

Chemical Aging Resistance of Electrical Insulation Materials for Railway Passenger Train

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To further improve the chemical aging resistance of Electrical Insulation Materials (EIM) for railway passenger trains, this paper prepares a modified polyvinyl chloride (PVC) with the UV Absorber (UVA) by the copper catalyzed azide-alkyne addition reaction. By analyzing the H-NMR (Nuclear Magnetic Resonance) and infrared spectrums, it is proved that UVA-modified PVC has been prepared successfully. In the end, based on the curve of the infrared spectroscopy as a function of carbonyl group content, the UV aging resistances of modified and common PVCs are compared. The findings show that the common PVC will turn into yellow after long-term ultraviolet irradiation, and the carbonyl in the compound rapidly increases, developing into severe aging; the insulation and physical structure properties has significantly deteriorated; while the modified PVC basically remains unchanged in color after 200h UV irradiation, and the carbonyl content increases at a rate much lower than the common PVC. Given the above, it is thus clear that the UVA-modified PVC prepared presents a better UV aging resistance.

1. Introduction

As of 2018, the mileage of G-series high-speed trains in the world has exceeded 40,000 kilometers, and the passenger capacity of railway passenger trains has ushered in an explosive growth. The power supply system for the railway passenger train is designed to supply power to the lighting, ventilation and entertainment devices for the passenger train, as a core working system that ensures the safe and stable operation, see Figure 1 for its general structure (Chen et al., 2016). The power generator for the railway passenger train is configured on the locomotive. During the operation, electrical equipment such as the integrated control cabinet and inverters are used to transmit electric energy to any passenger compartment of the railway train (Dai et al., 2012).

In recent years, the power equipment for railway passenger trains has become even more intricate. The power cables have gradually proliferated with high-voltage current and insulation properties of the external insulation materials as the basic precondition for protecting the safe operation of railway passenger trains (Benato et al., 2017). Currently, the external insulation materials for cables mainly include the polyvinyl chloride (PVC), crosslinked polyethylene (XLPE), silicone rubber, and ethylene propylene rubber. Among them, the PVC is widely used as cable insulation thanks to its low production cost, good insulation property and high acid and alkali corrosion resistance (Basfar, 2002). But unfortunately, in the process of direct sunlight, the PVC will react with oxygen, light energy, etc. to form HCl and other gases which helps degrade and age, and further leads to a significant attenuation of the physical and mechanical properties (Naïma, 2010; Brebu et al., 2000). So far, scholars have attempted to remove chemical aging defects of PVC by synthesizing high-gloss-stabilized PVC polymers or adding photo-heat stabilizers to PVC materials. Where the addition of photo-thermal stabilizers is currently adopted as a primary method (Decker, 2001). Photothermal stabilizers are mainly divided into lead salt stabilizer, metal soap stabilizers, ultraviolet (UV) absorbent, nano material stabilizers, and the like (Chai et al., 2012; Xiang et al., 2011; Santamaría et al., 2010). The UV absorbent can absorb plenty of UV light, and mix it into the PVC insulation, which can effectively inhibit the chemical aging of the PVC (Xiang et al., 2010; Fechine et al., 2002; Pickett, 2002). But, the UV light absorbent-PVC copolymer currently prepared has many defects, such as poor stability of the copolymer, easy volatilization of UV

absorbent, and the failure of the UV light absorbent due to its easy reaction with the substances in the environment (Braun et al., 2011).

To eliminate the above defects, the UV absorbent is directly linked to the PVC backbone via chemical reactions. It is proved that the UV-absorbent-modified PVC is successfully prepared by analyzing the HNMR and infrared spectrums as the chemical reaction products. In the end, the curve of carbonyl groups content as a function of the infrared spectrum is based to compare the UV aging properties of modified PVC and ordinary PVC. The findings can provide a theoretical reference for the safety and stability of the power system of railway electric trains.

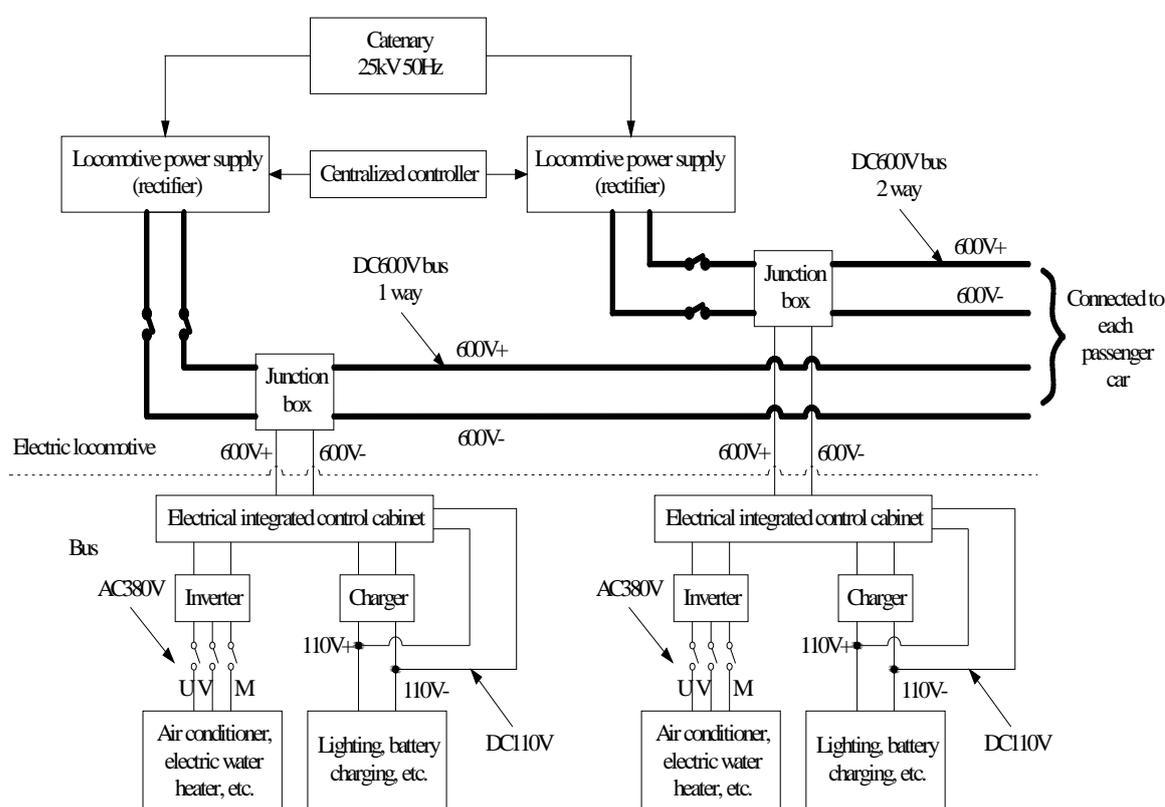


Figure 1: Power system for railway passenger train

2. Test materials and equipment

2.1 Test materials

Eluent: tetrahydrofuran, prepared on the spot every time the UV absorbent-PVC copolymer solution is configured; cuprous bromide, PVC, sodium azide, tetra-n-octyl ammonium bromide, 2,4-dihydroxy Benzophenone, potassium carbonate, propargyl bromide, distilled water.

2.2 Test equipment

NMR: superconducting nuclear magnetic resonance spectrometer; infrared spectroscopy test: Fourier transform spectrometer; solid powder is processed by the tableting method, and liquid samples are treated by liquid membrane method; the spectral resolution 4.0/cm; the polymer molecular weight test: the gel chromatograph, the refractive index detector, and ultraviolet detector.

3. Test results and analysis

3.1 Properties of modified PVC precursor compounds

The synthesis process of the UV absorbent-PVC copolymer prepared herein is shown in Figure 2. In order to make the resultant polymer have better photostability and chemical stability, the precursor compounds the

azide-substituted PVC-N₃ and 2-hydroxy-4-propargyl benzophenone (2,4-DHBP-P) should be synthesized before UV-absorbent-modified PVC is prepared.

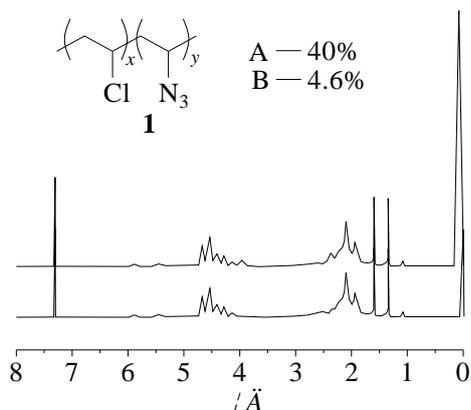
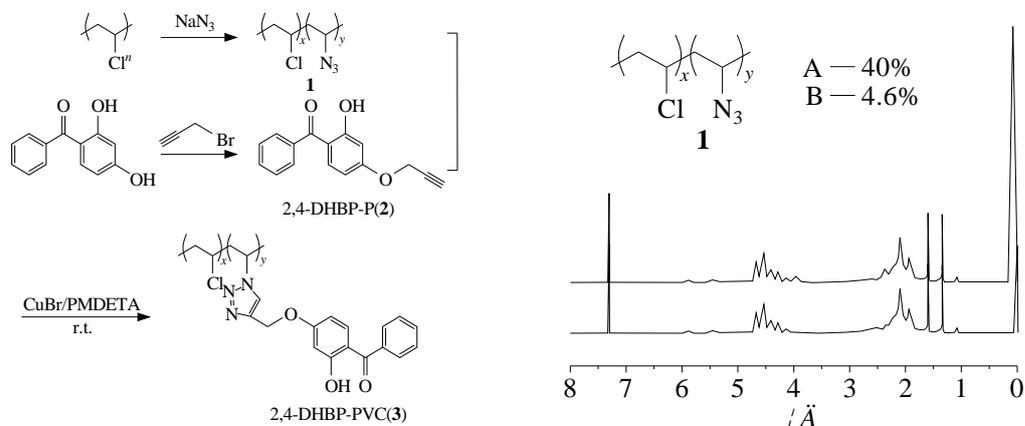


Figure 2: Synthesis process of modified PVC Figure 3: HNMR spectrums of PVC with different azide groups

NaN₃ and PVC reaction links the azide groups to the PVC, to prepare the PVC with different azide groups by controlling the reaction time. It was observed from the test results that PVC-N₃ will turn from light yellow to light brown as azide group content increases. The Figure 3 gives the HNMR spectrums of PVC with an azide content of 4.6% and 40%, respectively, Figure 4 shows the infrared spectrums of azide-substituted PVC and 2,4-DHBP-PVC.

As shown in Figure 3, there are the methylene peak at $\delta = 2.1$, the new diffraction peak at $\delta = 4.0$, representing the -N₃ group accessed; the methine peak at $\delta = 4.5$. It is proved from the HNMR spectrum that the PVC-N₃ prepared herein is effective, and the N₃ group does appear in the polymer. The N₃ substitution process occurs during the reaction. As shown in Figure 4, a new peak appears at 2110/cm in the infrared spectrum of PVC-N₃, corresponding to an azide group. The test results of infrared spectrum also demonstrate that PVC-N₃ is successfully prepared.

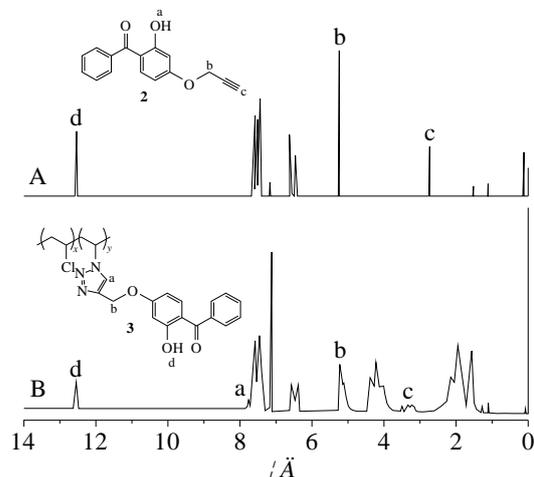
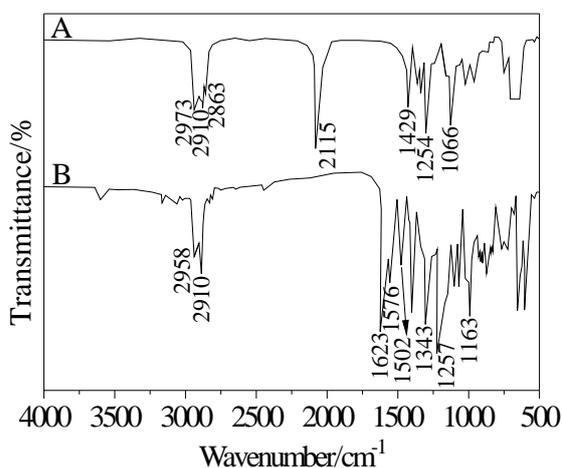


Figure 4: Infrared spectrum of two prepared

Figure 5: HNMR spectrums of 2,4-dihydroxybenzophenone

Copolymers

and its PVC polymer

As shown in Figure 5, HNMR spectrums of benzophenone-based UV-absorbent - 2,4-dihydroxybenzophenone, and a UV absorbent-modified polyvinyl chloride formed by reacting it with PVC are given. Theoretically, 2,4-dihydroxybenzophenone has a good stability, and it does not form a dihydroxy-substituted compound under the UV irradiation, thereby inhibiting the deactivation of UV absorption function of

2,4-dihydroxybenzophenone. As shown in Figure 5(A), the signal peaks at $\delta = 2.5$ and $\delta = 4.9$ represent the terminal alkynyl hydrogen and methylene hydrogen in 2,4-dihydroxybenzophenone, respectively; at $\delta = 6.3 \sim 7.8$, the peak group is the proton signal peak in the benzene ring; the peak at $\delta = 12.5$ represents the hydroxyl group. Observed from the color of the prepared solution, it has a tendency to turn into a significantly shallower color than 2,4-DHBP, and the absorption curves of the two are basically consistent in the UV absorption spectrum. Combined with the HNMR spectrum, this paper has successfully prepared the alkynyl-containing 2,4-DHBP-P, and the prepared 2,4-DHBP-P still retains a strong UV absorption function.

3.2 Preparation and properties of modified PVC

In this paper, the copper-catalyzed azido-alkynyl addition reaction lasting for 12h is used to modify the ordinary PVC. The nitrogen protection is performed in the whole process. By controlling the reaction time and the azide group content, a variety of modified PVCs with UV stabilizers can be produced. As shown in Figure 5(B), there are a methylene peak at $\delta = 2.3$, a methine peak at $\delta = 5.1$, triazole proton peak at $\delta = 7.7$, and a hydroxyl peak at $\delta = 12.8$. These typical signal peaks show that UV stabilizer modified PVC has been successfully prepared. It can also be observed from Figure 3(B) that the modified PVC adds a characteristic peak of the benzene ring at 1508/cm compared with ordinary PVC, but lessens a characteristic peak of the azide group at 2112/cm. It is also proved that the azide group has been completely removed by chemical reaction, and the UV absorbent has been successfully linked to the PVC polymer backbone.

As shown in Figure 6, there are the UV absorption spectrums of PVC, azido group PVC, and UV-absorbent modified PVC. It is obvious that the modified PVC prepared herein shows a strong UV absorption peak on the map, while the other two have none, showing the modified PVC prepared in this paper has a strong UV absorption capacity.

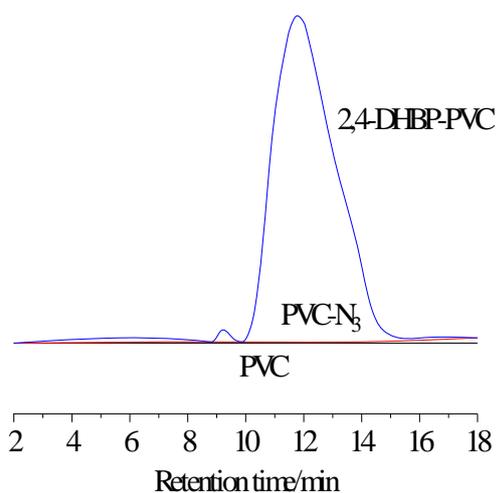


Figure 6: Ultraviolet absorption spectrums of PVC,

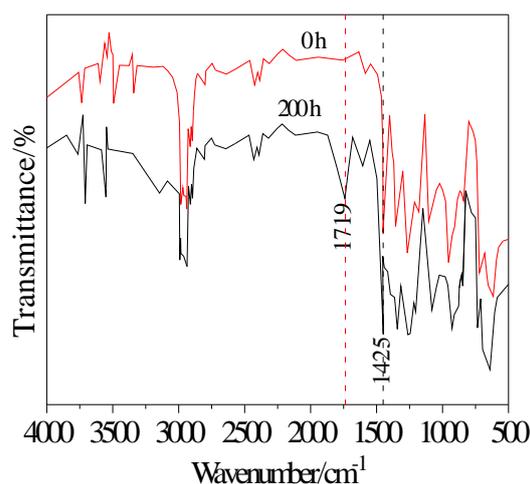


Figure 7: Infrared spectrum of PVC under UV

azido group PVC and ultraviolet absorbent modified PVC irradiation

3.3 Chemical aging resistance of modified PVC

As shown in Figure 7, the infrared spectrums of PVC materials under UV irradiations (0h, 100h, 200h) change. It can be observed from the test results that as the UV irradiation time increases, the PVC powder gradually turns yellow; from the infrared spectrum, compared to 0 h UV radiation, a significant carbonyl absorption peak appears at 1720/cm after 200 h UV irradiation, and an olefin characteristic peak appears at 3120/cm.

The carbonyl content is a direct parameter of the PVC photoaging. As shown in Figure 8, the carbonyl content of PVC is subjected to change with the UV irradiation. It is obvious that if the ultraviolet irradiation lasts for long time, the carbonyl content in the PVC increases gradually, but slowly when the irradiation time is less than 100h. When exceeding 100h, the carbonyl content increases rapidly. At this time, the severe aging appears on the PVC, while its insulation and physical structural properties significantly decrease.

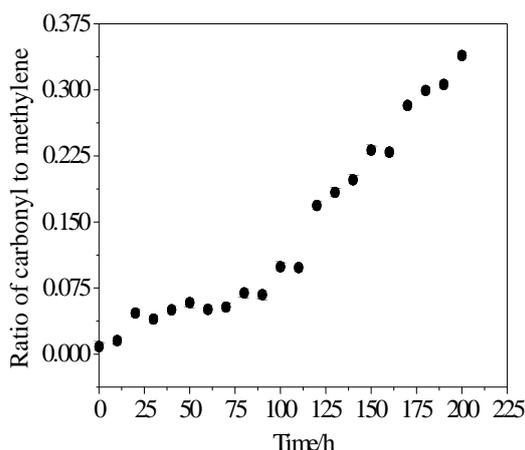


Figure 8: Change in carbonyl content of PVC under UV irradiation

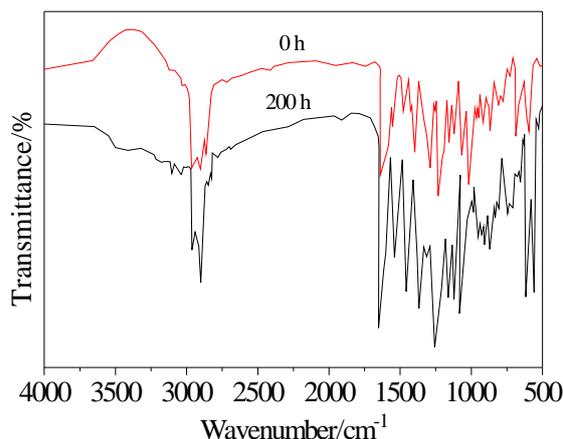


Figure 9: Infrared spectrum of UV-modified PVC under UV radiation

As shown in Figure 9, the infrared spectrum of the modified PVC under the UV irradiation is given. It is observed from the test results that the color of the modified PVC does not change substantially after 200 h UV irradiation. It is clear in the infrared spectrum curve that the carbonyl absorption peak of the modified PVC does not change significantly. These phenomena show that the prepared UV-absorbent-modified PVC has a better effect against UV aging.

4. Conclusion

This paper prepares a modified the polyvinyl chloride (PVC) with the UV Absorber (UVA) using the copper catalyzed azide-alkyne addition reaction, in order to further improve the chemical aging resistance of Electrical Insulation Materials (EIM) for railway passenger trains. By analyzing the H-NMR (Nuclear Magnetic Resonance) and infrared spectrums, it is proved that UVA-modified PVC behaves better. In the end, according to the curve of the infrared spectrum as a function of carbonyl group content, the UV aging resistances of modified and common PVCs are compared.

The contrast test shows that the common PVC turns into yellow after long-term ultraviolet irradiation, and the carbonyl in the compound rapidly increases, developing into severe aging; the insulation and physical structure properties significantly worsen; while the modified PVC basically remains unchanged in color after 200h UV irradiation, and the carbonyl content increases at a rate much lower than the common PVC. Given the above, it is thus clear that the UVA-modified PVC prepared had a better UV aging resistance effect.

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