

Article

Study on a Novel Recyclable Anticorrosion Gel Coating Based on Ethyl Cellulose and Thermoplastic Polyurethane

Hailong Zhang ¹, Junlei Tang ^{1,2,*}, Hongchang Han ³, Shengwei Zhang ⁴, Hu Wang ^{3,*}, Yingying Wang ¹, Tian Li ⁴ and Bing Lin ¹

- ¹ School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China; hailong0902@126.com (H.Z.); yingyingwanglyon@126.com (Y.W.); h1900@foxmail.com (B.L.)
- ² State Key Laboratory of Oil and Gas Reservior Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
- ³ School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China; hongchang_han@163.com
- ⁴ AECC Chengdu Engine Co., Ltd., Chengdu 610500, China; zswabc1111@163.com (S.Z.); dongwu_13@163.com (T.L.)
- * Correspondence: tangjunlei@126.com (J.T.); senty78@126.com (H.W.); Tel./Fax: + 86-028-8303-7323 (J.T.)

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Abstract: In this paper, ethyl cellulose, thermoplastic polyurethane, and mineral oil were used as the main raw materials to synthesize a recyclable thermoplastic gel for anticorrosion coatings by a hot melt method. In addition, the effect of thermoplastic polyurethane on the properties of the coating was discussed. The structure and corrosion protection properties of the coating were characterized and analyzed by a scanning electron microscope, transmission electron microscope, X-ray diffraction, infrared spectroscopy, dynamic mechanical analysis, salt spray test, and electrochemical measurements. The results show that the ethyl cellulose and oil in the coating can form a stable organic-gel structure by hydrogen bonding, and the mineral oil and castor oil are uniformly dispersed in the coating. The surface of the coating does not change after 3000 h of a salt spray test. During the repeated hot melting spraying and immersion in 3.5 wt.% NaCl solution for five times, the electrochemical impedance modulus of the coating was always above $10^9 \Omega \cdot cm^2$, the water absorption rate was always less than 1.5 wt.%, and the mechanical properties of the coating did not decrease. This novel coating could be used for the corrosion protection of flange and valve connections in pipeline and bolting connections in different industries. The disassembly and assembly operation of these connection structures during the regular maintenance will destroy the ordinary anticorrosion coating, and the irregular geometric shape of such places also make difficulties for the preparation of ordinary coatings onsite.

Keywords: thermoplastic; ethyl cellulose; anticorrosion coating; recyclable gel; corrosion resistance

1. Introduction

Metals are prone to corrosion in the marine environment. In particular, the profiled structure with gaps and connection structures are the most susceptible to localized corrosion such as flanges, valves, welds, and bolts. Therefore, these parts have higher requirements for corrosion protection. The heavy-duty anticorrosion coatings are usually used to protect metallic constructions in marine corrosion [1–4]. However, for the mentioned particular structures, the good shielding property of anticorrosion coating not only depends on the nature of coating material but also requires high thickness and good elasticity of coating to cover the crevice and to withstand the structural deformation [5–8]. The recycling property of coating is desired because the disassembly and assembly operation of these



connection structures during the regular maintenance will destroy the ordinary anticorrosion coating. In addition, it is beneficial for environmental protection.

At present, most of the heavy-duty anticorrosive coatings are solvent-based crosslinking curing resins, such as epoxy resin [5,6], polyurethane [9], and acrylic resin [8,10]. In the process of connection structures installation and later maintenance, the disassembly and assembly operation are easy to cause damage to these coatings and reduce the protection performance of the coating. The peeled coating cannot be reused and needs to be resprayed, which not only causes environmental pollution but also wastes earth resources. Moreover, it is difficult to clean the complex surface of the connections effectively on site, which brings great challenges and difficulties for respraying the new coatings with a desired quality. Therefore, the solvent-based crosslinking curing coating is not good for these specific places.

Compared with crosslinking curing resins, thermoplastic resins have the characteristics of low energy consumption, solvent-free, and recyclable, and it is often used in the preparation of powder spraying coatings, such as polyolefine [11,12], polyamide [13,14], polyester [13,15], and polycarbonate [16,17]. However, these typical thermoplastic resins as mentioned previously have the characteristics of high hot melting temperature, poor flowability, high requirement for surface cleanliness of materials, complex spraying equipment, and more. Therefore, they are often used for indoor fabrication of protective coating in different industries [16–19], but not suitable for on-site spraying of coatings.

Ethyl cellulose (EC) is a commonly used cellulose derivative, which has the characteristics of the thermoplastic polymer and can be prepared by etherification of natural cellulose. It has excellent film forming properties, chemical resistance, and degradability [20]. It is often used as a coating additive [21–23] and medical film [24–26]. It is reported that ethyl cellulose has good compatibility with mineral oil and castor oil to form a stable oil gel, and the mechanical strength of the oil gel can be adjusted by changing the proportion of oil components [23]. Juan Yu et al. [27] prepared a series of thermoplastic elastomers with different strength and toughness from ethyl cellulose, fatty acids, and furfural. Abbaspoor et al. [28] prepared an ethyl cellulose capsule containing linseed oil by an emulsion-solvent evaporation method, and dispersed the capsule in the polyurethane coating to improve the corrosion resistance of the coating. According to previous studies, it is possible to develop a thermoplastic gel material with good chemical stability and good elasticity based on the advantages of ethyl cellulose, oil, and elastomer components.

Therefore, a recyclable anticorrosion gel coating composed of ethyl cellulose, thermoplastic polyurethane (TPU), and mineral oil was developed on carbon steel substrate in our study. The features and properties of the coating were investigated by a scanning electron microscope, a transmission electron microscope, X-ray diffraction, infrared spectroscopy, dynamic mechanical analysis, a salt spray test, and electrochemical measurements. This novel environmentally-friendly coating could be used for the corrosion protection of flange and valve connections in pipeline, and the bolting connections in different industrial environments, especially in the marine environment.

2. Materials and Methods

2.1. Materials

Mineral oil and castor oil were supplied by Kelong Chemical Reagent Company (Chengdu, China). The mineral oil was selected of viscosity about 12 cSt at room temperature and the boiling point is 255 °C. Castor oil contains 80% ricinoleic acid and 10% oleic acid with a boiling point of 330 °C. Thermoplastic polyurethane was produced by Taiwan sheen soon Co., Ltd.(Taiwan, China). Ethyl cellulose and TiO₂ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

Carbon steel Q235 with the composition of 0.2 wt.% C, 0.35 wt.% Si, 1.40 wt.% Mn, 0.045 wt.% P, 0.05 wt.% S, and balance Fe was used in this study. It was cut into sheets with different scales for different experimental requirements, which will be introduced in the relative experimental part, respectively.

2.2. Preparation of Gel and Coating

The gel material was prepared by the melt blending method. A total of 6.0 g of EC, 4.0 g of mineral oil, 2.0 g of castor oil, and 0.12 g of TiO_2 with a particle size of about 100 nm were mixed and heated with stirring at 180 °C. When the raw material was completely melted and mixed uniformly, it was cooled to obtain a C-EC gel. Similarly, 6.0 g of ethyl cellulose, 4.0 g of mineral oil, 2.0 g of castor oil, 2.0 g of TPU, and 0.14 g of TiO₂ were mixed and heated with stirring at 180 °C. When the raw material was completely melted and mixed uniformly, it was cooled to obtain a C-EC gel. Similarly, 6.0 g of ethyl cellulose, 4.0 g of mineral oil, 2.0 g of castor oil, 2.0 g of TPU, and 0.14 g of TiO₂ were mixed and heated with stirring at 180 °C. When the raw material was completely melted and mixed uniformly, it was cooled to obtain a C-EC/TPU gel. Anatase-TiO₂ was added to the coating to absorb ultraviolet light to improve the aging resistance of the coating.

The coatings about 2 mm thick with a thickness deviation of about 0.1 mm were prepared by hot melt spraying gel materials using a hot glue gun (HB700KD, Buhnen, Germany) on a carbon steel substrate with different scales.

2.3. Material Characterization and Property Measurement

The samples were mounted on SEM stubs with double-sided adhesive tape, and then coated with gold. A SEM (EVOMA15, ZEISS, Aalen, Germany) was used to observe the morphologies of the surface and cross sections of the coating at an accelerating voltage of 20 kV.

The structure of the sample was observed using a transmission electron microscope (TEM) (Tecnai G2F20S-TWIN, FeieiECTRONOptics, OR, USA) at an acceleration voltage of 200 kV. The ultra-thin cryo-section of samples were prepared for testing.

Fourier transform infrared spectra (FT-IR) of samples were recorded on a Nicolet 740 infrared spectrophotometer equipped. The spectra were recorded by averaging 32 scans at a resolution of 2 cm^{-1} from 4000 cm⁻¹ to 500 cm⁻¹.

The possible crystal structures of the samples were analyzed by X-ray diffraction. It was recorded by X-ray Diffraction (XRD) (X'Pert PRO, PANalaytical) with Cu Ka radiation, and the scanning angle was from 10° to 90°.

The dynamic mechanical analysis (DMA) of the samples were tested by DMAQ800. The sample was scanned at a temperature of 3 °C/min under a dry nitrogen blanket from -50 °C to 100 °C. Tan θ and storage modulus were collected at a frequency of 1 Hz.

The corrosion resistance of the samples was characterized by a neutral salt spray test in a 35 °C, and a 5 wt.% NaCl solution environment, according to ASTM B117-90. The sample size was 40 mm \times 80 mm \times 2 mm. The corrosion resistance of the sample was evaluated by observing the surface change of the sample during the 3000-h test.

The UV aging test of the coating was performed using Q-Lab's Quv/Spray accelerated aging equipment. The ASTM standard G154-Cycle1 was used. The coated samples with a size of 7.5 cm \times 15 cm were alternately exposed to UV radiation at 60 °C for 8 h in a cyclic manner, and then condensed in water at 50 °C for 4 h. The irradiance of the ultraviolet light was 0.89 W/m². The distance between the center of the lap and the sample is about 50 mm.

Electrochemical impedance spectroscopy (EIS) was measured using a three-electrode system by the Corr-Test electrochemical workstation. Platinum was used as the auxiliary electrode. The coated steel sheet was used as the working electrode. The sample size was 70 mm \times 70 mm \times 2 mm. The saturated calomel electrode (SCE) was used as the reference electrode. The EIS experiment was tested after the stabilization of open circuit potential. The amplitude of disturbance voltage was 20 mV and the frequency ranged from 100 kHz to 0.01 Hz. All electrochemical measurements were performed in 3.5 wt.% NaCl solution at room temperature.

2.4. Cyclic Spraying and Performance Test of Coating

The schematic diagram of the fifth melting cycle test of C-EC/TPU coating is shown in Figure 1. The sample size is $70 \text{ mm} \times 70 \text{ mm} \times 2 \text{ mm}$. The hot melt spraying of coating at $180 \degree$ C is shown in Figure 2. A total of nine parallel samples were used for the cycle test, including three of which were

tested for EIS, three were tested for tensile strength testing, and three were tested for water absorption testing. First, the tensile strength and the weight of the coating were measured. Then, the coating was immersed in a 3.5 wt.% NaCl solution and the electrochemical AC impedance was tested at the beginning of the immersion, and the electrochemical AC impedance of the coating was again tested after 30 days of immersion. For one parallel sample, the surface of the coating was dried first. Then, the coating was peeled off from the surface of the substrate, and the weight of the coating was weighed to calculate the water absorption after 30 days of immersion. For another eight parallel samples, the tensile strength of peeled off coating was measured after 30 days of immersion. Then, each coating sample was melted and resprayed on the surface of the substrate again. Five cycles of testing were performed in sequence.



Figure 1. Schematic diagram of the cycle performance of C-EC/TPU coating.



Figure 2. The hot melt-spraying of C-EC/TPU coating at 180 °C.

3. Results and Discussion

3.1. FT-IR Spectra

Figure 3 shows the infrared spectra spectrum of C-EC, C-EC/TPU, EC, and TPU. The peak at 3470 cm^{-1} was attributed to the vibration of the –OH group [29]. As shown in Figure 4g, EC is the product of cellulose after etherification reaction, but there are still many –OH groups on the EC molecule. In addition, the castor oil molecule contains –COOH, –C=C– and –OH groups. The peaks at 1640 cm⁻¹ and 1376 cm⁻¹ were attributed to the vibration of –COO and –C=C– on the castor oil molecule [30,31], respectively. Compared with the EC spectrum, the peak at 1100 cm⁻¹ in the C-EC spectrum was attributed to the vibration of the –C–O–C– group on the EC molecule. Compared with the EC and TPU spectrum, the peak at 1637 cm⁻¹ in the C-EC/TPU spectrum was attributed to the vibration of the superposition vibration of the C–N group on the TPU molecule and the –C–O–C– on the EC molecule [32]. The peaks at 1747 cm⁻¹ in the C-EC and C-EC/TPU spectra were attributed to the vibration of the ester C=O group, which may be due to the reaction of –COOH with –OH. As indicated from the IR results, no clear chemical reactions occurred between the functional groups of different molecules in two coatings except a small esterification reaction.



Figure 3. FT-IR spectra of C-EC and C-EC/TPU.

3.2. SEM Observation

Figure 4a,d show the surface and cross-sectional microscopic morphology of C-EC and C-EC/TPU coatings. Figure 4e,f were the "groove" width profiles in Figure 4b,d, respectively. Figure 4a,c show that the C-EC and C-EC/TPU surfaces were smooth with no clear defects. The cross-section of the C-EC coating had a number of "groove" structures with a scale of 3–10 μ m from Figure 4b,e. Figure 4d shows the C-EC/TPU cross-sectional microstructure. The C-EC/TPU cross-section was flatter and denser than the C-EC cross-section. The "groove" scale was concentrated at 1–2 μ m.

Although there is no clear chemical reaction between the main compositions of coatings from FT-IR analysis. EC and castor oil molecules had many unsubstituted hydroxyl and carboxyl groups. A strong hydrogen bond can be formed between these hydroxyl groups and carboxyl groups to form a cage construction [23,33]. The "sponge" morphology was observed in Figure 4b,d. Then, the mineral oil was filled in the cage construction. For the C-EC/TPU gel coating, the TPU molecule contains an amino group, which could form a hydrogen bond with the hydroxyl group and the carboxyl group as well. A crosslinking structure was formed by the bonding of EC, castor oil, and TPU molecules. The crosslinking and interpenetration networks made the internal structure of the cage construction more compact [34] in C-EC/TPU gel coating, as confirmed in Figure 4d,g. It indicated that TPU have a strengthening effect on gel coating.

3.3. TEM Observation

Figure 5 shows TEM images and energy dispersive X-ray spectroscopy (EDX) spectrum of C-EC and C-EC/TPU. The TiO₂ particles had a diameter of about 100 nm, and its edge was relatively smooth with the polymer. Anatase-TiO₂ was added to the coating to absorb ultraviolet light to improve the aging resistance of the coating. It indicated that TiO₂ had good compatibilities with the two coatings. No impurities were observed in the images, which indicates that the gel coating formed a homogeneous micro-structure on a nanoscale.







Figure 4. SEM images of (**a**) the surface of C-EC coating, (**b**) the cross-section of C-EC coating, (**c**) the surface of C-EC/TPU coating, (**d**) the cross-section of C-EC/TPU coating, (**e**) the "groove" scale profiles in Figure 4b, (**f**) the "groove" scale profiles in Figure 4d, (**g**) The C-EC and C-EC/TPU materials model the diagram.





Figure 5. TEM micrographs of the (a) C-EC, (b) C-EC/TPU, and (c) EDX spectrum.

3.4. XRD Analysis

Figure 6 shows the XRD pattern of the C-EC and C-EC/TPU. It can be seen that two coatings have almost the same patterns, which displayed typical peaks of semi-crystalline, since both patterns have an extremely broadened peak at 20°. It had been reported that the pure EC had a broad diffraction peak at around 20 of 20° [35]. TiO₂ peaks could be found in two samples at $20^{\circ} = 25.7^{\circ}$, 38.1° , 48.4° , 54.1° , 55.4° , 63° , 69° , 70.6° , 75.3° and 83° [36]. Furthermore, peaks at $20^{\circ} = 22^{\circ}$ and 24° could be attributed to methyl stearate [37], which is in accordance with the C=O group identified in the IR spectrum at the peak 1747 cm^{-1} .

The XRD spectra indicated that the C-EC and C-EC/TPU coatings have a similar crystalline structure in the polymer phase. Because castor oil contains more ricinoleic acid [38], the carboxyl group in ricinoleic acid could be esterified by reacting with the hydroxyl group to form a crystalline stearate.



Figure 6. X-ray diffraction pattern of the C-EC and C-EC/TPU.

3.5. DMA Analysis

Figure 7 shows the DMA spectra of C-EC and C-EC/TPU. It can be seen from Figure 7a that the storage modulus of C-EC decreased rapidly from 175 to 75 MPa at -44° C, with a decrease of about 57%. It increased to 100 from 75 MPa first and then dropped rapidly with the increase of temperature. When the temperature rises to 70 °C, the storage modulus of C-EC was close to 0 MPa. The storage modulus of C-EC/TPU was higher than 230 MPa when the temperature was lower than 10 °C. Then, it decreased rapidly and approached 0 MPa at 90 °C. As can be seen from Figure 7b, the tan θ of C-EC reaches a maximum at 58 °C, and the tan θ of C-EC/TPU reached a maximum at 83 °C.

There were many small oil molecules in the two coatings. The oil molecules may flow through grooves when the temperature rises. The intermolecular force gradually decreases with the increase of temperature. The increase of molecular motion will result in the decrease of the storage modulus. As discussed previously, the EC and castor oil molecules formed hydrogen bonds with each other because of hydroxyl and carboxyl groups. As the temperature increased, the hydrogen bond force decreased, which leads to the storage modulus of the material decreasing gradually [23]. Compared with the C-EC, the C-EC/TPU contains the amino group, and the amino group also has the hydrogen bond with the hydroxyl group and the carboxyl group. Furthermore, the energy needed to break the binding was increased. Therefore, the storage modulus of C-EC/TPU was higher than that of C-EC. After the addition of TPU, the loss factor peak shifted to a high temperature because the TPU chain length is longer than other materials, and the intermolecular force is enhanced by the action of hydrogen bonding, which reduced the molecular mobility [39,40]. Consequently, the mechanical property and thermal stability of C-EC/TPU is better due to the strengthening effect of TPU.



Figure 7. The relationship between (**a**) storage modulus and (**b**) loss factor $(\tan\theta)$ and temperature of C-EC and C-EC/TPU coatings.

3.6. Salt Spray Test and Ultraviolet Aging Test

Figure 8 shows the surface morphology of C-EC and C-EC/TPU coatings during the 3000-h salt spray test. It was found that no clear changes, such as cracking and discoloration, were observed on the surface of the two coatings during the test process. Therefore, the two coatings have passed the 3000 h of the salt spray test, according to ASTM B117-90 standard, which indicated that the two coatings both have good corrosion resistance. This was attributed to the excellent chemical stability of EC and TPU, and the oily components in the coatings also blocked the penetration of corrosive media.

Figure 9 shows the morphology of the C-EC and C-EC/TPU during the UV aging test. It could be seen that the surface of C-EC showed significant damage after 240 h of testing, but the surface of C-EC/TPU only slightly yellowed after 400 h of testing. It can be seen from Section 3.2 that EC and castor oil form a cross-linked interpenetrating network structure through hydrogen bonding in C-EC materials. In addition, EC, castor oil, and TPU worked together to form cross-linking and interpenetrating in C-EC/TPU materials. Since castor oil contains more –COOH and –C=C–, these reactive functional groups are easily destroyed by ultraviolet light [41]. Therefore, the skeleton structure of the C-EC material is easily destroyed, whereas the skeleton structure formed by TPU and EC in the C-EC/TPU is relatively stable. Therefore, the C-EC/TPU gel coating has a better corrosion resistant property.



Figure 8. Surface morphology of sample after 500 h, 1000 h, 2000 h, and 3000 h salt spray test.



Figure 9. Surface morphology of coating samples before and after UV aging.

3.7. Cyclic Performance of Coating

Figure 10 shows the EIS plots of two coatings immersed in a 3.5 wt.% NaCl solution for 150 days. Only one semi-arc in the Nyquist diagram at the time of both coatings and the maximum mode value was always more than $10^9 \ \Omega \cdot \text{cm}^2$ in the Bode diagram, in which the phase angle is very close to 90° in a wide frequency range as well. Figure 10e shows the change in coating resistance for each coating over 150 days, which is calculated from the EIS spectrum using an equivalent electrical circuit, as shown in Figure 10f. R_S is the solution resistance, and Q and R_p are the coating capacitance and the coating resistance, respectively [42]. It can be seen from the figure that the R_p value has a certain decrease seven days before the start of immersion, and gradually increases during the immersion to 90 days, and finally gradually stabilizes. This may be due to the presence of some surficial graves in the coating that were not completely full filled with oil. In that case, the aqueous solution can quickly seep into

these graves during the initial immersion time. As the immersion time increased, the oil inside the coating gradually diffused toward the coating surface and some of the permeated aqueous solution was squeezed out. Lastly, the diffusion rate of oil to the surface and the penetration rate of the aqueous solution to the inside reached equilibrium.



Figure 10. The EIS measurements during 150 days immersion in 3.5 wt.% NaCl solution, (**a**) the Nyquist plot of C-EC gel coating, (**b**) the Bode plot of C-EC gel coating, (**c**) the Nyquist plot of C-EC/TPU gel coating, (**d**) the Bode plot of C-EC/TPU gel coating, (**e**) the coating resistance change, and (**f**) the equivalent electrical circuit.

However, the R_p values of C-CE/TPU gel coating were always higher than that of C-CE gel coating. The EIS measurement also revealed the C-CE/TPU gel coating had better corrosion resistance. Therefore, the recycling performance was further studied for the C-EC/TPU gel coating.

Figure 11 shows the electrochemical impedance spectroscopies of C-EC/TPU gel coating during five cycles in 3.5 wt.% NaCl solution. When the impedance data before 30 days of immersion of each cycle with the one after was compared, it could be seen that the diameter of the semi-arc decreases in the Nyquist diagram after immersion. This indicates that the water molecules have started to permeate from the coating surface to the inner surface with the extension of immersion time [43,44]. However, there was only one semi-arc in the Nyquist diagram at the time and the maximum mode value was always more than $10^9 \ \Omega \cdot cm^2$ in the Bode diagram, in which the phase angle was very close to 90° in a wide frequency range. It indicated that the corrosive solution had never permeated deep and far away from the coating/carbon steel substrate interface.

In order to further analyze the EIS results, all the electrochemical impedance spectroscopy were fitted with the equivalent circuit diagram model in Figure 10f. The fitting results are shown in Table 1. Figure 12 shows the variation of the R_p value and the sample weight change with the number of cycles. It could be observed that the value of R_p decreased to a certain extent and the coating weight increased to a certain extent after immersion in each cycle, which indicates the permeation of water molecules into the coating. However, the value of R_p was always greater than $10^9 \ \Omega \cdot cm^2$ in the process of five cycles, and the weight increase of the coating was less than 1.5% after immersion at the same time. As shown in Figure 13, the tensile strength of the sample was tested after each melting cycle. It could be seen that the tensile strength fluctuates 1.5 MPa and did not decrease significantly.

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Test Conditions		$R_s (\Omega \cdot \mathrm{cm}^2)$	Q (F·cm ⁻²)	$R_p (\Omega \cdot cm^2)$	n
Before the cycle	Before immersion	5.420×10^{-2}	1.3×10^{-9}	6.454×10^9	0.9523
	After immersion	4.01×10^{-3}	1.063×10^{-9}	4.331×10^9	0.9495
Cycle once	Before immersion	3.805×10^{-4}	1.033×10^{-9}	5.193×10^9	0.9517
	After immersion	1.023×10^{-2}	9.553×10^{-10}	3.357×10^9	0.9610
Cycle 2 times	Before immersion	2.45×10^{-3}	1.035×10^{-9}	3.402×10^9	0.9533
	After immersion	7.67×10^{-3}	9.929×10^{-10}	1.191×10^9	0.9590
Cycle 3 times	Before immersion After immersion	$\begin{array}{c} 1.487 \times 10^{-2} \\ 2.42 \times 10^{-3} \end{array}$	1.023×10^{-9} 1.021×10^{-9}	1.898×10^9 1.491×10^9	0.9553 0.9538
Cycle 4 times	Before immersion	8.07×10^{-3}	1.049×10^{-9}	3.102×10^9	0.9519
	After immersion	1.196×10^{-2}	1.07×10^{-9}	2.055×10^9	0.9506
Cycle 5 times	Before immersion After immersion	$\begin{array}{c} 1.953 \times 10^{-4} \\ 4.17 \times 10^{-3} \end{array}$	1.073×10^{-9} 1.029×10^{-9}	2.870×10^9 2.015×10^9	0.9512 0.9525

Table 1. The electrochemical fitting parameters of EIS of C-EC/TPU coating for five cycles.

Because the chemical components in the C-CE/TPU gel coating were aggregated by the hydrogen bond to form the gel coating and the hydrogen bond is reversible. The melting and spraying process will not change the microstructure of coating. Figure 14 is the FT-IR spectrum of C-CE/TPU after 10 times of melting. It shows that no functional group has changed during re-melting, which indicates that the chemical composition and chemical bonding are both stable during the cyclic melting. The boiling point of mineral oil is above 250 °C [45] and that of castor oil is above 330 °C [38]. There was no loss of oily components in the process of repeated heating and melting at 180 °C. At the same time, the water molecules, which have permeated into the coating, will evaporate to the air at the same temperature. It means the cyclic melting treatment has a healing effect on the gel coating. It is the reason why the decrease of coating weight and the recovery of coating resistance after each melt-spraying can been seen in Figure 12. From the above discussion, it could be concluded that the C-CE/TPU gel coating maintains good corrosion resistance and a stable mechanical property in cyclic tests because it has very good thermoplastic property, thermostability, and healing property due to the specific chemical composition and microstructure of this ethyl cellulose and TPU-based gel material.



Figure 11. Cont.



Figure 11. Electrochemical impedance spectra of C-EC/TPU coating for five cycles. The black square point stands for EIS of the initial state of coating while the red triangle point stands for the EIS after 30 days of immersion in 3.5 wt.% NaCl solution. The line was the fitting results: (**a**,**b**) cycle 0, (**c**,**d**) cycle 1, (**e**,**f**) cycle 2, (**g**,**h**) cycle 3, (**i**,**j**) cycle 4, (**k**,**l**) cycle 5.



Figure 12. The change of the R_p value and the weight change rate of the C-EC/TPU under different cycle test times.



Figure 13. The tensile strength of the C-EC/TPU changes under different cycle test times.



Figure 14. The FT-IR spectrum of the C-EC/TPU gel coating after 10 times of melting at 180 °C.

4. Conclusions

In this paper, a recyclable anti-corrosive coating was prepared on carbon steel using the melt spray method from a novel organogel, which is synthesized by melt blending ethyl cellulose, thermoplastic elastomer, and oil together. The crosslinking structure was formed by the hydrogen bonding effect of EC, castor oil, and TPU molecules with each other, which formed a cage construction. Then the mineral oil was filled in the cage construction to form a thermoplastic gel. SEM and TEM observations show that the gel coating was dense and uniform in the microstructure, and it is composed of amorphous phase and crystalline phase as detected by XRD. The DMA measurement and tensile strength test revealed the TPU can also strengthen the mechanical property.

The neutral salt spray test, ultraviolet aging test, and EIS measurement show that the gel coating has good corrosion resistance. The cyclic performance of C-EC/TPU was further studied by EIS, weight measurement, infrared spectroscopy, and tensile strength test. After five cycles, the impedance value of the coating in EIS test was always higher than $10^9 \Omega \cdot \text{cm}^2$, and the weight change rate of the coating was always less than 1.5% after 30 days of immersion. The tensile strength of the coating material did not decrease. They are attributed to the good thermoplastic property and the good chemical stability

of the gel coating. In addition, the healing property of the gel coating in the re-melting could improve the corrosion resistance in cyclic utilization.

The features of this novel coating are very different from the ordinary thermoplastic resin-based coating, that make it possible to be used for the corrosion protection of flange and valve connections in pipeline, and the bolting connections in different industries.

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