

Article

Preparation and Properties of Impact Resistant Polyurea Coating for Fluorochemical Pipeline

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Abstract: A new type of high elastic polyurea protective coating reinforced by nano silica is prepared by filler composite in order to avoid both the leakage of fluorine chemical pipelines containing highly toxic and dangerous media as well as the damage to fluorine chemical pipelines under impact loads. The aim is to improve the intrinsic safety of fluorine chemical pipelines and ensure the safety of the ecological environment, life and property. The effects of different processes and process parameters on the properties of polyurea coating were studied. The polyurea coating was blended and strengthened with nano silica modified by silane coupling agent KH-550. The suitable stirring speed, material addition sequence and nano silica concentration of the new polyurea material were put forward to prepare a new polyurea coating with excellent properties. The properties of the polyurea coating were characterized, including curing time, tensile strength, elongation at break and impact resistance. Then, by using the numerical simulation method, the protection law of polyurea coating on fluorochemical pipelines with or without polyurea coating under the impact of small balls with different speeds was studied, and the equivalent stress mitigation and energy absorption mechanism of polyurea coating were analyzed from the perspective of macro and micro mechanisms. The results show that silane coupling agent KH-550 has successfully modified nano silica, and the optimal filling concentration of modified nano silica is 4 wt%. At this time, the tensile strength of filled reinforced polyurea coating is increased to 15.7 MPa, the elongation at break is 472%, the hardness is 61 HA, and the impact resistance of the matrix material is increased by 9.7 kJ/m². This shows that the polyurea reinforced by nano silica has excellent mechanical properties and impact resistance. The simulation results show that the polyurea coating can slow down the impact caused by the equivalent stress of small balls at different speeds. When the ball speed is 5 m/s, the equivalent stress of polyurea coating slows down to 49.3%, and the percentage of reduction of the impact caused by the equivalent stress of the polyurea coating decreases gradually with the increase of ball impact speed.



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1. Introduction

As a sub industry of the chemical industry, the fluorine chemical industry has formed four categories of fluorine chemical product systems from the 1950s to the present [1]. There are many kinds of products with excellent performance in this industry, which are widely used in machinery, electronics, metallurgy, the military industry and other fields. In the process of producing these high-performance products, the materials between different process flows are generally transported through pipelines, as shown in Figure 1. Because most of the raw materials and products transported in the fluorine chemical pipeline are toxic, harmful, flammable, explosive and highly corrosive chemicals, once the pipeline leaks, it poses a great threat to the ecological environment and the safety of life and property [2].



Figure 1. Fluorochemical pipeline.

Generally, fluorine chemical pipelines will not leak in the normal service stage, but if the pipeline is subjected to impact loads such as accidental collisions and object drops, this will often produce large stress and energy in the contact area, resulting in material failure. At present, the protection of impact loads mainly includes the addition of lightweight materials outside the device that can weaken the external impact load. These kinds of materials generally have good mechanical properties and certain energy absorption [3]. Currently, most of the commonly used lightweight protective materials are fiber-reinforced polymers, which generally have the characteristics of high modulus and high strength [4–6]. However, during the use of this material, peeling and delamination with the matrix structure will occur, resulting in brittle fractures, which cannot meet the use requirements [7].

As a new lightweight protective material, polyurea coating has excellent mechanical properties, is green and pollution-free, is waterproof and anti-corrosive, and has vibration damping and wear resistance [8]. Scholars at home and abroad have studied the mechanical properties of polyurea materials and found that its mechanical behavior is complex and has obvious strain rate effects and pressure correlations [9–13]. Additionally, scholars have studied the protective performance of polyurea coating and found that it can effectively reduce the load peak and impact energy of impact loads on matrix materials [14–17].

In order to prepare polyurea coating for fluorochemical pipelines with excellent impact resistance, the polyurea coating needs to have appropriate mechanical strength and mechanical ductility and must effectively absorb impact energy. Adding different nano materials during preparation can enhance the mechanical properties of polyurea coating so as to enhance the impact protection performance of the coating [18,19]. As a common nano reinforcing material for rubber, plastics and polyurethane, nano silica has the advantages of being light weight, non-toxic and tasteless, with stable chemical properties and high temperature resistance. Its molecular structure is a three-dimensional chain structure, and hydroxyl groups in different bonding states exist on the surface, which can significantly enhance the mechanical properties of the matrix material [20–23]. In recent years, there has been considerable research on the use of nano silica to strengthen polyurethane, but the polyurethane main chain contains more polar groups that are easy to hydrolyze, and its water resistance is poor. Moreover, when the temperature is high, the hydrogen bond in polyurethane molecules will break. Because of its poor water resistance and thermal stability, polyurethane is not suitable for fluorochemical pipelines. As a new protective material, polyurea is waterproof, wear-resistant, aging resistant and has thermal stability. It has great prospects in the safety protection of fluorochemical pipelines. However, at present, there are few studies on the use of nano silica to strengthen polyurea coating. Due to the similar structures of polyurethane and polyurea, the strengthening effect of nano

silica on polyurea materials is explored by understanding the principle and method of nano silica's strengthening polyurethane. However, nano silica has large specific surface energy, small particle size, easy agglomeration and poor compatibility with polyurea. If nano silica is directly used to fill polyurea materials, the mechanical properties of polyurea materials will change little or even decline. Silane coupling agent KH-550 can be used to modify nano silica to increase the compatibility between nano silica and polyurea materials so as to improve the mechanical strength, toughness and aging resistance of polyurea materials.

At present, polyurea coating is widely used in the field of safety protection. For example, polyurea is mostly used in the waterproofing of internal and external walls of buildings, underground water transmission and sewage pipelines, as well as the anti-seepage and leak-proof treatment of water bodies such as large and small natatoriums, various plant sewage treatment reaction tanks, reservoirs and dams, and the construction of filling building cracks. Polyurea coating can also be used for corrosion and wear resistance in the petrochemical field, shock absorption protection in the automotive field and safety protection in the high-speed railway field. However, there is no research on the protection of fluorochemical pipelines. In order to obtain the polyurea coating with excellent performance and the ability to be used for fluorochemical pipelines, nano silica reinforcement is added in the preparation process of polyurea, and the properties of the prepared polyurea coating, such as curing time, tensile properties and impact resistance, are characterized. Finally, the finite element numerical simulation technology is used. The mechanical behavior of a small ball impacting the fluorochemical pipeline under different working conditions was studied. The research results of this paper will provide a new research direction for researchers in this field and provide a reasonable theoretical and experimental basis for future scientific work.

2. Preparation of Polyurea Coating

The preparation of polyurea material mainly includes three parts: the preparation of modified nano silica, the preparation of isocyanate prepolymer (component A) and the synthesis of polyurea coating. There are many kinds of raw materials and process methods for preparing polyurea coating. The properties of polyurea coating prepared under different group distribution ratios and process parameters are obviously different. To prepare polyurea coating with excellent performance, the group distribution ratio and process parameters of polyurea should be strictly controlled.

2.1. Main Raw Materials

Diethyltoluenediamine: analytical pure (Jiangsu Victory Chemical Co., Ltd, Jiangsu, China); nano silica: the average particle size is 12 nm (Shanghai Kaiyin Chemical Co., Ltd, Shanghai, China); KH-550: analytical pure (Chengdu Yuanda Chemical Co., Ltd, Chengdu, China); Diisocyanate prepolymer and deionized water: self-made; Ethyl acetate and absolute ethanol: analytical pure, Sinopharm Chemical Reagent Co., Ltd, Hangzhou, China); BYK-310, BYK-358N: surface additives, Shanghai Kaiyin Chemical Co., Ltd, Shanghai, China).

2.2. Test Process

2.2.1. Preparation of Modified Nano Silica

Weigh a certain amount of nano silica with a weighing scale, add it to the 1:1 mixed solution of absolute ethanol and water, stir it with a magnetic stirrer for about 10 min, and disperse it by ultrasonic for 15 min. Weigh an appropriate amount of silane coupling agent KH-550 and add it to the deionized aqueous solution for hydrolysis, then take a certain amount of modified aqueous solution and add it to the nano silica mixed solution, stir and ultrasonic disperse for 15 min. Heat the obtained uniform suspension and reflux it at 80 °C for 2 h, then centrifuge the suspension in a centrifuge. Wash the modified nano silica with absolute ethanol to remove KH-550 on the surface, then dry it in an oven at 80 °C for 12 h and grind it for standby.

2.2.2. Preparation of Component A

Diisocyanate prepolymer (component A) is one of the most important components of polyurea coating. It is necessary to strictly control the process parameters in the preparation process so as to ensure the product quality of polyurea coating.

Pour an appropriate amount of isocyanate prepolymer into a teflon beaker to weigh the mass of the isocyanate prepolymer. Place the mixing drum on the mixing table, center the mixing drum through the centering knob, and then add the isocyanate prepolymer into the mixing drum. Turn on the mixer and slowly increase the speed of the mixer until the speed is adjusted to about 200 r/min. Take a certain quality of modified nano silica, slowly add it into the mixing bucket and stir for 10 min. Then, add rheological additives BYK-310, BYK-358N and oleic acid into the mixing drum, keep the rotating speed unchanged and stir for about 3 min. After mixing evenly, weigh a certain mass of ethyl acetate with a weighing scale, and add ethyl acetate to the mixing barrel for mixing and dilution. Slowly increase the rotating speed to 500 r/min and stir for about 5 min. Weigh a certain amount of Sudan Blue II with a weighing scale and slowly pour it into the mixing bucket for color matching. Increase the rotating speed of the mixer to 800 r/min and stir for about 20 min to obtain component a of polyurea elastomer.

Preparation process control: The mixing speed of the mixer is an important factor to ensure the quality of component A. When the speed is too slow, the mixing vortex is relatively shallow, the contact degree between different particles is low, and it cannot be fully mixed or it may take a long time to mix evenly (as shown in Figure 2). Moreover, when the velocity is too low, the equilibrium particle size of particles will be relatively low, so it is difficult to achieve the enhancement effect. When the speed is accelerated, the equilibrium particle size of particles is reduced, and the contact probability between components is increased. However, if the speed is too fast, it will not only have requirements for instruments and working conditions that are too high, but it will also produce large stirring heat and affect the product quality. It has been verified by many tests that in order to obtain isocyanate prepolymer with uniform particle dispersion and appropriate particle size, the rotating speed of the mixer should reach at least 780 r/min.

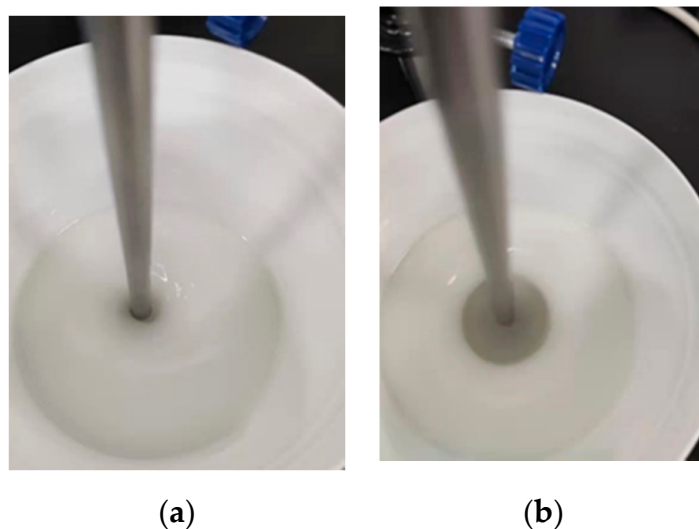


Figure 2. Stirring vortex of component A at different stirring speeds. (a) Low speed stirring; (b) high speed stirring.

The addition sequence of raw materials is also an important factor affecting the preparation of component A. Although different addition sequences will not lead to the formation of other products, if ethyl acetate, as diluent, is added too early, the viscosity of component A will be too low, the intermolecular shear force will be too small, and it will be difficult to obtain nano silica powder with uniform mixing and appropriate particle size.

If ethyl acetate is added too late, the viscosity of component A will be too high, and the friction heat between molecules will accumulate too much, resulting in the reduction of product quality.

2.2.3. Synthesis of Polyurea High Elastomer Coating

For the synthesis of polyurea, the prepared isocyanate component, a prepolymer shall be evenly mixed with component B amine curing agent to make the isocyanate group react with the amine group to form the urea group. The specific operations are as follows:

Take a certain amount of component A and pour it into a Teflon beaker. According to the concentration ratio, take out a certain amount of component B curing agent, mix and stir for about 15 min. Apply the mixture of component A and component B evenly on the polished sample plate and stand to obtain polyurea product (as shown in Figure 3).

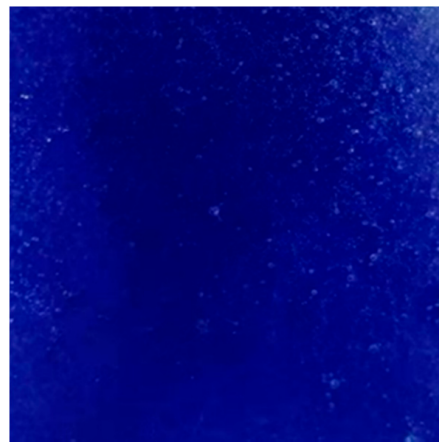


Figure 3. New polyurea coating.

3. Performance Test

3.1. Density

Density is an important physical property of polyurea coating, which greatly affects the product quality. As a lightweight protective material, the density of polyurea coating is generally much less than the matrix density. If the density of the polyurea coating is too high, it will increase the weight of the device and affect the service quality. Due to the small amount of modified nano silica, the density of the polyurea coating is basically the density of the matrix resin. Using pycnometer, the density of the polyurea coating is $1.06 \text{ g}\cdot\text{cm}^{-3}$.

3.2. Hardness

An appropriate coating hardness is the prerequisite to ensure that the polyurea coating has good energy absorption characteristics. According to the standard GB/T531.1-2008, the hardness of polyurea coating filled with different concentrations of modified nano silica is measured.

It can be seen from Table 1 that the hardness of the polyurea coating increases with the addition of modified nano silica. The hardness of the polyurea coating is generally negatively correlated with its flexibility and ductility. The smaller the hardness of polyurea coating is, the greater the flexibility and ductility. Greater flexibility and ductility are conducive to the energy absorption of the polyurea coating. However, the hardness of polyurea coating is positively correlated with the mechanical strength of the polyurea material. Generally, the higher the mechanical strength of the polyurea coating, the higher the hardness. Larger mechanical strength is also conducive to the energy absorption of the polyurea coating.

Table 1. Hardness of polyurea coating filled with different modified nano silica concentrations.

Addition Amount of Silica/(wt%)	Hardness of Coating/(HA)
0	59
1	60
2	60
3	60
4	61
5	61

3.3. Curing Time

When the polyurea coating is applied to the surface of the fluorinated pipeline, the influence of the curing time of the polyurea material on the construction process of the polyurea coating must be considered. If the curing time is too long, and the polyurea coating applied on the surface of the fluorination pipeline has not been cured in time, this will lead to the flow of the polyurea material coating under the action of gravity, resulting in uneven thickness of the polyurea material coating on the fluorination pipeline. When the curing time is too short, the requirements for processing equipment will be higher, and the polyurea material coating may not flow evenly. Furthermore, there will still be defects such as bubbles and bulges in the coating, which seriously affect the service quality of the polyurea coating on the fluorination pipeline.

According to the provisions of GB/T1728-79, it is necessary to take a certain amount of isocyanate prepolymer and amine curing agent B and mix and stir evenly according to a certain proportion. The average curing time is about 33 min.

3.4. Tensile Test

According to the requirements of GB/T528, the polyurea material for the fluorinated pipeline is made into dumbbell type and right-angle tear type samples for the performance test, and then the universal tensile machine is used for the tensile test of the polyurea material.

According to the data in Table 2, the tensile properties of the polyurea coating can be significantly affected by filling the polyurea coating with modified nano silica, and the additional amount of nano silica is an important factor affecting the quality of the polyurea coating. When the amount of silica is low, the tensile strength of the polyurea increases significantly with the increase of the amount of nano silica, and the enhancement effect is the most obvious when the amount of modified nano silica is 4 wt%. However, when the concentration of modified nano silica continues to increase, the tensile strength of the polyurea materials will be significantly reduced due to the agglomeration of nano silica in the polyurea coating materials. The elongation at the break of the polyurea coating is negatively correlated with the addition of modified nano silica. Due to the addition of nano silica, the elongation at the break of the polyurea material decreases, but the elongation at the break decreases to a lesser extent compared with the tensile strength. The tear strength of the polyurea is positively correlated with the amount of nano silica, but the change in the tear strength of the polyurea is not sensitive to the concentration of nano silica. The main material parameters of nano silica reinforced polyurea prepared this time are shown in Table 2.

Table 2. Tensile properties of polyurea coatings modified by nano-sized dioxide with different concentrations.

Addition Amount of Silica (wt%)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (kN/m)
0	10.1	489	55
1	12.7	486	57
2	13.6	480	57
3	14.8	475	58
4	15.7	472	58
5	13.9	463	58

3.5. Impact Performance Test

Under impact loads, the load action time is short, the load peak and impact energy are large, and the mechanism of load acting on the matrix is complex. In order to explore the enhancement effects of the new polyurea coating on the impact toughness of the matrix material, the new polyurea coating was coated on the surface of the matrix, and the impact sample was made with a cutting knife. The impact strength of the polyurea coating on the matrix material was studied by a drop weight tester.

Place the hammer head of the drop hammer tester at the same angle, and the samples adopt V-notch. First, the impact toughness of the matrix material without polyurea coating is measured to be 16.6 kJ/m^2 . Then, explore the influence of different nano silica additions on the impact toughness of the matrix (as shown in Table 3).

Table 3. Impact strength of matrix with different nano silica content.

Addition Amount of Nano Silica (wt%)	Impact Strength of Matrix (kJ/m^2)
0	22.9
1	23.7
2	24.5
3	25.9
4	26.3
5	26.1

The test results show that the impact strength of the matrix material is 16.6 kJ/m^2 compared with that without polyurea coating, and the impact strength of the matrix after polyurea coating is significantly improved. This is because the area density and bending stiffness of the matrix material will increase significantly after coating with polyurea, which increases the impact resistance of the matrix material. The impact resistance of the matrix is approximately positively correlated with the amount of nano silica, and the impact strength of the matrix is highest when the amount of nano silica is 4 wt%. This is because, with the increase of nano silica content, the tensile strength, hardness and tear strength of the polyurea coating increase, and the reinforcement effect is the best when the nano silica content is 4 wt%.

By continuously optimizing the preparation process parameters, the main raw material formula and main material parameters of the modified nano silica reinforced polyurea are shown in Tables 4 and 5.

Table 4. Main formula of new polyurea coating.

Component	Consumption (wt%)
Isocyanate prepolymer ($\text{-NCO} = 4.75\%$)	58.34
Diethyl toluene diamine	21.22
Modified nano silica	4.00
Ethyl acetate	15.88
BYK-310	0.13
BYK-358N	0.13
Oleic acid	0.15
Sudan blue II	0.15

Table 5. Main test parameters of polyurea coating.

Coating Properties	Material Parameters
Density/ $(\text{g}\cdot\text{cm}^{-3})$	1.06
Hardness/(HA)	61
Curing time/min	33
Tensile strength/MPa	15.7
Tear strength(kN/m)	58
Elongation at break	472%
Strengthening effect of matrix impact toughness(kJ/m^2)	9.7

4. Numerical Simulation Study

4.1. Example Verification

In order to verify the correctness of the finite element calculation model, the finite element simulation technology is used to establish the same mechanical model as in the literature [24] (as shown in Figure 4). The diameter of the impacted flat head cylinder is 15 mm, the length is 30 mm and the mass is 41 g. The thickness of the pipe is 3.46 mm and the outer diameter of the pipe is 115 mm. The Cowper–Symonds material model is selected, and the fracture strain failure criterion is adopted. The penalty function contact algorithm is selected. The friction coefficient between cylinder and pipe is set to 0.3, and the grid size of the pipe is set to 2.5 mm.

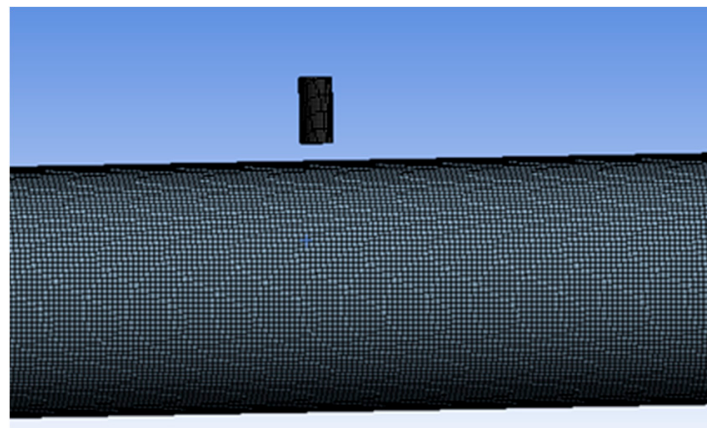


Figure 4. Simulation model.

The simulation results show that the critical fracture velocity of the pipeline is 185 m/s, and the critical fracture velocity of the experimental pipeline is 181 m/s, with an error rate of 2.21%. The critical failure energy of the pipeline is 701.59 J, the critical failure energy of the experimental pipeline is 671.6 J and the error rate is 4.47%. The simulation results are consistent with the experimental results in an acceptable range, which shows that the finite element mechanical model and finite element simulation results are reliable.

4.2. Establishment and Grid Division of Pipeline Model in Fluorine Chemical Industry

The mechanical response of fluorination pipelines under impact loads is simulated by finite element software ANSYS Workbench/LS-DYNA, and the deformation of the fluorination chemical pipeline during impact is analyzed. The Lagrange algorithm is adopted in this simulation. In order to improve the calculation efficiency of the numerical simulation and obtain the more regular mechanical behavior of the fluorinated pipeline, the feasibility of the simulation model is simplified, and the boss and rotation angle in the model that have no substantive impact on the simulation results are ignored. The three-dimensional model of the fluorination pipeline is established by Creo three-dimensional modelling software. The inner diameter is 10 cm, the outer diameter is 12 cm and the length is 100 cm. The next step is to establish the three-dimensional model of the polyurea coating shell, set its thickness as 0.5 cm, assemble the fluorochemical pipeline and polyurea shell as an assembly according to the assembly relationship, and then establish an impact ball with a radius of 5 cm and place it in a fixed position directly above the fluorochemical pipeline. Because there is no large-sized mutation in the appearance of the fluorine chemical pipeline, tetrahedral grid division is adopted, and the number of grids is 2086.

4.3. State Equation and Material Parameter Selection

Polyurea coating is a super viscoelastic body with obvious pressure sensitivity. Its stress–strain curve is nonlinear. It is generally expressed by the Mooney–Rivlin model with

2 parameters. The strain energy function expressed by the left Cauchy tensor invariant is used to describe the mechanical response characteristics of super elastic materials:

$$W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) \quad (1)$$

I_1 and I_2 are first-order and second-order strain invariants, respectively. C_{10} and C_{01} are material constants, which can be inversely calculated by the method in the literature [25]. The main material parameters of polyurea coating are shown in Table 6.

Table 6. Main material parameters of polyurea coating.

$\rho/(\text{g}\cdot\text{cm}^{-3})$	C_{10}	C_{01}	σ_b/MPa
1.06	0.03	0.48	15.7

The impact ball and fluorochemical pipeline are simulated by the structural steel material model, and the strain rate effect is reflected by the Cowper–Symonds model.

$$\sigma_Y = \left[1 + \left(\frac{\dot{\epsilon}}{C} \right)^{\frac{1}{P}} \right] \sigma_0 \quad (2)$$

where σ_Y is the dynamic yield stress, σ_0 is the static yield stress, $\dot{\epsilon}$ is the strain rate, C and P are the strain rate parameters and the main material parameters of the fluorochemical pipeline and impact ball are shown in Table 7.

Table 7. Main material parameters of pipeline and impact ball.

E/MPa	$\rho/(\text{g}\cdot\text{cm}^{-3})$	ν	C/s^{-1}	P
210	7.85	0.3	13.8	5

4.4. Impact Load Condition Simulation

The LS-DYNA module in the ANSYS Workbench is used to simulate the mechanical response of the fluorochemical pipeline with/without polyurea coating under impact loads. It is assumed that the fluorochemical pipeline is fixed on the ground surface, and the unit surface of the fluorochemical pipeline away from the impact ball is the fixed constraint. Because the polyurea coating has strong adhesion to steel, the polyurea coating is set to bind and contact with the fluorochemical pipeline. In order to simulate the impact load under real working conditions, it is necessary to give the small ball an initial velocity of 5 m/s along the Z direction and check the equivalent stress nephogram of the fluorochemical pipeline with/without polyurea coating (as shown in Figures 5 and 6).

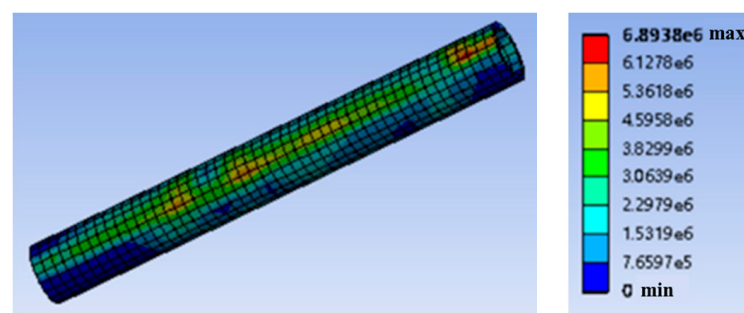


Figure 5. Cloud diagram of equivalent stress of fluorochemical pipeline without polyurea coating.

The simulation results show that the equivalent stress of the fluorine chemical pipeline without polyurea coating is 6.9 MPa when impacted by a 5 m/s small ball, and the equivalent stress of the fluorine chemical pipeline with polyurea coating is 3.5 MPa when impacted

by a 5 m/s small ball. This shows that polyurea coating on the fluorochemical pipeline can effectively reduce the equivalent stress of impact loads on fluorochemical pipelines. When the impact velocity of the small ball is 5 m/s, the equivalent stress is reduced by about 49.3%.

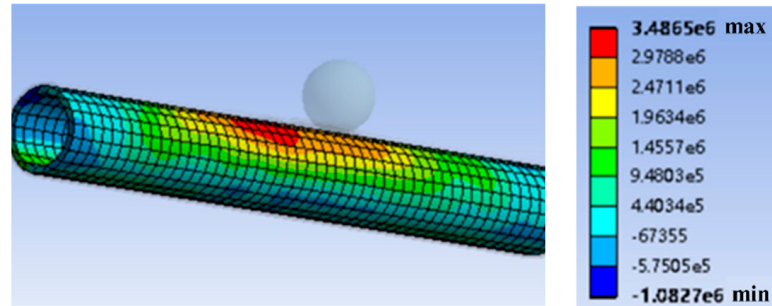


Figure 6. Equivalent stress cloud diagram of fluorochemical pipeline coated with polyurea coating.

In order to study the protective effect of polyurea coating on the impact of small balls with different speeds, the algorithm control, boundary conditions and contact type of the finite element solution are set to remain unchanged. Only the impact speed of the small balls is changed, and the ball speeds are set as 5 m/s, 6 m/s, 7 m/s, 8 m/s and 9 m/s, respectively, to view the equivalent stress response of the fluorochemical pipeline (as shown in Figure 7).

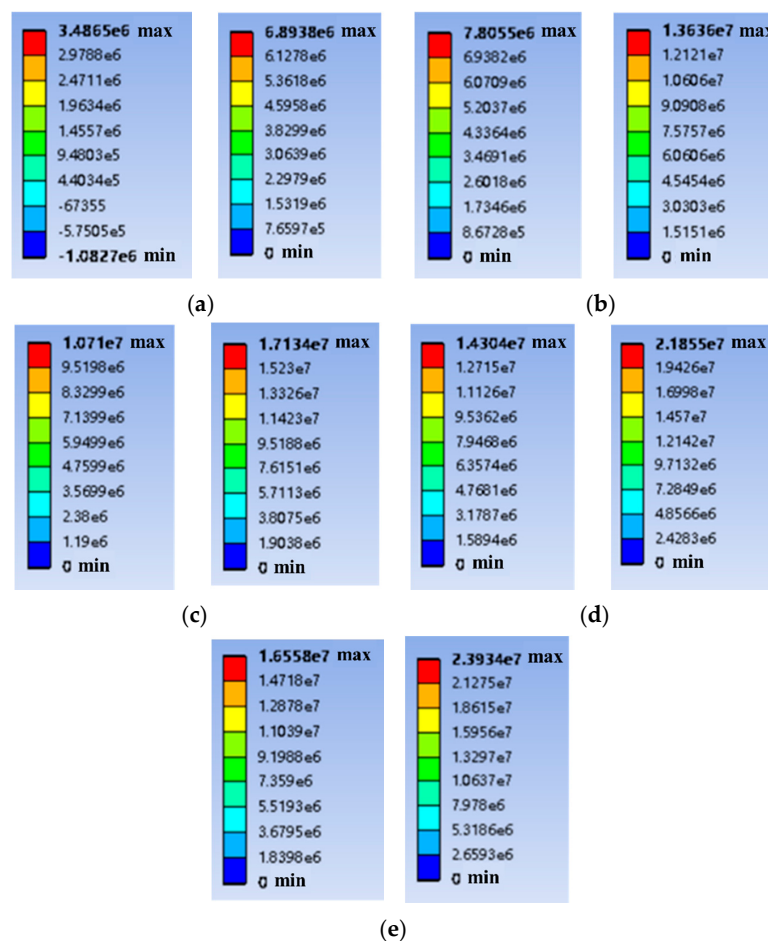


Figure 7. Equivalent stress response of fluorochemical pipeline with/without polyurea coating under different impact speeds. (a) $v = 5$ m/s; (b) $v = 6$ m/s; (c) $v = 7$ m/s; (d) $v = 8$ m/s; (e) $v = 9$ m/s.

It can be seen from the analysis results that the polyurea coating has an obvious buffer effect on the equivalent stress of small ball impact loads at different speeds. When the polyurea coating is not applied, the impact load of the small ball is directly applied to the fluorochemical pipeline. Under the impact of the small ball at different speeds, the equivalent stresses of the fluorochemical pipeline without polyurea coating are 7.8 MPa, 10.2 MPa, 14.3 MPa, 16.6 MPa and 21.9 MPa. When the polyurea coating is applied, the impact load of the small ball is buffered by the polyurea coating and transmitted to the fluorochemical pipeline. Under the impact of the small ball at different speeds, the equivalent stresses of the fluorochemical pipeline with polyurea coating are 3.5 MPa, 7.8 MPa, 10.7 MPa, 13.6 MPa and 17.1 MPa, respectively. However, the impact stress buffering effect of polyurea coating on small balls at different speeds is quite different. The buffering effect of polyurea on small balls at different speeds is shown in Figures 8 and 9.

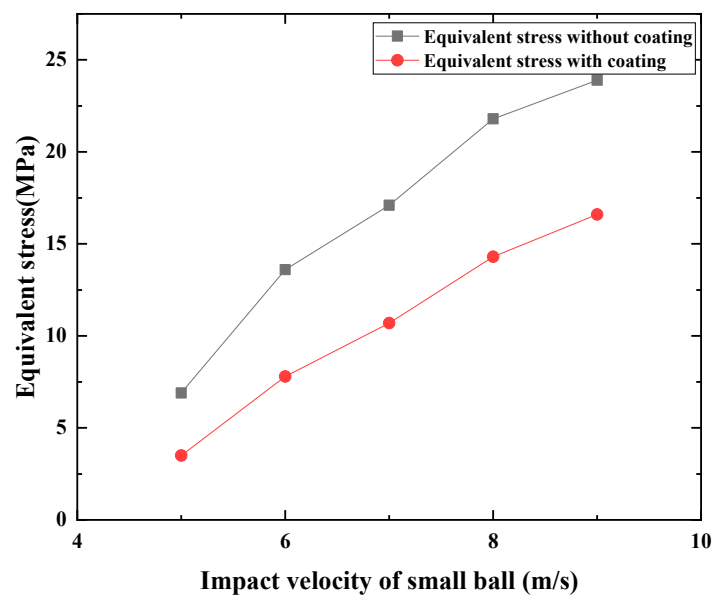


Figure 8. Equivalent stress of fluorochemical pipeline with or without polyurea coating under impact of small balls with different velocities.

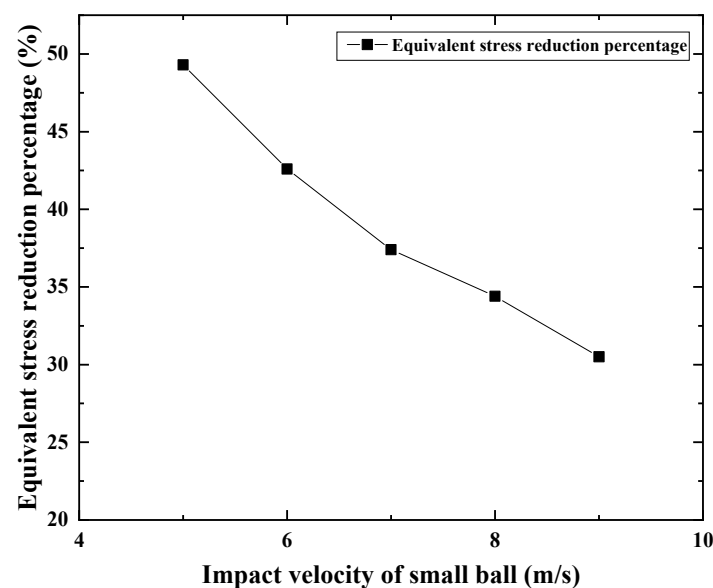


Figure 9. Cushioning effect of fluorochemical pipeline coated with polyurea coating under impact of small balls with different velocities.

It can be seen from Figures 8 and 9 that with the increase of impact ball speed, the maximum equivalent stress in the fluorochemical pipeline with/without polyurea coating increases, but the stress reduction percentage of polyurea coating on small balls with different impact speeds is different. When the ball speed is 5 m/s, the equivalent stress reduction percentage of polyurea coating is 49.3%, and when the ball speed is 9 m/s, the equivalent stress reduction percentage of polyurea coating is 30.5%. It can be seen that the equivalent stress reduction of polyurea coating on small ball impacts at different speeds is negatively correlated. In a certain speed range, the percentage of stress buffer decreases gradually with the increase of small ball impact speed.

5. Analysis of Protection Mechanism

Macroscopically: when the small ball impacts the fluorochemical pipeline without polyurea coating at a certain speed, the impact energy is mainly absorbed through the plastic hinge line of the fluorochemical pipeline at the initial moment of impact, and in the subsequent stage, the energy is mainly absorbed through the bending deformation at both ends of the fluorochemical pipeline. When the fluorochemical pipeline is coated with polyurea coating, the stress deformation of polyurea coating can absorb a considerable amount of impact energy. The polyurea coating also improves the area density and plastic hinge line of the fluorochemical pipeline, which can effectively reduce the impact stress of the small ball on the fluorochemical pipeline. Because of its high elasticity, polyurea coating can distribute the impact more evenly through its own coordinated deformation, increasing the instantaneous stress area of the fluorochemical pipeline and reducing the instantaneous maximum equivalent stress of the impact load.

Microscopically: polyurea is a micro phase separated polymer material, which is composed of a hard segment and a soft segment. When the shock wave propagates in the polyurea coating, the impact energy will be partially dissipated into the potential energy and kinetic energy in the polyurea material. The dissipated kinetic energy is the heat dissipation generated by the thermal effect of the polyurea material, and the dissipated potential energy is the thermal expansion of the polyurea coating, the incomplete relaxation of molecular chain caused by the viscosity of the polyurea material, the fracture and reorganization of hydrogen bonds and the ring breaking of microstructure. Under the impact load, a large number of microstructure changes, internal friction and conformational changes will occur in the polyurea material, which is conducive to the dissipation of impact energy.

When small balls with different velocities are used to impact fluorochemical pipelines, the equivalent stress reduction percentage of the polyurea coating will decrease with the increase of the small ball impact velocity, because polyurea material has a complex microphase separation structure, complex mechanical response behavior and obvious stress-strain nonlinearity, which shows pressure sensitivity. The flow modulus of the polyurea material increases with the increase of stress. Furthermore, the polyurea coating is a viscoelastic material, which has an obvious strain rate effect. The larger the strain rate is, the more the flow elastic modulus will increase. When the impact velocity of the ball increases, the instantaneous stress and strain rate in the polyurea coating will increase, resulting in the increase of the flow modulus of the polyurea material, and the material tends to transform into a "glass state". The viscosity of the polyurea material will reduce the energy dissipation of the molecular chain, the internal friction of the material and the rearrangement and crystallization of the soft and hard segments of the polyurea, resulting in the reduction of the energy dissipation efficiency of the polyurea coating to the impact load. Moreover, the "glass state" transformation of the polyurea material will also change the stress wave impedance of the polyurea material, thus affecting the peak value and energy transmission and reflection of stress waves in the composite medium. Under higher impact loads, the hardening of the polyurea material will reduce the impact deformation and the stress area of impact, resulting in the increase of equivalent stress of the fluorinated pipeline under impact.

6. Conclusions

The filler composite polyurea polymer was prepared by adding modified nano silica to polyurea material, and the properties of polyurea coating were characterized, including curing time, tensile strength, elongation of section and impact properties. Through many tests, it was found that when the amount of silica is 4 wt%, the comprehensive mechanical properties of polyurea coating are the best. The measured tensile strength of polyurea material is 15.7 MPa and the elongation at break can reach 472%. After coating with polyurea coating, the impact strength of the matrix is increased by 9.7 kJ/m², indicating that the polyurea coating modified by silica has excellent properties and good ductility. It can buffer the effect of impact loads on the fluorochemical pipeline.

The effects of different process parameters on the properties of polyurea coating were studied. It was found that different mixing speeds of the mixer and material addition order would greatly affect the quality of the polyurea coating. In order to obtain polyurea coating with excellent performance, when preparing component A, the stirring speed of the mixer should reach 780 r/min, and ethyl acetate and nano silica should be added alternately.

In order to explore the protective effect of the new polyurea coating on small balls with different impact speeds, it is necessary to obtain the law of equivalent stress reduction percentage of the new polyurea coating on small balls with different impact speeds and the protective mechanism of polyurea coating on the fluorochemical pipeline, the mechanical response behavior of the fluorochemical pipeline with or without polyurea coating is analyzed by finite element simulation software. The results show that polyurea coating can effectively buffer the impact stress of small balls with different impact velocity on fluorochemical pipelines, and with the increase of small ball impact velocity, the flow modulus of polyurea material gradually increases, and the equivalent stress reduction percentage of polyurea coating on the fluorochemical pipeline gradually decreases.

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