Performance Study on Acrylic Pressure-Sensitive Adhesive Modified with Metakaolin

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Abstract: This paper takes butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) as the soft monomers, vinyl acetate (VAC) as the hard monomer of pressure-sensitive adhesive and acrylamide (AM) and acrylic acid (AA) as the raw materials of modified monomer to synthesize pressure-sensitive adhesive to carry out Fourier Transform Infrared Spectroscopy (FTIR) characterization. In order to satisfy some special requirements and improve its adhesive property, this paper uses metakaolin and metakaolin modified with silane coupling agent KH570 to carry out mechanical blending with pressure-sensitive adhesive respectively and prepare composite acrylic pressure-sensitive adhesive. This paper tests the viscosity of composite pressure-sensitive adhesive with metakaolin and modified metakaolin. It is found that with the increase of doping content, the viscosity will be increased accordingly and the viscosity of composite pressure-sensitive adhesive with modified metakaolin has a larger growth. The adhesive property indicates that composite pressure-sensitive adhesive with KH570 modified metakaolin has an obviously better adhesive property than that with unmodified metakaolin, and when 0.8wt% of modified metakaolin is added, inorganic/organic composite acrylic pressure-sensitive adhesive has the best comprehensive adhesive property.

1. Introduction

With the high-speed economic development, all walks of life can not be separated from packaging while packaging can not leave the adhesive[1]. Science and technology have been developing with each passing day, which provides the possibility for the development of pressure-sensitive adhesive. Pressure-sensitive adhesive [2] (PSA) is a kind of special viscous-elastic material which can rapidly wet the adherend without heating, adding solvent or curing agent and other methods, and form a solid adhesive strength at the interface between adhesive and adherend while not destroying the surface structure of adherend once it has been laminated or applied to the bonding plane. There is a serious shortage of functional pressure-sensitive adhesives in the fields of electronics, aviation, military affairs and so on. It has become an urgent need of the current society to develop new functional monomers, improve polymerization technology and select new materials to produce new pressure-sensitive adhesives to expand their application fields[3,4]. Acrylic pressure-sensitive adhesive is a kind of artificially
synthesized resin polymer adhesive formed by free radical polymerization of various acrylic acid monomers. Polyacrylic acid pressure-sensitive adhesive has numerous advantages such as excellent low temperature resistance and high temperature resistance, no harmful gas volatilization in the application process, etc.\textsuperscript{[5-7]}, which has made acrylic acid pressure-sensitive adhesive become the most widely used application product in the pressure-sensitive tape industry. Jin X\textsuperscript{[8]} is used as the acrylic acid pressure-sensitive tape for liquid crystal display under the synthesis condition of taking 2-ethylhexyl acrylate as the viscous monomer, methyl methacrylate as the cohesive monomer, acrylic acid as the crosslinking monomer and benzoyl peroxide as the initiator.

Due to the poor properties of solvent acrylic acid pressure-sensitive adhesive such as weather fastness, thermal endurance, durability and so on, it needs to be carried out modification. Inorganic nanoparticles have many excellent properties, such as unique high temperature resistance, high hardness, high strength, solvent resistance and so on. In addition, there are microscopic quantum size effect, surface effect and photo-electromagnetic effect that make them have a complete development. A homogeneous and heterogeneous material which has not only the rigidity and dielectricity of inorganic matter, but also the transparency, workability, plasticity and other advantages of organic matter is obtained through organic/inorganic nanocomposite, so that composite material has become a new material which has a great development prospect in the field of material science. The inorganic nanoparticles are mixed into the acrylic acid pressure-sensitive adhesive, and the composite acrylic acid pressure-sensitive adhesive with inorganic nanoparticles is obtained by combining their advantages.

2. Material and Methods

2.1 Experiment

BA, 2-EHA and VAC are blended in ethyl acetate with the ratio of 1:6:1 and the reaction temperature is 82℃. 2.5% of initiator BPO, functional monomer AA and AM are added into the reaction system in twice. The reaction lasts 8 hours and the material is obtained after cooling.

Modification of Metakaolin

This experimental design uses silane coupling agent γ-methyl propyl trimethoxy silane to carry out surface modification for nano-metakaolin(MK) and the modified nano-metakaolin(mMK) is obtained.

Preparation of Inorganic/Organic Composite Pressure-Sensitive Tape

Metakaolin with the ratio of 0.2wt%, 0.4wt%, 0.6wt%, 0.8wt% and 1.0wt% and modified metakaolin are carried out blending reaction with acrylic acid pressure-sensitive adhesive for 2h. The reaction temperature is 40℃ and the pressure-sensitive tape is produced by 35 um coating.

2.2 Test

Fourier Transform Infrared Spectroscopy(FTIR) is used to carry out characterization analysis of basic pressure-sensitive adhesive and metakaolin. Surface tension meter is used to test the contact angle of modified and unmodified metakaolin and DJ-1 rotational rheometer is used to test the viscosity of basic pressure-sensitive adhesive.

The initial adhesion, permanent adhesion and 180° peel strength of the composite pressure-sensitive adhesive are tested according to the international standard.

3. Result and Conclusion

3.1 FTIR Characterization of Basic Pressure-Sensitive Adhesive

Figure 1 is the FTIR characterization diagram of basic pressure-sensitive adhesive. From the test results and characteristic peak values of each vibration group in characteristic peaks of 3200-3600cm\(^{-1}\), 2960cm\(^{-1}\), 2870cm\(^{-1}\)and so on, we can draw the conclusion that five monomers have copolymerization and produce the copolymer acrylic acid pressure-sensitive adhesive.
3.2 FTIR Analysis of Modified Metakaolin
Figure 2 is the infrared spectroscopic analysis chart of unmodified and modified metakaolin. Through observing the modified metakaolin spectrogram, we find that there are two small peak values in large peak 3000-2800cm\(^{-1}\) compared with unmodified metakaolin. It is speculated that it should be the peak value of methylene-CH\(_2\). The KH570 molecules contain methylene, which indicates that the two peaks of the modified metakaolin comes from KH570, thus it can be explained that KH579 has successful modification to metakaolin. It is found that there is a larger peak value pf modified and unmodified metakaolin in the wave number 3442cm\(^{-1}\), which shows that it should be the stretching vibration peak of hydroxyl groups on the surface of particles. Through comparison, it is found that the peak value of modified metakaolin is decreased and it is inferred that silane coupling agent has a chemical reaction with some hydroxyl groups of metakaolin, but most reactions should be physical absorption.

3.3 Water Contact Angle Analysis of Modified Metakaolin
Figure 3 and Figure 4 are water contact angle diagrams of unmodified and modified metakaolin. The contact angle changes from 19° to 81.12°. The larger the angle, the stronger the hydrophobicity, which indicates that the modification is successful. This is because the unmodified metakaolin has a large surface, abundant hydroxyl groups and excellent hydrophilicity, while KH570 has a soft and long alkyl chain with hydrophobicity and has low interface energy. Therefore, through the modification of me-
takaolin by KH570, metakaolin has long-chain alkyl groups with hygrophobicity by surface grafting, which makes modified nano-metakaolin have better hydrophobicity, so the contact angle becomes larger.

Figure 3. Water contact angle of unmodified metakaolin

Figure 4. Water contact angle of modified metakaolin

3.4 Viscosity Analysis of Composite Pressure-Sensitive Adhesive
As shown in Figure 5, as the addition volume of inorganic particles is increased, the viscosity is enlarged and the viscosity of modified metakaolin is larger. Rheology believes that metakaolin with inorganic particles is the undeformable solid granule with poor fluidity. Its addition encroaches on a part of free volume of the macromolecular chain segment, and the reduction of free volume will make the segment motion of macromolecular chain become worse, while the modified metakaolin will disperse more uniformly in the system, so that the acting force between the modified metakaolin and the hydrogen bond of molecular chain of acrylic acid pressure-sensitive adhesive will be strengthened. The increase of viscosity can indirectly reflect the storage modulus and loss factor of the polymer will become larger, which will also reflect the viscoelasticity of polymer. Viscoelasticity has a close relation with cohesiveness of polymer.
Figure 5. The impact of adding modified and unmodified metakaolin on viscosity

3.5 Adhesive Property Analysis

3.5.1 Initial Adhesion Analysis
As shown in Figure 6, whether the modified metakaolin by KH570 or the unmodified metakaolin, the initial adhesion shows a variation tendency of rising at first and declining later with the increase of addition volume. However, pressure-sensitive adhesive with modified metakaolin has better cohesive-ness. It is analyzed that the initial cohesion of metakaolin modified by KH570 is significantly better than unmodified metakaolin, and has the best property when the addition volume is at 0.8wt%. This is because the modified metakaolin makes the surface introduce the oily groups, thus the oil phase composite improves the affinity between organic matters and it, which makes it have better dispersibility in the acrylic acid pressure-sensitive adhesive. In addition, because the metakaolin with surface modification will introduce more polar groups, the modified metakaolin surface will introduce double bonds after modification, so that the molecular polarity of pressure-sensitive adhesive will be enhanced, which will form more hydrogen bonds with adherend and have a better adhesive property.

Figure 6. The impact of metakaolin on the initial cohesion of solvent pressure-sensitive adhesive
3.5.2 Permanent Cohesion Test
As shown in Figure 7, with the increase of content, the permanent cohesion maintains the tendency with continuous growth, and the metakaolin modified by KH570 has obvious increase effect of permanent cohesion. The increase of permanent cohesion should be taken into account the cohesion factor, which should be caused by the increase of cohesion. Considering that metakaolin is a kind of rigid particle, the addition of metakaolin will inevitably lead to the increase of its modulus. In addition, the increase of metakaolin is bound to form more crosslinking of hydrogen bonds, which will improve the cohesion of acrylic acid pressure-sensitive adhesive and increase the permanent cohesion. The metakaolin modified by KH570 has better dispersibility and stronger polarity. The hydrogen bonds formed are more uniformly distributed, which obviously makes the permanent cohesion have a better increase effect.

![Figure 7](image)

Figure 7 The impact of metakaolin on the permanent cohesion of solvent pressure-sensitive adhesive

3.5.3 180° Peel Strength Test
Figure 8 is the impact effect diagram of metakaolin on the 180° peel strength of solvent pressure-sensitive adhesive. It is found that its change law is similar to the initial cohesion, which shows the tendency of increasing at first and decreasing later, and the modified metakaolin by KH570 has a better effect than that without modification. The reason should be similar to that of initial cohesion, which can be explained by free volume, hydrogen bond, better dispersibility after modification and introduction of polar groups.

![Figure 8](image)

Figure 8. The impact of metakaolin on the 180° peel strength of solvent pressure-sensitive adhesive

4. Conclusion
This paper analyzes the adhesive property between composite pressure-sensitive adhesive with unmodified metakaolin and modified metakaolin by KH570. The results show that the adhesive property of composite pressure-sensitive adhesive with modified metakaolin by KH570 is significantly better
than that with unmodified metakaolin. When the addition volume of modified metakaolin is less than 0.8wt\%, the curves of peel strength and initial cohesion of composite pressure-sensitive adhesive rise with the addition volume increase of modified metakaolin. While its admixture amount is more than 0.8wt\%, the peeling strength and initial cohesion show a decreasing tendency with the increase of its admixture amount, but the permanent cohesion is enlarged with the increase of its admixture amount. To sum up, when the content of modified metakaolin reaches 0.8wt\%, inorganic/organic composite acrylic acid pressure-sensitive adhesive has the best comprehensive adhesive property.

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