

12-1-2013

Section: Chemistry

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How to Cite This Article

ELKADY, G.; EL-SHAFIE, M.; FAREED, USAMA; ELNAGGAR, ELSAYED; SALEH, A.; and SHOHIDE, MOSTAFA (2013) "SYNTHESIS AND EVALUATION OF NOVEL BITUMINOUS MATERIALS FOR USING IT IN CONSTRUCTION APPLICATIONS," *Al-Azhar Bulletin of Science*: Vol. 24: Iss. 2, Article 12.
DOI: <https://doi.org/10.21608/absb.2013.6414>

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Abstract

Recently, the application of asphalt in coating purposes presented in different ways. On the other hand polymers are used to improve the properties of asphalt to use in coating purpose. Although asphalt has low cost, high cohesive nature, rheological properties and high thermal resistance but it is not practically used in coating, this because the long curing time of asphalt on the surface of the substrate which inappropriate industrially, also asphalt need to additives to improve resistance to chemicals. So the aim of this research is to use polyurethane to improve asphalt properties to produce low cost, high qualified asphaltic materials for coating application. To achieve this aim, after characterization of raw materials by FT-IR for both asphalt and polyol (caster oil), determination of OH number for caster oil, caster oil has mixed with asphalt of type 60/70 in different percentages as 5, 10, 15, 20&25 % by the total weight of mixture. After determining the OH number, these samples act as polyol to prepare asphalt-PUR materials with different ratios of isocyanate material (MDI) to polyol material (caster oil). The ratios were (1.1:1, 1.2:1, 1.3:1, 1.4:1). After adding the equivalent amounts of MDI, different samples of asphalt-polyurethane coating materials were obtained. These samples were applied as coating materials on the surface of carbon steel, and then visually, mechanically, chemically tested. The results revealed that the 1.3:1 NCO/OH is the best ratio.

Keywords: asphalt, polyurethane, polymer modified asphalt, asphalt polyurethane coating,

1. Introduction

Asphalt material is a complex mixture of four main families of compounds, referred to as SARAs fractions (saturates, aromatics, resins, and asphaltenes)^(1, 2). It can be considered as a colloidal system in which micells of high molecular weight organic molecules (asphaltenes), surrounded by a shell of resins, are dispersed in an oily phase (maltenes), consisting of low molecular weight saturated and aromatic hydrocarbons together with the remaining resins⁽³⁻⁵⁾. The composition of asphalt varies with the source of crude oil and the method of manufacturing^(6,7). Asphaltenes represent the heaviest part of asphalt, with hydrogen-to-carbon ratios low as 1.15 (per mole)⁽⁸⁾. Thus, bitumen composition and temperature strongly influence the mechanical properties and microstructure of bitumen⁽⁵⁾. Asphalt's properties that make it particularly suitable for use in different purposes are versatility, stability, flexibility, durability and acceptability (inert in the presence of water)^(9,10). Recently, polymer-modified asphalt increases the level of field performance of asphalt. The polymer should form a continuous network within the asphalt, for this reason, the polymer and asphalt need to be compatible. Among these polymers; polyurethane is one of the most popular modifiers. It is used in modification the asphalt for using in coating applications. However, polyurethanes include polymers containing a significant number of urethane groups, regardless of the composition of the rest of

the molecule⁽¹¹⁾. For example polyurethane (PUR) modifiers, especially prepolymers, used for asphalt modification to be used as coating layers comprising from 5 to 25 % by weight of polyurethane prepolymer. The prepolymer/bitumen ratio is from 30/70 to 70/30. This mix has more both the creep and solvent resistance comparing to polymers that prepared by conventional methods⁽¹²⁾.

Also a polyurethane modified bitumen composition produced for coating purpose. The composition includes bitumen; a minor modifying amount of polyurethane prepared by the reaction of polyisocyanate and polybutadiene; a tackifier; and a filler material⁽¹³⁾. However, polyurethane is used for asphalt modification to produce new compounds suitable for use in different applications^(14, 22).

2. Experimental Work

2.1. Materials used

- a- Asphalt cement of penetration grade 60/70 was obtained from Al Nasr for petroleum Co. in Suez city, Egypt.
- b- Laboratory synthesized polyurethane composed of:
 - 1) Castor oil (commercial grade) produced by Algomhuria company for drugs and chemicals, Cairo city, Egypt.
 - 2) Methylene diisocyanate (MDI) obtained from DOW Chemical Company.
- c- Carbon steel specimens of grade BG37 were obtained from Belayim Petroleum Company, Port-Fouad station.
- d- Miscellaneous:
 - 1) Pyridine (commercial grade) obtained from Algomhuria Company for drugs and chemicals, Cairo, Egypt.
 - 2) Acetic anhydride, Benzene, Potassium hydroxide, cyclohexane, Sodium hydroxide, hydrochloric acid, sulfuric acid, nitric acid, acetic acid and sodium chloride were obtained from El-Nasr pharmaceutical company, Cairo, Egypt.

2.2. Experimental Procedure

2.2.1. Characteristics of raw materials

2.2.1.1. Characteristics of asphaltic material

A. Physical characteristics⁽²³⁾

The virgin asphalt sample was characterized by conventional asphalt tests as penetration test (ASTM D5), softening point test (ASTM D36), kinematic viscosity test (ASTM D2170) and chemical constituents (ASTM D 3297).

B. Infrared spectroscopic analysis

FTIR infrared spectroscopy (ASTM E1252) was used to determine the functional groups in both asphalt and castor oil. The IR-spectra was conducted using ATI Mattson-Genesis Series. The wave number and intensities of the IR bands of the different types of the functional groups were determined in a range of 4000-1500cm⁻¹. The model of used instrument is (NICOLET IS 10).

2.2.1.2. Characteristics of castor oil

The hydroxyl group content for castor oil was determined according to (ASTM D4274). Based on test result, this content was found to be 180.

The chemical formula of castor oil is shown in figures (1).

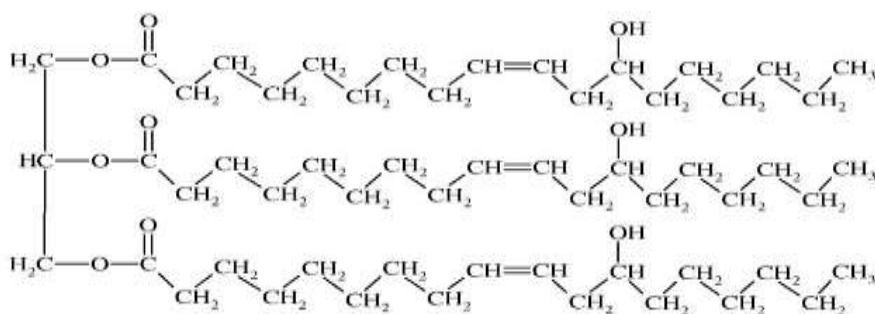


Figure (1): Chemical formula of castor oil

2.2.2. Preparation of polyurethane coating^(24, 25)

In this step, the NCO/OH ratio was chosen to be ranging from 1.0 to 1.5. The calculated amount of castor oil (according to the desired NCO/OH ratio) was added to a fixed chosen amount of MDI (equals 10g) with stirring. The mixture was then heated to a temperature of $60 \pm 5^\circ\text{C}$ with stirring for 30 minutes. The used weights of castor oil according to chosen NCO/OH ratio are illustrated in table (1).

Table (1): Required weights of Castor Oil for polyurethane polymer preparation

NCO/OH Ratio	Wt. Of MDI(g)	WT. Of C.O*(g)
1.0	10	24.93
1.1	10	22.66
1.2	10	20.77
1.3	10	19.17
1.4	10	17.80
1.5	10	16.62

NB: (*): castor oil

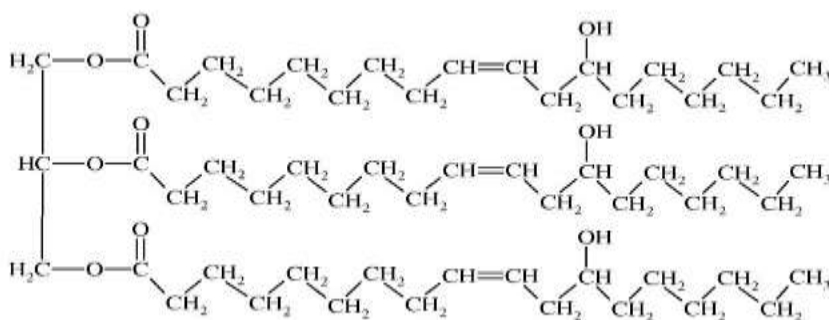
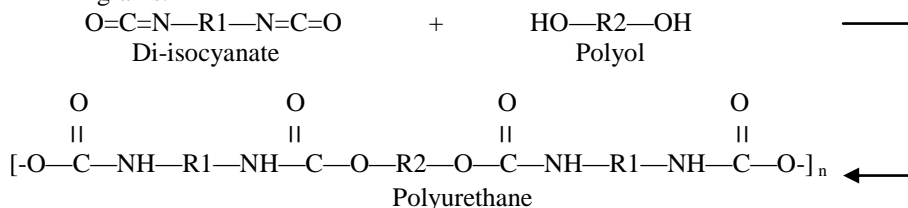
The prepared polyurethane samples were used in coating of carbon steel specimens and left for complete curing in air. The steel specimens were cut as regular edged cuboids with dimensions nearly of $8 \times 15 \times 0.5$ cm. Each specimen was cleaned and polished with emery paper in one side before applying the coatings.

The polyurethane preparation calculation in as follows:-

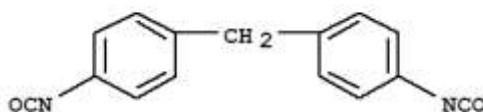
- Number of hydroxyl groups in polyol (caster oil) = 180
- Hydroxyl equivalent weight for castor oil = $56100/180 = 311.66$
- The equivalent NCO groups is calculated from MDI of molecular weight = 250 as follows:
 - Equivalent weight for MDI = $250/2 = 125$
 - 10g from MDI contain $10/125 = 0.08$ equivalent NCO group.
 - In order to obtain polyurethane of ratio 1.2 (i.e. NCO/OH = 1.2) Which mean that $0.08 / \text{OH} = 1.2$
 - OH equivalent = $0.08/1.2 = 0.0666$

- Weight of polyol (caster oil) which contains 0.0666 OH equivalent = $0.0666 \times 311.66 = 20.77$ gm.

Where: 56100 is the molecular weight of KOH used in the analysis expressed in milligrams.



Triglyceride of ricinoleic acid



MDI

Fig.2: shows the structures of the diisocyanate and the polyol: ricinoleic acid (the major component in castor oil) used in this work for producing polyurethane and MDI.

2.2.2.1. Choosing the optimum ratios of NCO/OH

The optimum ratios of NCO/OH to be used in modified asphalt preparation were used based on measuring the suitable drying time of PUR polymer prepared. The time was measured on three stages. The first stage when the films were tacky; in the second stage when the films turn to slightly tacky (finger print); and in the third stage in case of the films became hard (completely cured). This process represents a chemical reaction between the functional groups of each component of polyurethane (NCO groups in MDI and OH groups of castor oil).

2.2.3. Preparation of modified asphaltic materials

In this step, asphalt and castor oil were mixed for used as a mixed polyol in the modified coating preparation. The polyol blend was prepared as following: Castor oil was added to heated asphalt, in different ratios of (5, 10, 15, 20, 25) % by total weight of mixtures, at a temperature ranging from 135-145°C until it become

pourable. The blend was tested for hydroxyl group contents (ASTM D4274). According to the desired NCO/OH ratio a fixed amount of MDI equals 10 g was added to the calculated amount of the previous samples. Knowing that; the modified samples were denoted as PMA_x, where PMA and x represent the polymer modified asphalt and oil content in the total mix respectively.

2.2.4. Application and evaluation of prepared coatings

2.2.4.1. Mechanical characteristics

The formed coatings were applied on the steel plates using a brush for one time at one direction. The coatings were tested for curing time (ASTM D-1640), dry film thickness (DFT) according to ASTM (D-1186 and 1005) by using Posit-Ector, model 6000-FT₂ coating thickness with probe gauge 6000- FT₂, Adhesion test (ASTM D3359), Impact test ASTM (D-3029) and (G14-88) by using Richmond Road, Kingstone type KT2 5BQ and bending test (ASTM D522) using Richmond Road, Kingstone type KT2 5BQ.

2.2.4.2. Chemical resistance

The resistance of coated carbon steel to various chemical reagents was detected. It was carried out by immersion the coated specimens in selected reagents (3% NaOH, 3% HCl, 1% H₂SO₄, 1% HNO₃, 5% CH₃COOH, and 10% NaCl) for 24 hrs at ambient temperature. The samples were removed and washed with running water and wipes them with a soft and clean cotton cloth or paper tissue. The appearance of specimen was visually inspected according to ASTM D883.

3. Results and discussions

3.1. Characteristics of raw materials:

3.1.1. Characteristics of asphaltic material

3.1.1.1. Physical characteristics

From table (2) it is noticed that, the sample analysis results comply with the Egyptian standard specification.

Table (2): Characteristics of used asphalt

Property	Result	ESS*
- Penetration (25°C,100g,5s),0.1mm	65	60/70
-Softening point, °C	47	45/55
- Kinematics viscosity at 135C°, cSt.	465	>320
- Chemical constituents		
-- Oil (% wt)	32	
-- Resins(% wt)	42	
-- Asphaltenes (% wt)	26	

NB:-(*)Egyptian Standard Specification limits for Roads, Bridges and Land Transportation item No102.01 (***) Not standardized

3.1.1.2. FT-IR analysis

Figure (3) shows FT-IR spectroscopic analysis of virgin asphalt. It was detected that; at wave number of 2921.26 cm⁻¹ high intensity stretch peak indicating the presence of C-H stretch, at wave number of 1603.97 cm⁻¹ weak stretch peak indicating the presence of (C=C) of aromatic ring, at wave number of 1455.63 cm⁻¹ bending peak indicating the presence of C-H bending.

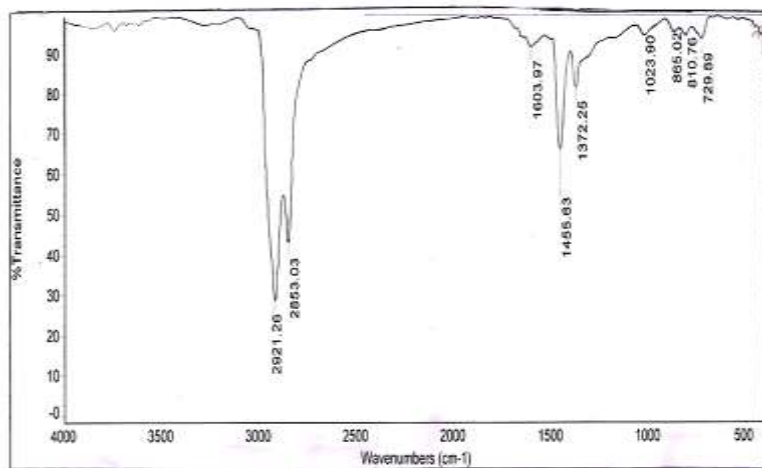


Figure (3): FT-IR spectroscopy of asphalt

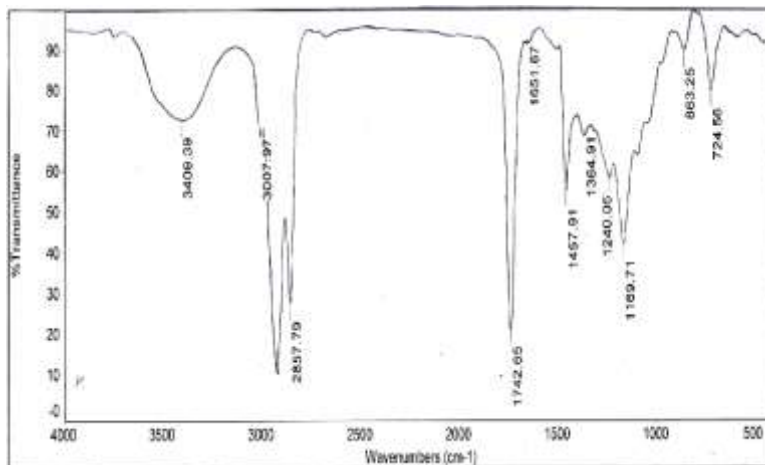


Figure (4): FT-IR spectroscopy of castor oil

Figure (4) shows FT-IR spectroscopic analysis of castor oil. It was detected that; at wave number of 3409.93 cm^{-1} medium intensity stretch peak indicating the presence of (OH) group, at wave number of 3007.97 cm^{-1} high intensity stretch peak indicating the presence of SP^2 (alkene) C-H group, at wave number of 2857.79 cm^{-1} high intensity stretch peak indicating the presence of SP^3 (alkane) C-H group, at wave number of 1742.65 cm^{-1} high intensity stretch peak indicating the presence of (C=O) group of ester, at wave number of 1651.67 cm^{-1} weak intensity stretch peak indicating the presence of isolated (C=C) group.

3.2. Evaluation of the prepared polyurethane films

3.2.1. Curing properties of the PUR films prepared

Table (3) illustrates the curing time of polyurethane films at room temperature.

Table (3): Curing time of prepared polyurethane films

Sample ID	NCO/OH ratio	Curing time, hr.		
		1 st Stage (Tacky)	2 nd Stage (Finger Print)	3 rd Stage (Cured)
PUR ₁	1:1	2	11	N.D
PUR _{1,1}	1.1:1	1.4	8.3	23
PUR _{1,2}	1.2:1	1.0	7.0	20
PUR _{1,3}	1.3:1	0.6	6.0	15
PUR _{1,4}	1.4:1	0.4	4.1	12
PUR _{1,5}	1.5:1	N.D	N.D	N.D

Test results illustrated that, PUR₁ has very long curing time until it can not be determined. As the NCO/OH ratio increased, it was noticed that the curing time is decreased, this may be attributed to the nature of PUR as of thermosetting polymers depends in its curing on the chemical cross linking between the chains. This is proved from the sample that has NCO/OH value of 1:1.5, it was difficult for processing and coagulation is denotes. So, the NCO/OH ratio was chosen to ranging from 1.1:1.4

3.3. Characteristics of asphalt polyurethane films

The hydroxyl number and the weight of required of asphalt polyol blend are illustrated in tables (4) & (5) respectively.

Table (4): Hydroxyl number of PMA prepared samples

Sample ID	Hydroxyl number
PMA ₅	60
PMA ₁₀	56
PMA ₁₅	50
PMA ₂₀	44
PMA ₂₅	40

Table (5): Required weights of asphalt – castor oil blends

Sample ID	NCO/OH ratio	Weight of MDI,(g)	Weight of blend,(g)
PMA ₅	1.1	10	68.00
	1.2	10	62.30
	1.3	10	57.30
	1.4	10	53.42
PMA ₁₀	1.1	10	72.86
	1.2	10	66.80
	1.3	10	61.65
	1.4	10	57.24
PMA ₁₅	1.1	10	81.60
	1.2	10	74.80
	1.3	10	69.00
	1.4	10	64.10
PMA ₂₀	1.1	10	92.72
	1.2	10	85.00
	1.3	10	87.46
	1.4	10	72.85
PMA ₂₅	1.1	10	102.0
	1.2	10	93.50
	1.3	10	86.30
	1.4	10	80.14

3.4. Evaluation of the prepared modified asphalt films

3.4.1. Curing properties

Table (6) illustrates the curing time of the prepared modified coating.

Table (6): Curing time of asphalt polyurethane films

Sample ID	NCO/OH ratio	Curing time, hr.		
		1 st Stage (Tacky)	2 nd Stage (Finger print)	3 rd Stage (Cured)
AC	0	14	21	ND
PMA ₅	1.1	6.00	16.00	32
	1.2	5.10	14.00	30
	1.3	4.00	13.00	27
	1.4	3.80	12.00	26
PMA ₁₀	1.1	7.00	17.00	34
	1.2	6.00	16.00	32
	1.3	5.10	14.00	30
	1.4	4.00	13.00	27
PMA ₁₅	1.1	8.00	18.00	36
	1.2	7.00	17.00	34
	1.3	6.80	16.00	33
	1.4	5.80	15.00	32
PMA ₂₀	1.1	8.50	20.00	37
	1.2	8.20	18.50	36
	1.3	8.00	18.00	35
	1.4	7.00	16.50	34
PMA ₂₅	1.1	9.00	21.00	38
	1.2	8.60	20.00	37
	1.3	8.20	18.50	36
	1.4	8.00	17.50	35

The test results detected that, the process of curing passes through three stages. From the obtained data it is noticed that, the curing time decreases with increasing the value of NCO/OH ratio. This means that with increasing the value of NCO/OH ratio, the reaction between NCO group in MDI and OH group in polyol (asphalt-aster oil mixtures) would have the possibility to proceed more readily, leading to the formation of excessive cross-links, more quick approach towards complete curing, and consequently a decrease in curing time. On the other hand, it was noticed that, the curing time increases with increasing the percentage of PUR with the same NCO/OH ratio. As for an example, final curing time was increased from 26 hr in case of PMA₅ to 35 hrs in case of PMA₂₅ at the same NCO/OH ratio equal to 1.4; this may be explained by that PUR has longer final curing time than virgin asphalt.

3.4.2. Mechanical properties

Table (7) illustrates the mechanical properties of asphalt polyurethane films comparing to virgin asphalt while figures (5:10) show the bending test result.

From table (7); it was noticed that:

- AC is flexible material, by increasing the proportions of cross-linking agent MDI (NCO/OH) ratio; the flexibility of the produced material is decreased.

- All samples showed good adhesion behavior, this is due to the adhesive property of both AC and PUR as a result of the polar groups exist in both asphalt and PUR.
- Addition PUR improved the impact resistance of the produced PMA, as a result of polymeric matrix formation.

Table (7): Physical properties of asphalt polyurethane films

Sample ID	NCO/OH ratio	DFT (mm)	Adhesion test	Impact resistance	Bending
AC	0	0.12	Pass	Fail	Pass
PMA ₅	1.1	0.11	Pass	Fail	Pass
	1.2	0.12	Pass	Fail	Pass
	1.3	0.13	Pass	Pass	Pass
	1.4	0.15	Pass	Pass	Fail
PMA ₁₀	1.1	0.12	Pass	Fail	Pass
	1.2	0.14	Pass	Fail	Pass
	1.3	0.14	Pass	Pass	Pass
	1.4	0.15	Pass	Pass	Fail
PMA ₁₅	1.1	0.12	Pass	Fail	Pass
	1.2	0.14	Pass	Fail	Pass
	1.3	0.15	Pass	Pass	Pass
	1.4	0.16	Pass	Pass	Fail
PMA ₂₀	1.1	0.13	Pass	Fail	Pass
	1.2	0.14	Pass	Fail	Pass
	1.3	0.16	Pass	Pass	Pass
	1.4	0.18	Pass	Pass	Fail
PMA ₂₅	1.1	0.14	Pass	Fail	Pass
	1.2	0.15	Pass	Fail	Pass
	1.3	0.17	Pass	Pass	Pass
	1.4	0.20	Pass	Pass	Fail



Figure (5): Bending test results for Virgin AC

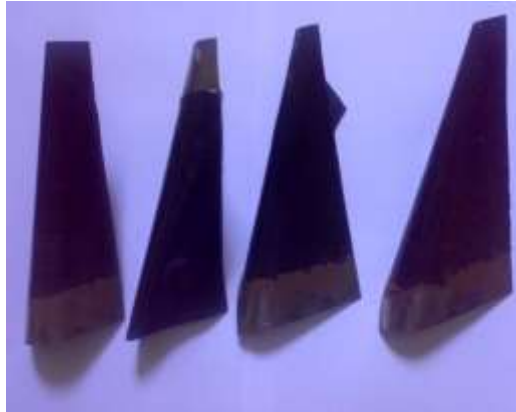


Figure (6): Bending test results for PMA₅ at different NCO/OH ratio



Figure (7): Bending test results for PMA₁₀ at different NCO/OH ratios



Figure (8): Bending test results for PMA₁₅ at different NCO/OH ratios



Figure (9): Bending test results for PMA₂₀ at different NCO/OH ratios



Figure (10): Bending test results for PMA₂₅ at different NCO/OH ratios

3.4.3. Chemical resistance

The chemical reagents includes; acids (3% HCl, 1% H₂SO₄, 1% HNO₃ and 5% CH₃COOH), alkali (3% NaOH), salt solution (10% NaCl).

The results in table (8) show that:

Table (8): Chemical resistance of asphalt polyurethane films

Sample ID	NCO/OH ratio	NaOH (3%)	HCl (3%)	H ₂ SO ₄ (1%)	HNO ₃ (1%)	CH ₃ COOH (5%)	NaCl (10%)
Virgin AC	0.0	F	F	F	F	G	G
	1.1	F	F	G	G	G	G
	1.2	G	G	G	G	E	E
PMA ₅	1.3	E	G	E	E	E	E
	1.4	E	E	E	E	E	E
	1.1	F	F	G	G	G	G
PMA ₁₀	1.2	G	G	G	G	E	E
	1.3	E	E	E	E	E	E
	1.4	E	E	E	E	E	E
PMA ₁₅	1.1	F	F	G	G	G	G
	1.2	G	G	G	G	E	E
	1.3	E	E	E	E	E	E
	1.4	E	E	E	E	E	E
PMA ₂₀	1.1	G	F	G	G	G	G
	1.2	G	G	E	G	E	E
	1.3	E	G	E	E	E	E
	1.4	E	E	E	E	E	E
PMA ₂₅	1.1	G	F	G	G	G	G
	1.2	G	G	G	G	E	E
	1.3	E	G	E	E	E	E
	1.4	E	E	E	E	E	E

Where: P = Poor, F=Fair, G= Good, E= Excellent

- The resistance of AC to alkali was improved with adding of PUR resin, this is due to PUR has higher resistance to alkali than AC as a result of presence of isocyanat group, and more improved with increasing of NCO/OH ratio due to the increase in cross-linking in the produced polymer.
- AC resistance to acid is improved with the addition of PUR resin, and more improved with increasing the ratio of NCO/OH due to the increase in the urethane cross-linking in the produced polymer.
- AC resistance to salt solution is improved with the addition of PUR resin, and more improved with increasing the ratio of NCO/OH due to the increase in the urethane cross-linking in the produced polymer.

4. Conclusion

The data obtained from the study reveals that the polyurethane is improve the asphalt cement as a coating material. The asphalt-polyurethane coating material is prepared by the reaction of isocyanate material (MDI) with asphalt-caster oil blend mixes. The high content of isocyanate material (MDI) (i.e. NCO/OH ratio) increase cross-linking urethane reaction. This reduces the curing time to make it suitable, also improve the chemical resistance, adhesion and impact resistance. Flexibility remains suitable at a certain extent, then decrease with increasing of isocyanate material.

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