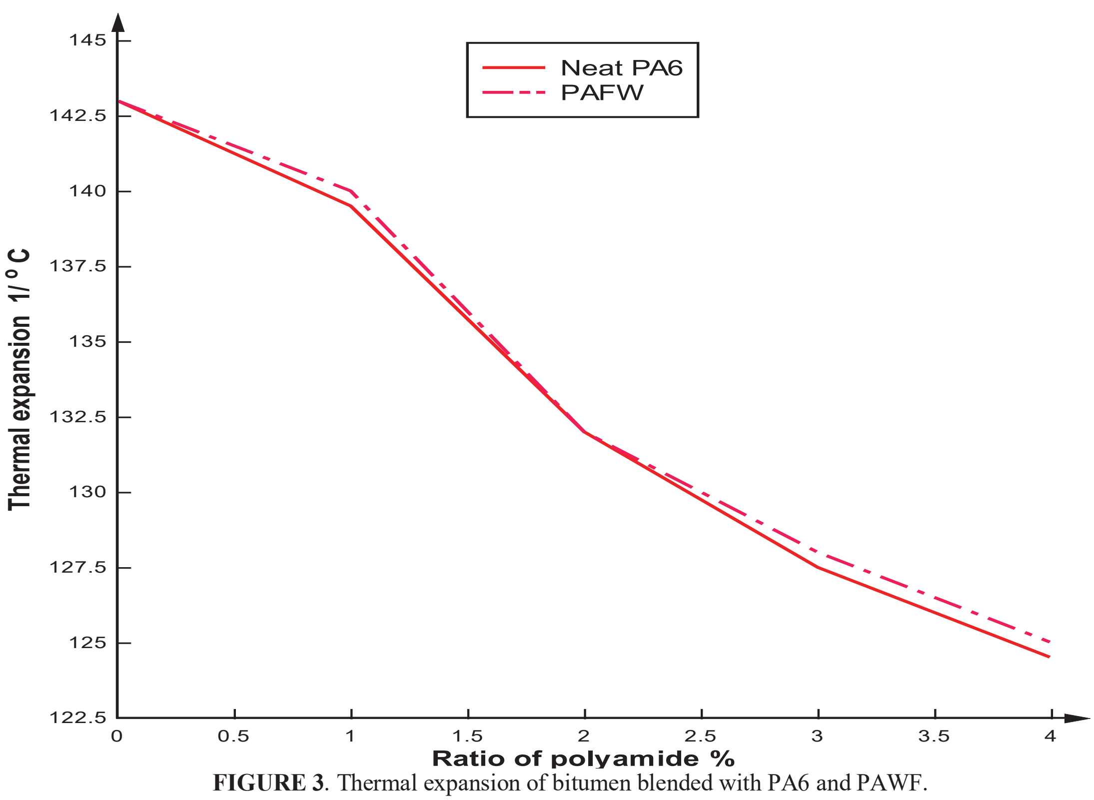

FIGURE 3. Thermal expansion of bitumen blended with PA6 and PAWF.

This results of the bitumen blended with polyamide have identical with the results of previous researches, that added different polymers to the bitumen, where these mechanical changes had attributed to the ability of low percentage polymers to swell in maltene molecules of the bitumen and formation of continuous blended phase[10.11]. The miscibility of blended polymers depends on ability of these polymer to interpretations for each other's. Therefore, the appearance of negative values of the PA6 and 4% PAFW mixture indicates that a portion of the polyamide remains without any physical or chemical change and will be as a filler in the binary polymer system. Accordingly, when the temperature rises, the polyamide will be more ductile, which makes the blend less responsive to the applied elastic force, i.e. it becomes more ductile and deformable [6].

It is important to note that the modulus values remained positive for the mixture containing 1% of PAFW in bitumen despite the rise in temperature to 47 ° C. To understand this single behavior of this ratio, the results of the rheological examinations should be noted as they are shown in the table (1).

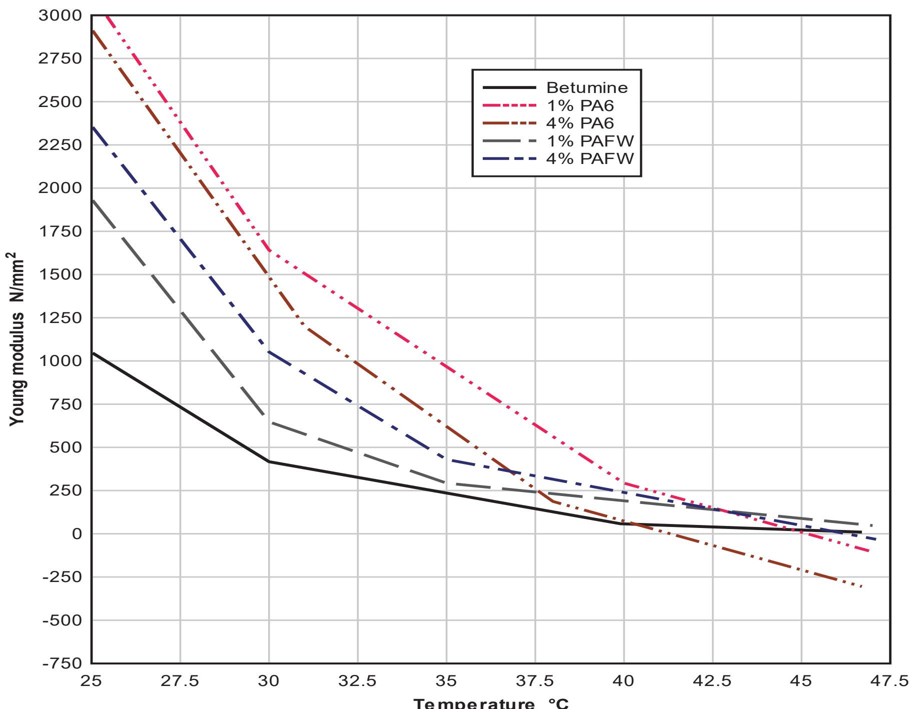

FIGURE 4. Young modulus of bitumen blended with PA6 and PAFW.

The softening point increased to 56°C with the addition of PAFW, but in the case of adding PA6 to the bitumen declined again when its ratio is more than 1% to the bitumen. The penetration test showed a clear improvement in the polyamide-bitumen blends but it was noted that adding PAFW gave better values than PA6 in ratios that exceeded 1%.

TABLE 1. Rheological properties of PA6 and PAFW

Ratio of polyamide	Neat bitumen	1% PA6	2% PA6	3% PA6	%4 PA6	1% PAFW	2% PAFW	3% PAFW	4% PAF W
Softening point °C	51	52.5	52	51.5	51.5	55	55.5	55.5	56
Penetration mm at 25°C	45	13.9	15.3	15.5	16	12.4	12	10.1	8.9
Penetration Index	-1.2	-2.85	-2.83	-3	-2.23	-2.6	-2.92	-2.84	-2.94

The mechanical and rheological tests have proven that adding PAFW has a continuous effect with an increase its ratio in blends, while the increasePA6 ratio more than 1% has no distinctive effect on physical behavior of blends. The difference in behavior of these two phases of polyamide – bitumen blends can be explained depending on the results of previous researches witch confirmed that there are a chemical reactions occurs between the polyamide hydrogen and the epoxy ring or its oxygen when the temperature of the mixing exceeds 200 ° C, and forming a thermosetting complex compounds, these reactions are the responsible of the miscibility improvement of bitumen-polyamide blend [16, 17].Another previous study diagnosed, the crystalline growth of a solution (polyamide - formic acid) in water produces polyamide films containing microscopic pores, while the PA6 surface obtained from the melt -cast process does not contain pore [18]. That means polyamide-epoxy resin reactions in the bitumen and the surface morphology difference between PA6 and PAFW were the reasons of differences of mechanical and rheological properties of bitumen blends.

The penetration index (PI) values for the prepared sblends obtained by using the equation below [19]:

$$\mathrm{PI} = \frac{1952 - 500\ \mathrm{Log\ Penetration} - 20\ \mathrm{softening\ point}}{50\mathrm{Log\ Penetration} - \mathrm{softening\ point} - 120}$$

Where values of the softening point and penetration at a temperature of 25 ° C were compensated from Table (1). It can be clearly observed that PI values were reduced to be more negative and near-3 when adding both polyamides. However, it is worth noting that the addition of PA6 more than 3% has made the values decrease negatively, this concentration can be considered critical and that the increase in the polymer will act as an unreacted filling with the bitumen, while adding PAWF has strengthened this reaction even when the ratio has reached 4%.

The penetration index is an important specification for choosing bitumen type when used in paving traffic roads. Their values are usually between -3 and +7, when bitumen is used for paving roads in cold climatic zones it should be close to +7, while its value should approach -3 in hot climates [20].On this basis, the PI results obtained from the addition of low percentages of polyamide to the bitumen are considered a good enhancer in the bitumen specification when used in the hot climate regions.

CONCLUSIONS

The interaction between the micro-pores in PAWF morphology and the epoxy in the bitumen made the mixtures more miscible, therefore, Young Modules and the softening point temperature of these blends possess higher and more stable values at temperatures up to 45 ° C. On the other hand, the weakness of the PA6 reaction with epoxy makes it a mere thermoplastic filler in the bitumen when its ratio increases and therefore, it had no apparent effect on the properties of the blends. Accordingly, the results of the rheological properties, Young modules and the thermal expansion coefficient of the bitumen showed an improvement in their value with the addition up to 4% weight ratios of PAWF, while the addition of PA6 to bitumen decreased again when the rate of addition was more than 1% in the blends.

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