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Synthesizes And Performance Of Poly (Ethylene Glycol Terphthalate Dimethyl Siloxane) Compound As Protective Material For Carbon Steel Alloy Of Petroleum Pipelines

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ABSTRACT

The poly (ethylene glycol terphthalate dimthylsiloxane) compound [PEGTDMSO] was prepared and confirmed by FTIR, NMR and GPC techniques. The carbon steel alloy specimens were provided from unused petroleum pipelines. The surfaces of specimens were prepared by polishing with different grade emery paper. PEGTDMSO was formulated with TiO_2, ZnO_2 and different ratios of silica gel as inorganic additives to produce seven formula designated from Y_0- Y_6. The toluene diisocyanate (TDI) was used as curing agent. The visual inspection, physical, mechanical and chemical properties such as, wet film thickness (WFT), dry film thickness (DFT), adhesion forces, bending, impact, hardness and thermal stability at 150 - 400 ºC at intervals of 50 ºC. Acid effect (10% H_2SO_4) at period time of 480 hr and the sealant water effect at period time of 1440 hr for the formed dry films were studied. The surfaces of films were visualy inspected by magnification power after chemical tests. The results indicated that the corrosion spots did not detect on the surface of the formed dry films from formula Y_2-Y_6. These films approved to be a protections agent for the surface of petroleum pipelines against corrosion.
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KEYWORDS

PEGTDMSO;
Unused petroleum pipelines.

INTRODUCTION

The carbon steel alloys are used at high temperatures in large scale for production and maunfacture of petroleum, petrochemical equipments and different industries. The carbon steel alloys are corroded quickly when subjected to both chemical and physical environmetal conditions[1-11].

The types of protective coatings must be compate the metal surfaces without any change. The formation films are provided a barrier between the metallic surfaces and the surrounding corrosive medium. These include paints, varnishes, enamels, plastics and metals which were applied by brushing, electroplating, hot dipping flame spraying, etc.[4-15].

Paintings are one of the most suitable, less expensive, and more efficient method for corrosion and wear control, which could be more suitable binders source and high efficiency as protective compounds[4-18].

The aim of this work depends on the preparation of PEGTDMSO and is formulated with inorganic ZnO, TiO_2, and silica gel. The different ratio of curing agent TDI is used. The preparation surface of carbon steel alloy specimens AG-15 are coated by these formula. The visual inspection, physical, mechanical and chemical properties of the formed dry films are evaluated and discussed.

EXPERIMENTAL

Preparation of PEGTDMSO

The preparation of PEGTDMSO was carried out by reacting of 1.0 mol of terphthalic acid with 1.0 mol of ethylene glygol in three necked flask under mechanical sterrier. The water produced was collected and measured. After cooling the reaction mixture the dichlorodimethylsilane was added dropwise under inert media. The product PEGTDMSO was purified and confirmed by infrared analysis (FTIR), nuclear magnetic resonance (^{1}HNMR) and molecular weight determination (M.Wt) by gel permeation chromatograph (GPC).

Preparation of the painting formula

45 parts of PEGTDMSO compound were mixed with 35 parts of zinc oxide, 5 parts of TiO_2 and different ratios of silica gel. The 5 parts of organic solvent mixture of (xylene, toluene and methylethyl ketone) were used. The toluene-di-isocyanate (TDI) was used at three concentrated ratios(5, 10 and 15%) as a curing agent, which were mixed with each other to form various formulation designated from Y_0-Y_6. These formulations were applied on the prepared surface of carbon steel alloy specimens by brushing method.

Preparation of the surface metal specimens

Unused tubes of carbon steel alloy type AG-15 were provided from petroleum pipelines of belayim petroleum company at Port -Fouad station to be used as specimens supplier. The specimens were cut as regular edged cuboids with dimensions ≈ 8, 15, 0.1 cm average. Each specimen was cleaned, polished with 150, 400, 600 emery paper, rinsed with distilled water, degreased with acetone, weight and finally stored under vacuum after wrapping with adhesive thin paper into sets. Each set includes specimens having nearly similar weight and surface area.

The optimization steps

To obtain the optimum PEGTDMSO coatings were carried out under static air, at ambient pressure and temperature within a selection formula from Y_0 to Y_6. A set of specimens were coated with these formula and cured by curing agent TDI at ambient condition. The coating specimens were gradually inspected to recorded the optimization conditions for each formula. The coating films over the surface of specimens were examined by measuring the WFT, DFT, adhesion, thermal stability, impact, bending, hardness and chemical tests.

The formation of the best coating was achieved in steps and kept constant through the optimization procedure.

The characterization techniques

Visual inspection

The visual inspection for the formation coating as sealing, sagging, fish eyes, shirinking, cogulastion, smoothes and homogeneity were inspected and tabulated.

Physical properties

Wet film thickness(WFT), dry film thickness (DFT), adhesion, thermal cycling test, electrical conductivity, and pinhole test of the formed coatings were carried out according to ASTM (D-1212), (D-1186 and 1005), (D 3359), BS-6670 Part 5 BS-6670 Part 5, ASTM (D-4399) and (D-5162), respectivily.

Mechanical properties

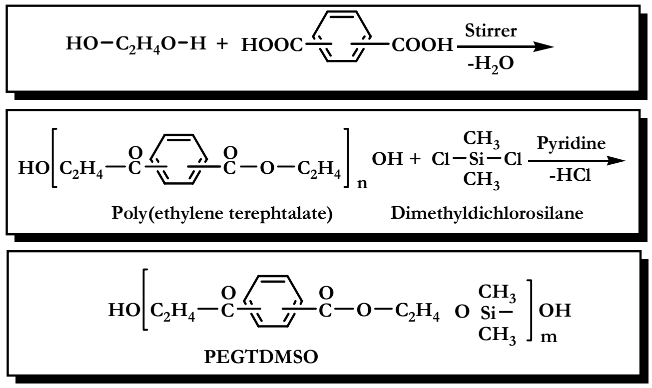
Bending, adhesion forces, hardness, and impact tests were carried out according to ASTM (D-522), (D-3363) and ASTM (D-2794 and G14-88), respectivily.

Chemical properties

The effect of organic solvents, 10% H_2SO_4 and synthetic sea water 3.5% NaCl were carried out according to ASTM D-44, 4752, 468, 610, G-31 and BS-6670, respectively. The data of results were recorded and investigated.

RESULTS AND DISCUSSION

The PEGTDMSO was prepared through the reaction of ethylene glycol, terphthalic acid and dimethyl-dichlorosilane in presence of pyridine as acid acceptor according to the following equation:



Where, n = M.Wt of poly (ethylene terephtalate) and m = M. Wt of PEGTDMSO

The evaluation of the physical and chemical structure of PEGTDMSO compound was carried out according to the following characterization techniques

Infra Red technique (FTIR)

Figure 1 illustrates the FTIR spectrum for preparation of PEGTDMSO. The characteristic bands at 945.6 and 1101.5 cm^{-1} represent the stretching vibration of CH_2-O-Si groups, the band at 2875.6 cm^{-1} for stretching vibration of Si-O and $-CH_2$ groups, the bands at 2957 cm^{-1} for CH aromatic, the bands at 1245.4 cm^{-1} for stretching vibration of Si-C group

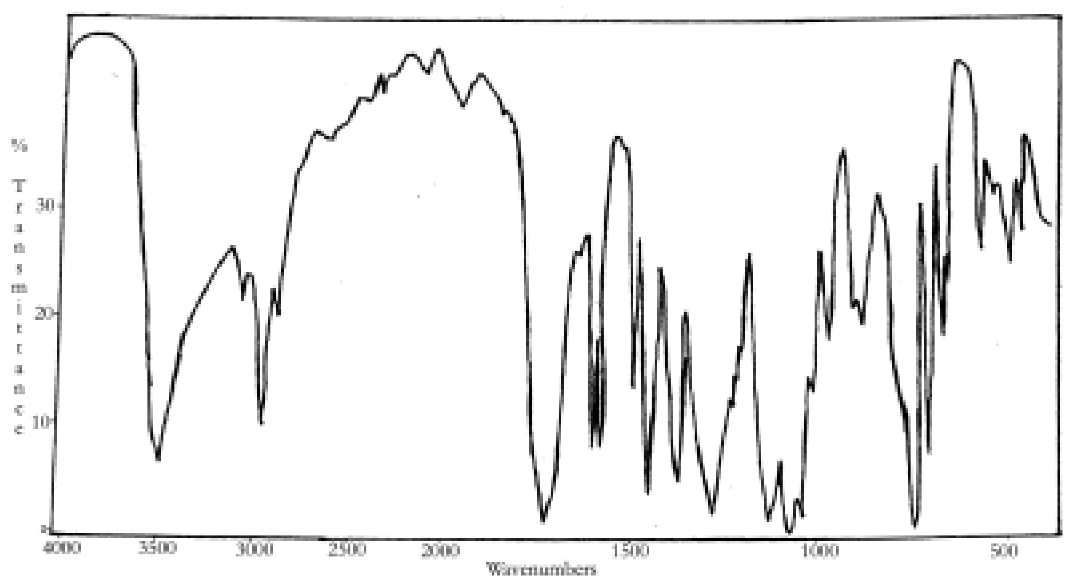


Figure 1: FTIR spectrum diagram for PEGTDMS compound

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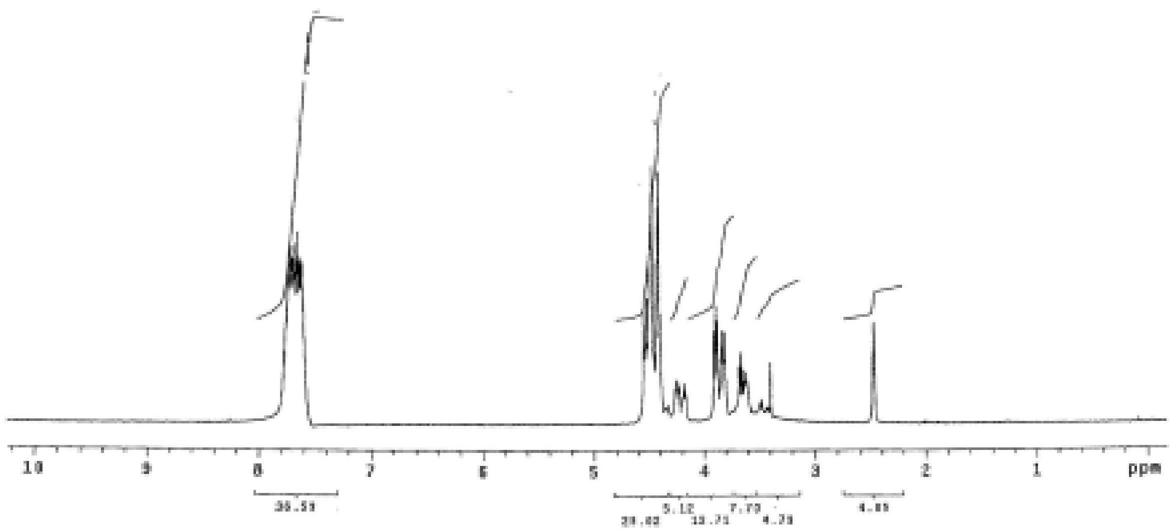

Figure 2: [1]HNMR spectrum diagram for PEGTDMS compound

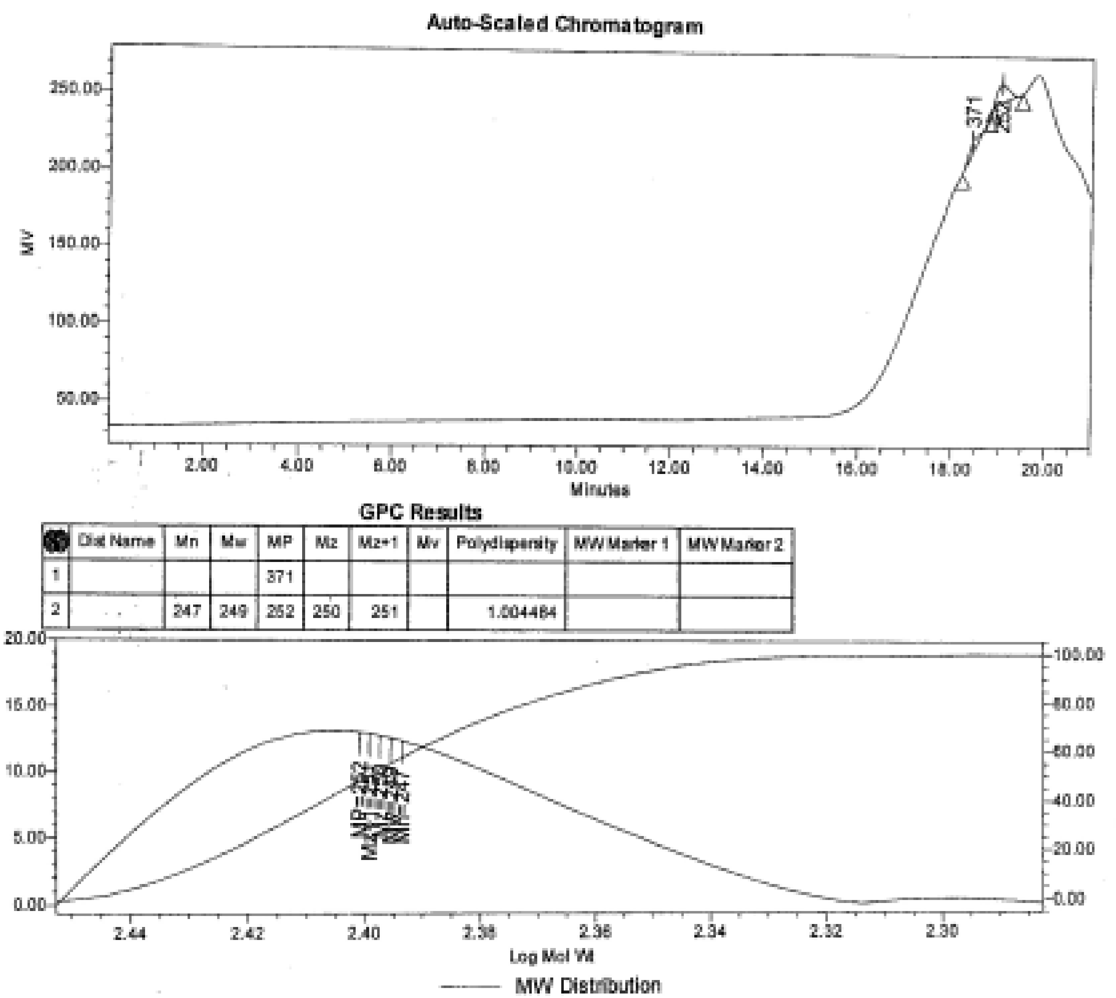

Figure 3: GPC spectrum diagram for PEGTDMS compound

and the band at 3400 cm^{-1} for stretching vibration of –OH groups.

Nuclear magnetic resonance (^{1}HNMR)

Figure 2 illustrates the ^{1}HNMR spectrum for PEGTDMSO. The integration 21.98, for the siloxane groups and 67.23, for ethylene glycol groups.

Gel permeation chromatograph (GPC)

Figure 3 illustrates the typical GPC spectrum of PEGTDMSO. The number average molecular weight Mn for PEGTDMSO was 247, which was highly sensitive to the presence of small number of fraction of low molecular weight. The weight average molecular weight Mw of PEGTDMSO compound was 249, which was highly sensitive to the presence of small amounts by weight of high molecular (weight macro-molecules). The Z and Z+1 were average molecular weights or molar mass. From different molecular weights average. These observed that the Mn < Mw < Mz < Mz+1 have 247 <249 <250 <251. The polydispersity index was 1.004 for PEGTDMSO compound as the ratios of weight average molecular weight Mw/Mn. This ratio was unity for a polymer of uniform molecular weight and become larger as distribution become broader.

Chemical composition of the paintings formula Y_0–Y_6

The synthetic PEGTDMSO compound was blended with inorganic materials zinc oxide, TiO_2 and silica gel as in TABLE 1. Toluene diisocyanate (TDI) was used as a curing agent at 5, 10 and 15 parts for each formula. The PEGTDMSO was used as a binder and it has also dispersant phenomena.

TABLE 1: Chemical formulae of PEGTDMSO cured by different ratios of curing agents TDI

Formula composition/parts	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
PEGTDMSO	45	45	45	45	45	45	45
ZnO	0	35	35	35	35	35	35
Tio_2	0	5	5	5	5	5	5
Silica gel	0	0	1	2	3	4	5
Solvent	5	5	5	5	5	5	5
Curing agent%	5	5	5	5	5	5	5
	10	10	10	10	10	10	10
	15	15	15	15	15	15	15

The formulae $Y_0 – Y_6$ were brushed on the prepared surface of carbon steel alloy specimens. The visual inspection, physical, mechanical and chemical properties for each formed film from formula $Y_0 – Y_6$ will be investigated.

Optimization conditions for curing agent

TABLE 2 illustrates the optimum conditions for the curing agent ratio of TDI. The touch dry time was the main factor, which determines the TDI concentration for curing the formed films on the surface of carbon steel alloy specimens. The inorganic additives affected each formula of $Y_0 – Y_6$. From the optimization studies of the curing agent TDI ratios. These indicated that the time of touch curing for formula $Y_0 – Y_6$ were decreased by increasing inorganic additives.

TABLE 2: Data of the optimum condition for the curing agent TDI respect to time for PEG TDMSO formula at ambient condition.

The ratio of curing agent (TDI)	Touch dry time for each formed films from the formula (hr)						
	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
5%	16-22	10-12	9-10	9-10	8-9	8-9	6-8
10%	6-10	5-8	5-8	3-7	3-7	3-6	3-6
15%	3-5	2-4	2-4	2-3	1-3	1-3	1-3

Physical properties

Visual inspection

The formed films from formula Y_0-Y_6 for PEGTDMSO compound were visually inspected and listed in TABLE 3. These data were showed that, the sealing was observed at Y_0 only. On the other hand the formation films from formula Y_1-Y_6 were not sealing, sagging, fish eyes, shrinkable, coagulation, smoothes and homogeneity for formed coatings.

Calculation and measuring the WFT and DFT

The results of normalization weight of wet and dry films respect to surface area were calculated and given in TABLE 4. These data indicating that the DFT were increased with increasing the inorganic additives. Also, the measuring data of WFT and DFT were given in TABLE 5. These data indicates that, the DFT were increased by increasing the inorganic

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TABLE 3: Data of the visual inspection after application of the painting films formed by formula $Y_0 - Y_6$ of PEGTDMSO compound

Formula	Sealing	Sagging	Fish eyes	Shrinking	Coagulation	Smoothes	Homogeneity
Y_0	Sealed						
Y_1	no sealed						
Y_2	no sealed						
Y_3	no sealed	Not sagging	Not fish eyes appeared	No shrinking	No coagulation	High smooth	Homogeneity of the formed films
Y_4	no sealed						
Y_5	no sealed						
Y_6	no sealed						

TABLE 4: The physical measurements for each formed film from PEGTDMSO wet and dry films at ambient condition and using curing agent TDI 10%

Sym.	Wt. of cleaning specimens (g)	Specimens area of one surface (cm^2)	Wt. of wet coating (g)	Normalized wt. of wet coating per unit area (g/cm^2)	Wt. of dry coating (g)	Normalized wt. of the formed dry coating per unit area (g/cm^2)	Curing temp. (°C)	Relative humidity	Touch dry time (hr)	Complete dry time (days)
Y_0	71.2375	111.8631	4.5621	0.0407	2.2825	0.0204			6-10	
Y_1	71.5037	112.0357	5.1125	0.0456	3.3885	0.0302			5-8	
Y_2	72.0183	112.7895	5.1245	0.0301	3.4015	0.0301			5-8	
Y_3	70.9951	111.0053	5.1337	0.0462	3.4107	0.0307	Ambient temp.	>50	3-7	3-5
Y_4	71.3891	111.9837	5.2015	0.0464	3.4791	0.0310			3-7	
Y_5	71.5961	112.0007	5.2321	0.0467	3.5103	0.0313			3-6	
Y_6	71.9315	112.0933	5.2817	0.0471	4.5601	0.0406			3-6	

TABLE 5: The physical and mechanical properties of the dry films formed from PEGTDMSO

Symp.	WFT	DFT	Bending	Pinhole	Adhesion	Hardness	Impact	Electrical conductivity
Y_0	145	50	fail	fail	fail	HB	fail	
Y_1	110	67	pass	pass	pass	F	fail	
Y_2	103	69	pass	pass	pass	F	pass	Insulating
Y_3	95	70	pass	pass	pass	H	pass	at200 'Ω
Y_4	95	72	pass	pass	pass	H	pass	
Y_5	93	75	pass	pass	pass	2H	pass	
Y_6	93	78	pass	pass	pass	2H	pass	

additives, but the WFT were decreased.

Adhesive forcing

The data of adhesive forces for the formed films from formula $Y_0 - Y_6$ with the surface of carbon steel alloy specimens were given in TABLE 5. From these data, the adhesive forces of the formed dry films from formula Y_0 was failed. On the other hand, the adhesive forces of the formed films from formula Y_1–Y_6 were passed. These data showed that, the adhesion forces increased by increasing the inorganic additives.

Electrical conductivity

The electrical conductivity data of the formed dry films on the surface of carbon steel alloy specimens were given in TABLE 5. The formation dry films from all formula were resisted the electricity until 200 ohm^{-1}.

Holiday (pinhole) detection

The data of holiday (pinhole) detection for the formed dry films from formula $Y_0 - Y_6$ were given in TABLE 5. These data were matched with the net results obtained from electrical conductivity. These films have good insulating properties and promising as insulators (protected) to the surface of carbon steel alloy at 275 Volt.

Thermal cycling test

The thermal cycling data for the formed films from the formula $Y_0 - Y_6$ were showed in TABLE 6.

TABLE 6: Thermal cycling tests (stability) of the dry films formed from PEGTDMSO at temperature ranged from 50 to 400°C and curing agent TDI

Temp. °C	Period time	Weight losses for each formed films x 10^{-4}						
		Y_0	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
50		3.1	1.7	1.6	1.5	1.5	1.5	1.4
75		3.9	2.1	1.9	1.7	1.7	1.7	1.9
100		6.1	2.5	2.3	2.1	2.1	2.1	1.9
125		6.5	2.0	2.1	2.1	1.7	1.7	1.5
150		5.7	1.9	1.7	1.5	0.9	0.9	0.7
175		4.3	1.2	1.0	0.9	0.5	0.5	0.3
200		3.1	0.9	0.7	0.5	0.0	0.0	0.0
225	6 hr's	1.1	0.7	0.2	0.2	0.0	0.0	0.0
250		failure	0.3	0.0	0.0	0.0	0.0	0.0
275		failure	0.0	0.0	0.0	0.0	0.0	0.0
300		failure	0.0	0.0	0.0	0.0	0.0	0.0
325		failure	0.0	0.0	0.0	0.0	0.0	0.0
350		failure	0.0	0.0	0.0	0.0	0.0	0.0
375		failure	failure	0.0	0.0	0.0	0.0	0.0
400		Failure	Failure	Failure	Failure	Failure	Failure	Failure

The degree of temperature was ranged from 50 to 400 ^{0}C by increasing 50^{0}C intervals. The formation a film from formula Y_0 was failed at 250^{0}C, while the formation films from Y_1 is failed at 375^{0}C and from Y_2 to Y_6 was failed at 400^{0}C.

Volatility of organic compounds

The volatility of organic compounds from the paints after curing was either estimated from the formulations and/or the use of organic solvent. In this situation the volatile organic compound were defined as blended organic solvent (toluene and xylene) and PEGTDMSO. Also, some methyl groups of the PEGTDMSO compound were hydrolyzed and evaporated (emission) during the curing process and the thermal effect on the formed films. Thus, the weight of the formed films decreasing until the weight was established.

Mechanical properties

The mechanical properties were investigated through hardness, bending and impact technique. The evaluation data of the mechanical properties for the formed dry films from formula Y_0 to Y_6 were given in TABLE 5. The mechanical properties data for the formed dry films on the surface of carbon steel alloy specimens were improved with increasing the amount of fillers / inorganic additives.

Mechanism

The presence of silicon on the surface of cured films were improved the properties of the formed dry films. Mar resistance, anti-blocking and other features were enhanced by the presence of silicon. Although PEGTDMSO gives very good properties to the surface of a cured coating. This was sufficiently compatible with formulation to provide adequate storage stability. The structure of PEGTDMSO compound was terminated by hydroxyl groups in the form of Si–OH / C-OH. Which was cured by cyano groups in TDI. The polyurethane siloxane films were formed as follow:

The PEGTDMSO urethane films include the variation of very important groups, such as ester, siloxane and urethane groups. These groups were played an important role in improvement of the physical, mechanical and chemical properties of the formed dry films on the surface of carbon steel alloy specimens.

Too, the traces of cyano groups of TDI were reacted with hydroxyl groups of silica gel, humidity and minor hydroxyl groups on the surface of specimens. Thus, the formation films of the polyurethane on surface of carbon steel alloy were highly compacted, adhesive, internal cohesion, hardness and also free from any pinholes. The silicon atom has tetra, penta- and hexavalent, these gives good physico-chemical properties.

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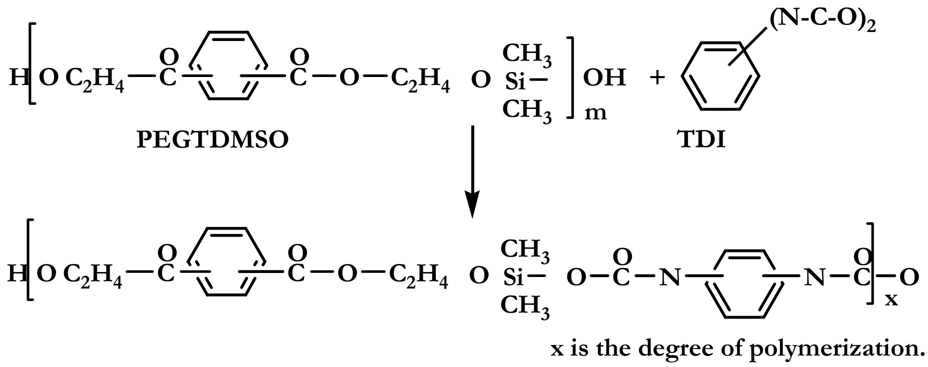

Poly(ethylene terephthalate urethane) film

Chemical properties

The effect of organic solvents

The effect of the mixture of benzene, toluene, xylene(ASTM D-44) on the texture morphology of the formed dry films of formula $Y_0 - Y_6$ were givenin TABLE 7. These data were indicated that, organic solvents do not affect the texture of the formed dry films from formula Y_1-Y_6. These were indicated on the compatibility of the binder with the inorganic filler/pigments and complete reaction with curing agent TDI. Thus, the formation of dry PEGTDMSO urethane films was resistant to the organic solvent, and can be applied in organic and petroleum media.

The formed dry PEGTDMSO urethane films from formula $Y_1 - Y_6$ did not affected on rubbing by MEK from 15-20 times (ASTM D-4752). These results were indicated that, the stability of zinc oxide and good compatible with the formed dry films.

Evaluation of the performance of the protected films

Effect of 10 % H_2SO_4

The data of the effective of 10% sulfuric acid (ASTM D 468 and 610) on the formed films from formula $Y_0 - Y_6$ are given in TABLE 8 . From these data, it is observed that the formed dry films from formula Y_0 are affected by 10 % H_2SO_4 after 10 days. On the other hand, the formation dry films from formula Y_1- Y_2 and Y_3-Y_4 were chalking only up to 16 and 20 days respectively, while the formed films from

TABLE 7: Visual inspection of the effect of the organic solvents (toluene, benzene, xylene) on the formed dry films from PEGTDMSO and curing agent TDI

Perior of immersion time (days)	Effect of the texture of the formed dry films						
	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
6	No charge	No charge	No charge	No charge	No charge	No charge	No charge
12	No charge	No charge	No charge	No charge	No charge	No charge	No charge
24	No charge	No charge	No charge	No charge	No charge	No charge	No charge
48	No charge	No charge	No charge	No charge	No charge	No charge	No charge
72	Partially swelling	Partially swelling	No charge	No charge	No charge	No charge	No charge

TABLE 8: Data of corrosion tests for the dry films formed from PEGTDMSO and curing agent TDI on the surface of carbon steel alloy specimens in 10% H_2SO_4 for 20 days

Period of immersion time (days)	Visual inspection for the dry films formed in 10% H_2SO_4						
	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
1	no spots	no spots	no spots	no spots	no spots	no spots	no spots
2	no spots	no spots	no spots	no spots	no spots	no spots	no spots
3	no spots	no spots	no spots	no spots	no spots	no spots	no spots
4	no spots	no spots	no spots	no spots	no spots	no spots	no spots
8	no spots	no spots	no spots	no spots	no spots	no spots	no spots
12	chalk surface	no spots	no spots	no spots	no spots	no spots	no spots
16	chalk surface	chalk surface	chalk surface	no spots	no spots	no spots	no spots
20	5 spots	3 spots	2 spots	chalk surface	chalk surface	no spots	no spots

TABLE 9: Corrosion tests data of the formed dry films on the surface of carbon steel alloy specimens in sea water for 60 days

Period time (days)	Visual inspection for the formed dry films						
	Y_6	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
3	no spots	no spots	no spots	no spots	no spots	no spots	no spots
6	no spots	no spots	no spots	no spots	no spots	no spots	no spots
9	no spots	no spots	no spots	no spots	no spots	no spots	no spots
12	1-5 spots	no spots	no spots	no spots	no spots	no spots	no spots
15	5-10 spots	no spots	no spots	no spots	no spots	no spots	no spots
18	10-14 spots	no spots	no spots	no spots	no spots	no spots	no spots
21	middle spots	no spots	no spots	no spots	no spots	no spots	no spots
24	middle spots	1-4 spots	no spots	no spots	no spots	no spots	no spots
36	much spots	low spots	no spots	no spots	no spots	no spots	no spots
48	covered spots	low spots	no spots	no spots	no spots	no spots	no spots
60	covered spots	much spots	1-5 spots	1-3 spots	1-3 spots	1-3 spots	1-2 spots

Y_5 and Y_6 were not affected. The 1-3 corrosion spots were appeared on the surface of the formed films from formula Y_1- Y_2 at 20 days. These ratios of corrosion spots were very low and should be neglected, (rust grade 8B ASTM D- 610), so that the formed dry films from formula Y_3- Y_6 were valid to protect the surface of carbon steel alloy against aggressive acidic media.

Effect of synthetic sea water (3.5% NaCl) on the formed PEGTDMSO urethane films

The data of the effect of synthetic sea water (3.5% NaCl) on the formed dry PEGTDMSO urethane films for 1440 hr (60 days) were given in TABLE 9. These results were indicated that the films formed from formula Y_2–Y_6 were valid for protecting the surface of carbon steel alloy against aggressive media. Generally, due to the ratio of spots to the total surface area was less than 0.1 %, (rust grade 8B ASTM D- 610), these spots should be neglected.

CONCLUSION

- The prepared PEGTDMSO purified and confirmed by ^{1}HNMR, FTIR and GPC.
- PEGTDMSO blended with inorganic additive ZnO_2, TiO_2, and silica to form formula Y_1 – Y_6.
- The preparation surface of carbon steel alloy specimens painted by formula Y_0 – Y_6.
- The physical, mechanical and chemical properties for the forming films from formula Y_0 Y_6 recorded and discussed.
- The net results indicating the validity of the formed dry films for protection of carbon steel alloy.

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