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Modification of RTV Silicone

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Owing to their broad spectrum of properties, silicone sealants are used in a large variety of purposes in Egypt. However, among the drawbacks of their use are low abrasion resistance, low tensile properties and high cost owing to the fact that they are completely imported. In the presented research, silicone sealants [Room Temperature Vulcanized (RTV)] have been formulated using local expertise and raw material (silicone polymer, ethyl silicate and dibutyl tin diacetate). In addition, two types of asphalt locally produced in Egypt (asphalt cement of penetration grade 60/70 and blown asphalt of type 115/15) as well as asbestos, fumed silica and reclaimed rubber have been used to produce modified silicone sealants thereby overcoming their high cost and producing high quality local cheap sealants. Results show the wide range of mechanical properties and chemical resistivities of the produced products.

Keywords: Silicone, RTV, Asphalt cement.

Introduction

It is a recognized fact that joints are generally needed in construction to minimize some of the defects that sometimes occur as result of movement Frank *et al* 1990. Accordingly, the introduction of joints creats openings which must usually be sealed using sealing systems dependent on the kind of joint. Sealants are usually used in joints to prevent the passage of gases, liquids or other unwanted substances into the openings or through them. The selection of an adequate joint sealant material depends on several factors such as joint material type and movement needed in addition to weather conditions, chemical environment, sealant and lifetime. Both sealing and sealant cost materials represent a fraction of 1% the total cost of a building (Klosowki 1990).

The first silicone sealants were developed in the early 1940's (Klosowki and Gant 1979) and resembled putties since they did not cure to elastomeric solids. Actually, elastomeric silicone sealants were first prepared in the early 1950's (Seymour 1979) and patented by (Hyde and Brown 1967) this involved a two part system consisting of a hydroxyl ended polysiloxane and polysilicate.

Silicone sealants exhibit a number of unusual properties (Cahill 1966). They are breathable and resistant to oxidation (especially ozone attack), water damage, photochemical reaction and hardening or cracking. In addition, they are usable in both hot and cold climates and finally they have surpassed 15-20 years without a significant change (Melody 1989).

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Because silicone sealants have a broad spectrum of properties, they are used in several purposes as coating for roofs, glazing, electrical applications, domestic applications, automotive industries, gaskets and taps. The draw back of silicone sealants is their high price. Accordingly, the main objective of this study is to produce silicone sealants-similar to imported ones using local experts and imported raw materials, also, using low priced asphalt locally produced-as well as asbestos, fumed silica and reclaimed rubber to produce specific modified high quality local cheap silicone sealants thereby overcoming their high cost.

Experimental

Raw materials used. The raw materials used for the production of silicone rubber are; hydroxyended dimethylsiloxane polymer, ethylsilicate as crosslinker and dibutyltindia-cetate as catalyst. Two types of asphalt [penetration grade 60/70 and blown asphalt of type 115/15], reclaimed rubber fumed silica and asbestos are used to produce modified silicone sealants.

Preparation of silicone rubber sealants (RTV). It is important to mention that, to date and as far as could be traced in literature there is no patented standard method for the preparation of silicone rubber sealant available. Accordingly, the rubber sealant was prepared by a rather simple technique, depending on silicone rubber properties. The percentages of the reactants mixed were suggested by Bruner (1963). The technique could be outlined as follows:

Table 1
Properties of silicone polymer

Property	Result
- Molecular weight	130000.00
- Specific Gravity at (25/25)°C	1.85
- Kinematic Viscosity at 25 °C	59828.80
- Rheological Properties at 25°C (c.St)	
Viscosiy (cP)	70500.00
Yield Stress (mPa)	990.00

1) 100 g of hydroxylended silicone polymer were weighed in a beaker and mixed with 20g of toluene solvent for nearly 5 min. The solvent was added to decrease the viscosity of the polymer and to help the reaction between the polymer and the crosslinker to be attained. Several trails were performed before selecting the appropriate amount of solvent to be used and the suitable time of mixing.

2) The selected amount of crosslinker (7% and 10% of polymer weight) and catalyst (0.1%, 0.25%and 0.5% of polymer weight) were reacted with the polymer solution. The reactants were thoroughly mixed for nearly 5 min in suitable container.

3) The reactants were placed in a dessicator for degassing purpose for about 5 min

4) The product was then poured in petridishes (of 10 cm diameter) and left to cure at room temperature. Care was taken to obtain a sample of thickness suitable for undergoing the tests needed to determine both the mechanical and chemical properties. The properties of silicone polymer as well as composition and mechanical properties of silicone sealants are illustrated in Table 1 and 2 respectively.

Preparation of modified silicone sealants. In this part of the work 15% asbestos was added while fumed silica and reclamied rubber were both added in different amounts namely 1%,2%and 5% of the former and 5%, 10% and 15% of the latter. On the other hand the procedure adopted for the manufacture of modified silicone sealants using asphalt can be summerized as follows. The calculated amount of each type of selected asphalt was heated in a suitable container until it softened and became pourable. The heating temperatures ranged from 130-140 C for AC 60/70 and 180-200 C for blown asphalt type 115/15. The properties of asphalt used and the mechanical properties of modified silicone sealants are illustrated in Table 3 and 4 respectively.

Results and Discussion

I) Mechanical properties of silicone sealants. Hardness, abrasion resistance (%loss by weight), tensile strength at rupture, elasticity modulus and % elongation at break were determined for all silicone sealants prepared. Table 2 shows values of such mechanical properties. It is worth mentioning that SSx indicates the silicone sealant number were:

SS = Silicone sealant
x = Sealant number

As seen from Table 2 the mechanical properties of the final silicone sealants vary with change in the amount of crosslinker and the amount of catalyst used.

II) Variation of the amount of crosslinker. For the same percent of catalyst used, the amount of crosslinker used is of primary importance in controlling the properties of the final product. Furthermore, for the same percent of catlyst, increasing the amount of crosslinker results in forming amorphous polymers that more rigid sealants.

Such aspect is illustrated by the higher tensile properties, the greater hardness, the lower loss in weight and lower elongation at break. The afroementioned effects may be attributed to the increase of crosslinking centers in the given mass of polymer.

Table 2
Composition and mechanical properties of silicone sealants

Silicone sealant number	Sealant composition		Hardness shore (A) (0.002mm)	Abrasion (%wt)	Tensile properties		
	Crosslinker (%wt)*	Catalyst			Tensile strength ($N\ cm^{-2}$)	Elasticity modulus ($N\ cm^{-2}$)	Elongation at break (%)
SS_1	7	0.10	19	8.99	299.4	261.9	165
SS_2	7	0.25	22	3.76	427.1	256.4	215
SS_3	7	0.50	20	5.96	336.1	326.1	115
SS_4	10	0.10	21	7.82	435.2	390.1	133
SS_5	10	0.25	25	2.78	527.5	334.8	225
SS_6	10	0.50	22	4.00	370.9	333.9	105

(*) NB: Polymer weight is 100g

Table 3

Properties of the asphalt used

Property	Result	
	AC*60/70	BA**115/15
1- Physical properties		
- Penetration (@ 100g, 25 °C, 5s), 0.1mm	63	14
- Kinematic viscosity (@ 135°C), cSt	342	ND
- Absolute viscosity (@ 60 °C), poise	1974	ND
- Softening point (Ring & ball), °C	46.5	114
- Ductility (@ 25 °C, 5 cm^{-1} min), cm	+150	8
- Flash point (Cleveland open cup), °C	287	304
- Solubility in trichloroethylene, (% wt)	99.9	99.9
- Specific gravity at 25°C (using pycnomete)	1.0196	1.0234
- Thin film oven test:		
• Weight loss on heating (@ 163 °C, 5 h), %	0.4	0.1
• Retained penetration after TFOT, %	56	ND
• Ductiliy (@ 25 °C, 5 cm-1 min) after TFOT, cm	75	ND
- Rheological properties:		
• Yield stress (@ 120 °C***), mPa	42000	ND
• Viscosity (@ 120 °C), cp	2000000	ND
2-Chemical constituents:		
• Oils (%wt)	37.7	23.0
• Resins (% wt)	49.0	35.
• Asphaltenes (%wt)	13.2	41.4
• Wax+ (%wt)		

(*) Asphalt cement of penetration grade 60/70; (**) Blown asphalt of type 115/15; (***) Mixing temperature of asphalt and polymer; (ND) Not determined; (+) This % is excluded from oil phase.

III) Variation of the amount of catalyst. Increasing the amount of catalyst from 0.1 to 0.25% causes the sealant to become more rigid. This may be attributed to the increase in the rate of crosslinking reaction.

Using a higher amount of catalyst (0.5%) results in a product that has lower mechanical properties compared to the end product resulting from the use of only 0.25% catalyst. Such results may be attributed to the increase in the content of inorganic materials of the catalyst compound in the mixture that may affect the homogeneity of the final product.

Finally, it is rather apparent that the sealant number 5-having 0.25% catalyst and 10% crosslinker seems to be the best sealant prepared. This sample has been modified using diffret modifiers as previously mentioned.

IV) Modified silicone bituminous sealant using oxidized asphalt and SS_5. From Table 4 it is clear that increasing the amount of blown asphalt in the sealant up to 20% results in decrease in the mechanical properties of the final products. This decrease in flexibility could be the results of a high content of solids and friable asphaltenes.

Using 30% blown asphalt, the flexibility of the final product increases and shows a maximum increase after which a decrease is noted. Such behaviour may be attributed to the initial homogeneity of the mixture which results in the increase in the first place. On the other hand, when adding 40% blown asphalt, the presence of high amount of asphaltenes caused incomplete homogeneity that resulte in a decrease in flexibillity.

The final product resulting from the use of 30% blown asphalt has the highest mechanical properties. On comparing those results to the mechanical properties of pure $SS_5$the former product shows higher tensile properties at rupture (5.3%), elasticity modulus (42.2%) and higher loss in weight (137.4%) but lower hardness (4%) and elongation at break (20%).

V) Modified silicone sealants using asphalt cement and SS_5. Table 4 indicates that increasing the % AC results in final products of higher mechanical properties as compared to the original (SS_5). This could be resulting from the flexibility of asphalt which contains high percent of oil and low percent of asphaltenes. The oil phase actually increases the homogeneity of silicone in asphalt.

The lowest mechanical properties were determined for the final product produced using 10% asphalt. Such result may be attributed to the incomplete solvation (inhomogeneity) of the asphalt and the silicone.

The highest mechanical properties however, are noted for the final product produced when 40% asphalt is used, due to the presence of a high percent of oil. On comparing such mechanical properties with those of pure SS_5, it is clear that there is an increase in hardness, tensile strength at rupture, elasticity modulus and elongation at break by 48%, 33.4%, 43.88% and 68.8% respectively coupled with a decrease in weight loss by 57.2%. Such effects may be attributed to the chemical composition of asphalt.

VI) Modified silicone sealant consisting of silicone and asbestos. From Table 4, it is clear that the mixing of asbestos with silicone results in a modified silicone sealant having higher mechanical properties as compared to the original values of pure SS_5 i.e: asbestos is considered a "reinforcement addition".

On comparing those results of mechanical properties with those of pure SS_5, it is clear that there is an increase in hardness, tensile strength at rupture and elasticity modulus by 76%, 0.3% and 42.2% respectively. The results presented may be attributed to the chemical constituents of asbestos having a chemical bond of type Si-O-Si. Accordigly, there is an increase of (Si-O) bond added to the sealant resulting.

VII) Modified silicone sealant consisting of silicone and fumed silica. The mixing of fumed silica with silicone results in a modified silicone sealant having higher mechanical properties as compared to the original values of pure SS_5 as clear from Table 4. It is a well known fact that fumed silica is considered a "work power ad reinforcement addition".

Increasing the content of fumed silica from 1% to 5% in the new sealant increases the value of hardness, tensile strength and elasticity modulus and decreases the values of loss in weight and elongation at break in relation to the original values by (4% to 32%), 16.8% to 87.8%), (52.3% to 107%), (2.9% to 51.1%) and (4.4% to 17.7%) respectively. Such behaviour may be attributed to the chemical constituent of fumed silica as it contains silicone bonded hydroxyl groups that interact with the

Table 4

Mechanical properties of modified silicone sealants using SS_5

Additive type & content (*)	Hardness shore (A) (0.002 mm)	Abrasion resistance (Loss %wt)	Tensile properties		
			Tensile strength (N cm^{-2})	Elasticity modulus (N cm^{-2})	Elongation (%)
Asbestos					
15%	44	1.54	634.9	476.2	165
Fumed silica					
1%	26	2.70	616.3	510.2	215
2%	29	2.63	654.7	535.7	200
5%	33	1.36	990.6	693.1	185
Reclaimed rubber					
5%	20	23.6	135.2	127.5	145
10%	22	18.3	152.7	138.6	130
15%	24	13.8	222.2	194.4	125
Blown Asphalt					
10	22	8.9	500.8	416.6	185
20	18	9.71	330.9	294.1	125
30	24	6.60	555.5	476.1	180
40	22	7.29	476.2	416.7	170
Asphalt cement					
10	22	4.07	518.5	418.5	195
20	24	3.84	572.9	416.6	215
30	32	2.60	594.0	346.5	295
40	37	1.19	703.7	481.5	380

(*) Based on total weight of polymer.

hydroxyl siloxane groups of the polymer chains in order to increase the Si-O-Si bonds and in this manner create a mechanical reinforcement for the original sample.

VIII) Modified silicone sealant consisting of silicone and reclaimed rubber. From Table 4 it is clear that the mixing of reclaimed rubbr with silicone results in a modified silicone sealant having lower mechanical properties as compared to the original values of pure SS_5 owing to the incompatibility of rubber and silicone.

Generally increasing the content of reclaimed rubber from10% to 15% in the new sealant results in sealants having higher mechanical properties but still lower as compared to SS_5. Such behaviour may be as a result to the increasing of the mixing power of rubber in silicone.

IX) Choice of the best modified silicone sealant. From Table 4 it is clear that the best samples possessing the best mechanical properties are those consisting of (SS_5+ 15% asbestos), (SS_5+5%fumed silica), (SS_5 + 15% reclaimed rubber), (SS_5 + 40% AC) and (SS_5 + 30% BA).

a) Chemical resistivity of modified silicone sealants to different chemical reagents. In this section, changes in weight and tensile properties of the best modified silicone sealants prepared were determined after complete immersion for 4 weeks in the chemical reagents distilled water, kerosene, NaOH solution (10%) of pH=8, NaOH solution (60%) of pH= 12.9, Conc. H_2 SO_4 of pH= 1 and H_2 SO_4 (30%) of pH = 5.5. The results are given in Table 5.

a) Effect of distilled water. Table 5 shows that the increase in weight is 4.4%, 1.36% and 11.27% for the samples using asbestos., fumed silica and reclaimed rubber respectively. Obviously, the difference in the values of the % increase could be attributed to the difference in chemical structure of those additives as well as to the differene in their grain size.

Also, Table 5 shows that the increase in weight is 1.02% and 0.82% for AC and BA with SS_5 respectively. Such increase in weight is due to the fact that water repellency is not unique to asphalt as for siloxane molecule.

For the tensile properties, water is generally found to have a negative effect i.e. a reduction of the tensile properties of all modified sealants is noted. An extent of reduction of the tensile properties differed for the different additives according to composition of each one of them.

The only exception was for the modified sealant using reclaimed rubber wherein the sealant became more flexible wih lower elongation; such behaviour may be as a result of the increasing homogeneity (solvation power) and the final curing conditions.

The lowest% decrease in tensile properties is observed for the BA type of asphalt due to its chemical composition as compared to AC type of asphalt.

b) Effect of Kerosene. As in the case of pure silicone sealents Table 5 generally indicates that the weights of modified sealents are generally increased as a results of immersion in kerosene. The increase in weight is found to be higher for modified sealents when using asbestos and reclaimed rubber. This is due to the chemical constituents of all the additives as well as to the effect of osmotic pressure of the kerosene. Also, the increase in weight using "AC" is lower when using "BA" This variation may be attributd to the difference in the solubility power of both types of asphalt in kerosene. From this table it is noticed that kerosene has a greater negative effect on the tensile properties of all sealents which could be attributed to the weakness and softness of the sealent resulting from the hydrocarbon solvation effect.

c) Effect of NaOH. Table 5 shows that the use of 10% NaOH has a limited effect on weight of all samples as that of distilled water. This is due to the weak basicity of that alkali and also to the fact that asphalt is a relatively inert material that resists alkaline attack.

Also, in case of 60% NaOH, the samples are found to degrade and their weight decreases upon immersion in this alkali. This could be attributed to the attack of the alkali medium under cleavage of Si-O bonds as well as Si-C bonds. The only expection is for modified sealent using asbestos, since an increase in weight rather than a decrease of 3.55% took place. Such opposing manner maybe attiributed to the chemical constituents of asbestos. A reduction in the tensile properties of all samples is quite apparent after immersion in both NaOH (10%) or (60%). Exception to the aforementiond sealant is for modified sealant using reclaimed rubber and asphalt when immersed in both NaOH solution and when using asbestos and reclaimed rubber in case of immersion in 60% NaOH. Such exceptions may be attributed to increasing the flexibility of the sealant as a result of improvement of homogeneity of reclaimed rubber in the two alkaline solution. On the other hand, whilst there is decrease in elongation when using reclaimed rubber yet, the increase in tensile properties may be attributed to the chemical nature of this additive.

d) Effect of H_2SO_4. Table 5 shows a slight increase in weight for all samples. Obviously the difference in the values of the % increase could be attributed as previously mentioned to the difference in their chemical compositions, grain size of fillers as well as to the fact that asphalt is considered a non polar inert material to weak acids.

Table 5

Change in weight and tensile properties of silicone and modified silicone sealant after immersion

		SS_5	SS_5+15% Asbestos	SS_5+5% F. Silica	SS_5+15% Rubber	SS_5+40% AC	SS_5+30% BC
Distilled water wt%		+0.36	+4.40	+1.36	+11.20	1.02	0.82
Tensile	T.S	-5.60	-13.70	-6.50	+50.00	-4.30	-3.70
Properties(*)	E.M	+18.8	-19.20	-16.60	+67.90	-12.50	-8.50
	E.	-6.60	+6.60	-4.30	-4.00	-2.30	-13.00
Kerosene wt%		+85.5	+97.70	+83.6	+100.1	+63.00	+73.3
Tensile	T.S	-50-8	-72.40	-59.1	-21.00	-33.50	-67.5
Properties(*)	E.M	-44.7	18.90	-67.6	-54.80	-51.50	81.2
	E.	-16.3	-6.00	-13.5	+40.00	-27.60	+25.0
Chemical reagent wt%		+1.5	+5.04	+4.79	+8.77	+4.24	+3.71
NaOH (10%)	T.S	-0.20	-15.00	-26.50	-74.90	+35.00	+4.00
Tensile	E.M	+17.9	-42.60	+47.50	+118.50	-35.90	-18.60
Properties(*)	E.	-4.40	+9.00	-18.90	-14.40	+57.0	+48.00
NaOH 60% wt%		-2.76	+3.55	-10.41	-3.80	-2.58	-2.59
Tensile	T.S	-27.90	+34.60	+19.40	+58.50	-20.10	-12.60
Properties(*)	C.M	-2.50	-10.30	+59.60	---	-38.80	-35.40
	E.	-17.70	+38.30	-40.50	-28.00	-27.60	-17.10
H_2SO_4 (30%) wt%		-0.85	+1.49	+1.38	+1.54	+1.17	+1.93
Tensile	T.S	-6.00	+20.80	-5.70	+164.1	+32.00	+2.20
Properties(*)	C.M	+19.5	-3.30	-4.50	+156.90	-20.70	+20.30
	E.	-9.70	+45.40	-5.40	-12.00	+88.0	+55.00

SS_5 + 15% Asbestos SS_5 +5% F. silica SS_5 + 15% Rubber SS_5 + 40% AC SS_5 +30% BA SS_5.

The Table 5 indicates that the effect of diluted H_2SO_4 on the tensile properties is very similar to the effect of distilled water due to the weak acidity of the solution. Once again, all samples were corroded in Conc. H_2SO_4 within a period of 2-5 h.

Conclusion

In view of the afroementioned analyses and within the limits investigation the following general highlights may be outlined:

The use of either AC or BA with silicone results in sealants that are more resistant to all chemical reagents (except kerosene) used in this study.

The use of B A results in more chemical resistant sealants as compared to the sealants produced using AC.

The use of either asbestos or fumed silica with silicone results in sealants that have higher mechanical properties and better chemical resistivity as compared to pure silicone.

The use of reclaimed rubber with silicone results in sealants having lower mechanical properties as compared to pure silicone. In case of immersion in different chemical reagents the tensile properties increases with increase in time.

Silicone is considered a flexible agent to asphalt, while asphalt is considered a reinforcement agent to silicone.

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