PREPARATION AND PROPERTY ANALYSIS OF SOLVENT-FREE FLEXIBLE PACKAGING ADHESIVES BASED ON HYBRID POLYURETHANE-ACRYLATE

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High-viscosity acrylate polyol copolymer (Component A) was synthesized employing polyether polyol (PPG400) as the reaction medium, methyl methacrylate (MMA) serves as the primary hard monomer, while butyl acrylate (BA), combined with hydroxyethyl acrylate (2-HEA), function as the soft monomers. Polyurethane (PU) prepolymers with terminal -NCO groups (Component B) were derived from the synthesis of polyether polyols (PPG) of varying molecular weights and isophorone diisocyanate (IPDI). A solvent-free polyurethane-acrylic flexible packaging adhesives(FPA)was then formulated using various ratios of Components A and B, the FPA was analyzed and characterized utilizing Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC) techniques. The study investigated the effects of three synthesis schemes for Component B and the amount of Component A on the viscosity and the glass strength. The research findings indicate that employing Scheme 2 for the preparation of Component B, with Component A comprising 40% of the mixture, results in peel strengths of 2.971 N/15mm for paper/aluminum foil and 3.567 N/15mm for paper/paper. Conversely, when Component B was prepared to do Scheme 3 and Component A constitutes 70%, the peel strengths achieved are 1.068 N/15mm for paper/PE film and 0.803 N/15mm for aluminum foil/PE film.

Keywords: Solvent-free, flexible packaging adhesives, Acrylic, Polyurethane

1. Introduction

Adhesive for flexible packaging is extensively utilized in the packaging sectors of food, pharmaceuticals, and daily necessities, primarily for adhering materials such as paper/paper, paper/aluminum, aluminum/plastic, and plastic/plastic [1]. The majority of current flexible packaging adhesives are either water-based or solvent-based [2-3]. These adhesives possess excellent water resistance and outstanding adhesion qualities. Among the notable representatives of water-based adhesives, waterborne polyurethanes and waterborne acrylic esters were the famous ones. At ambient temperatures, water evaporation occurs gradually. To accelerate this process, additional heat input is required, which

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consequently leads to concerns about energy consumption. On the other hand, solvent-based adhesives, which contain volatile organic solvents like benzene and esters, have the potential to infiltrate into both the human body and the environment. Health can be damaged by prolonged exposure to these substances and environmental pollution challenges are also posed. Additionally, some of these products suffer from stability issues [4-5]. Solvent-free adhesives are produced under specific conditions via swift reactions among various polymers. Given that no organic solvents are employed during this manufacturing process, they circumvent the issues typically associated with the utilization of such solvents, thereby rendering them a highly eco-friendly product. Numerous studies have demonstrated that solvent-free adhesives are viable replacements for conventional water-based solvents. [6-7]. To meet the demands of the extensive Flexible packaging adhesives market, it is essential to develop non-toxic, solvent-free adhesives which have high adhesion capabilities, are cost-efficient, and are environmentally friendly. This endeavor is crucial not only for the environment but also for human development. [8-11].

Solvent-free adhesives, devoid of any solvents, eliminate the necessity for drying equipment during production, thereby drastically cutting down on drying costs. Throughout the manufacturing process, they refrain from emitting harmful gases, obviating the requirement for extensive and intricate heating, ventilation, and exhaust treatment systems. The production apparatus remains uncomplicated, leading to minimal maintenance costs, heightened production efficiency, and substantial economic gains [12-13]. Since the groundbreaking introduction of the solvent-free adhesive synthesis process, Herbert, in 1974, these adhesives have consistently undergone advancements and enhancements. The concept of solvent-free synthesis was capitalized on by Houton et al [14] to develop supramolecular solvent-free polyurethane adhesives. Offering a valuable insight into the research realm of solvent-free polyurethane adhesives in production processes. The modification of polyurethane with Al2O3 was delved into by Hadavand et al [15] and their colleagues, and an adhesive that boasts remarkable heat resistance was crafted. They also elucidated the thermal motion mechanism involved in the composite adhesive's preparation process through the lens of mathematical models. In another groundbreaking study, Nanomaterials were harnessed by Dong et al[16] to be integrated with polyurethane, and a novel material that excels in both mechanical strength and corrosion resistance was successfully yielded. This achievement holds significant promise for economic applications. Epoxy resin was integrated with polyurethane by Chen et al [17] to develop a two-component, solvent-free adhesive modified with epoxy resin. Analysis revealed that this adhesive forms a densely crosslinked polymer network between molecules, leading to a substantial enhancement in mechanical strength and heat resistance. The influence of incorporating epoxy resin into polyurethane on its properties was

examined by Sivanesan et al [18]. Experimental evidence demonstrated that the inclusion of epoxy resin enhances the tensile strength, impact resistance, and flexural strength of polyurethane, while also augmenting the flexibility of the polyurethane adhesive. Blending and in-situ polymerization techniques were employed by Jia et al [19] to modify polyurethane with epoxy resin. Their findings indicated that the epoxy resin-polyurethane composite material produced through in-situ polymerization excels in peel strength and heat resistance. The modification of polyurethane with epoxy resin was leveraged by Chen & Chen [20] and polyacrylate was further introduced to create a tri-network crosslinked adhesive. Tests confirmed that this material demonstrates outstanding mechanical strength, heat resistance, and hydrolysis resistance.

However, the absence of assistance from organic solvents during the preparation of solvent-free adhesives poses numerous challenges, including low viscosity, inadequate peel strength, excessive volatile content, and cost control difficulties. These shortcomings underscore the pressing need for the further refinement and optimization of the synthesis process for solvent-free soft packaging laminating adhesives. [21-22]. In response to these concerns, this paper endeavors to conduct research encompassing the following key aspects: The utilization of acrylic ester and polyurethane composite hybrids in the formulation of solvent-free soft packaging adhesives, specifically a two-component system. Polyether polyol (PPG400) is employed as the reaction matrix by Component A which is comprised of acrylic ester. Within this matrix, methyl methacrylate (MMA) serves as the hard monomer, while butyl acrylate (BA) and hydroxyethyl acrylate (2-HEA) function as soft monomers. Furthermore, the process is facilitated as azobisisobutyronitrile (AIBN) is acted as the initiator. This approach primarily harnesses the principles of multicomponent copolymerization and free radical polymerization, To synthesize high-viscosity acrylic ester copolymers, it is crucial to precisely control the synthesis ratio. A reaction with polyether polyols (PPG) of varying molecular weights is undergone by Component B which consists primarily of polyurethane, and isophorone diisocyanate (IPDI) is utilized as the reactant. The addition of dibutyl tin dilaurate (DBTDL) as a catalyst facilitates this reaction, which leads to the formation of an NCO - terminated polyurethane (PU) prepolymer.

The study delves into the influence of both the molecular weight of PPG and the catalyst on the viscosity characteristics of the synthesized prepolymer. Notably, while maintaining the production process of Component A (acrylic ester) constant, various production methodologies for Component B (polyurethane) are employed, adhering to the principle of single variable alteration. This involves manipulating the molecular weight of PPG and adjusting the catalyst addition, subsequently assessing the temperature-viscosity correlation of Component B.

Furthermore, the viscosity of the solvent-free flexible packaging adhesive (FPA) is examined through the utilization of differing compounding ratios of the

two components. Additionally, the peel strength of the resulting mixed adhesive is meticulously measured.

The impact of the preparation method of Component B and the incorporation level of Component A on the molecular weight of polyether polyols (PPG), as well as the influence of catalyst type and acrylate hybrid ratio on viscosity and tensile strength is primarily delved into by this article. Furthermore, optimized the formulation of solvent-free flexible packaging adhesive (FPA). A solvent-free polyurethane acrylate adhesive with excellent viscosity and tensile strength was successfully formulated. achieving peel strengths of 2.971 N/15mm and 3.567 N/15mm for paper/aluminum foil and paper/paper interfaces, respectively, and 1.068 N/15mm and 0.803 N/15mm for paper/PE film and aluminum foil/PE film interfaces, respectively. The salient benefits of this production method lie in its absence of harmful gas emissions and environmental footprint, coupled with its water-free nature, which eliminates the need for water removal. Consequently, it represents an environmentally benign, energy-efficient, and emission-mitigating manufacturing process with immense application potential.

2. Preparation and performance analysis of the FPA

2.1 Materials

Methyl methacrylate (MMA), hydroxyethyl acrylate (2-HEA), butyl acrylate (BA), polyether diol (PPG1000), polyether diol (PPG3000), azodiisobutyric nitrile (AIBN), and isophorone diisocyanate (IPDI) were procured from Shanghai Ehn Chemical Technology Co., Ltd. Dibutyltin dilaurate (DBTDL) was procured from Shanghai Aladdin Biochemical Technology Co., Ltd., and tetrahydrofuran (THF) was procured from Tianjin Damao Chemical Reagent Company.

2.2 Design of experiments

In this study, a solvent free polyurethane-acrylic adhesive for food packaging was prepared. A two-component system was used to engineer the adhesive, and each component was individually sealed to ensure an extended shelf life. This innovative production process obviates the need for solvents, thereby preventing the emission of unnecessary gases and rendering it an eco-friendly alternative. The film coating under investigation is a two-component system. Ethyl ester (2-HEA) as the soft monomer and polyether diol (PPG400) as the reaction medium are comprised in Component A. It includes 60% acrylic monomer, 39.8% polyether diol (PPG400), and 0.2% azodibutyl nitrile (AIBN). The mass ratio of the various acrylic acid monomers is established in accordance with their individual glass transition temperatures (Tg): methyl methacrylate at 35.13%, butyl acrylate at 49.14%, and hydroxyethyl acrylate at 15.73%. The Tg value for this blend is -10.21℃. In component A, the hydroxyethyl acrylate interacts with the -NCO group

of isophorone diisocyanate, serving as a link between the acrylate chain segment and the polyurethane chain segment.

Component B: The hydroxyl value of the synthesized polyether diol (PPG1000/3000) was determined to be 1.5 times that of the isocyanate value of isophorone diisocyanate (IPDI), and the formulation was designed accordingly. The viscosity was evaluated by using dibutyltin dilaurate (DBTDI) as a catalyst and changing the molecular weight of the polyether diol. The two-component mixture was blended in proportions of 25%, 40%, 55%, 70%, and 85% of the volume of component A, and the adhesion to paper/aluminum foil, paper/paper, paper/PE film, and aluminum foil/PE film was evaluated after the formulation. Tg calculation formula is shown in (1):

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}} \tag{1}$$

Among them:
W1 ---- mass fraction of methyl methacrylate;
W2 ---- mass fraction of butyl acrylate;
W3 ---- mass fraction of hydroxyethyl acrylate;
Tg1 ---- glass transition temperature of methyl methacrylate at 378.15 K;
Tg2 ---- glass transition temperature of butyl acrylate at 217.15 K;
Tg3 ---- glass transition temperature of hydroxyethyl acrylate at 258.15 K.

The calculated glass transition temperature for acrylic ester copolymer is -10.21 ℃.

The following copolymers are obtained based on the free radical polymerization reaction mechanism. Among them, component A is obtained through radical addition co-polymerization of acrylic monomer. Component B polyurethane prepolymer is obtained by nucleophilic addition of -NCO and polyether diol. FPA is obtained by copolymerization of -NCO and -OH in components A and B. The reaction format and structure formula of the copolymer are shown in Fig. 1 – Fig. 3.

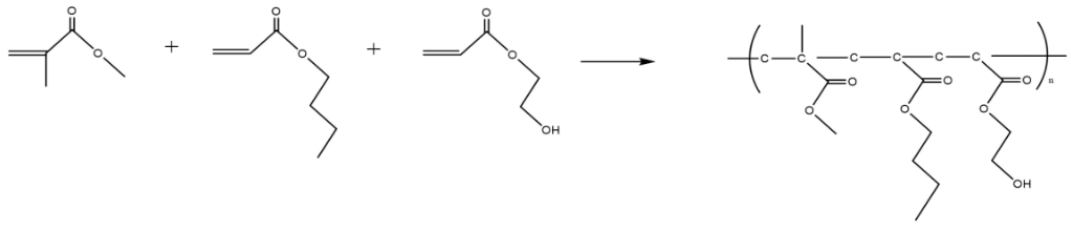

Fig. 1. The Reactions format and structural formula of component A

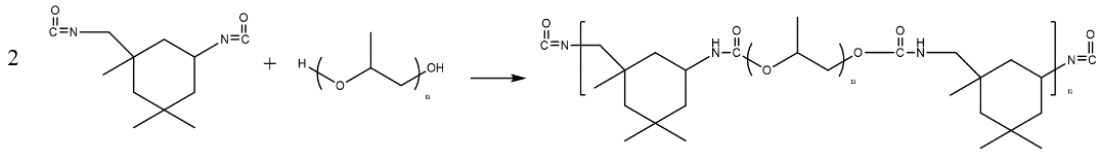

Fig. 2. The Reactions format and structural formula of component B

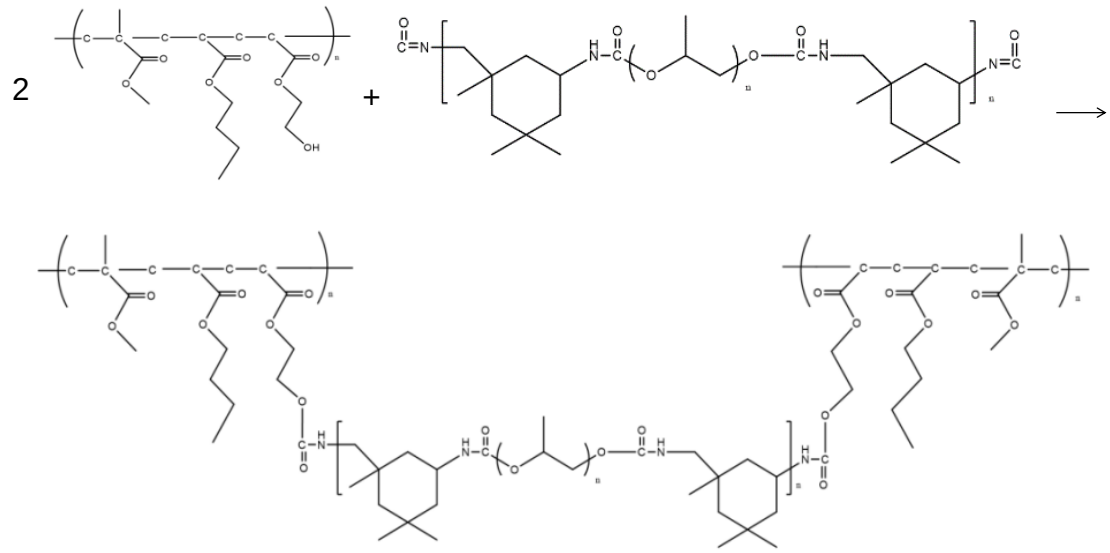

Fig. 3. The Reactions format and structural formula of the FPA

2.3 Preparation of FPA

2.3.1 Preparation of component A

Add a suitable quantity of polyether diol (PPG400) to a four-necked round bottom flask. Heat it up to 95℃ under water bath conditions.In a beaker, prepare the appropriate amounts of methyl methacrylate (MMA), butyl acrylate (BA), ethyl acrylate (2-HEA), and Ao diisobutyric nitrile (AIBN). They are gradually dripped into the four-neck round bottom flask using a split funnel while mechanical agitation is maintained at a rotational speed of 250 r/min. Continue this process for approximately 2 hours. Insulate the reaction mixture for 0.5 hours, then add trace amounts of azo dibutyronitrile (AIBN). The reaction is allowed to proceed at 95℃ for 1 hour to ensure thorough mixing of the remaining acrylate monomers. After completion of the reaction, cool down the mixture to room temperature in order to measure its viscosity accurately. Finally, seal the product for storage.

2.3.2 Preparation of component B

Scheme 1: Add the appropriate amounts of polyether diol (PPG1000) and isofolone diisocyanate (IPDI) into the four-neck round bottom flask respectively.

The appropriate amounts of polyether diol (PPG1000) and isofolone diisocyanate (IPDI) are added into the four-neck round bottom flask respectively. Mechanical stirring is kept at 300 r/min, and it is slowly heated to about 50℃. The heating is discontinued and it is allowed to exotherm to 70 - 75℃. The temperature is maintained at 75℃, and the reaction is carried out for 4 hours. Then the mixture is cooled to room temperature to assess the viscosity of the polyurethane. Once cooled, it is sealed for storage.

Scheme 2: Appropriate amount of polyether glycol (PPG1000) and isofolone diisocyanate (IPDI) are put into a four-neck round bottom flask, It is slowly heated to about 50℃ and stirred at 300 r/min, The heating is discontinued and it is allowed to exotherm to 70~75℃, and the reaction is carried out for 2 hours. Then 0.5 mL butyl digluric tin (DBTDL) is added to the reaction unit for 2 hours. Upon completion of the reaction, the mixture is cooled to room temperature and measure the viscosity of the polyurethane. Finally, seal the product for storage.

Scheme 3: The appropriate amount of polyether diol (PPG3000) is added into the four-neck round bottom flask; The appropriate amount of isofolone diisocyanate (IPDI) is put into the four-neck round bottom flask, Mechanical stirring is kept at 300 r/min, and it is slowly heated to about 50℃. The heating is discontinued and it is allowed to exotherm to 70~75℃. The temperature is maintained at 75℃, and the reaction is carried out for 4 hours. Upon completion of the reaction, the mixture is cooled to room temperature and the viscosity of the polyurethane is measured. Finally, the product is sealed for storage.

2.3.3 Preparation of FPA

Component A (acrylate) and Component B (polyurethane) are combined in various being proportions, with the composite ratio determined by volume. The volume fractions of Component A (acrylate), which 25%, 40%, 55%, 55%, 70%, and 85%, respectively,are set. Based on these ratios, 15 distinct sets of FPA are prepared.

2.4 Characterization and performance determination

2.4.1 FT-IR Analysis

The potassium bromide crystal was analyzed using a Fourier transform infrared spectrometer (SHIMADZU IRPrestige-21) to obtain the baseline spectrum. Subsequently, 2 to 3 drops of tetrahydrofuran (THF) were used to dissolve the test samples, which were then deposited onto the potassium bromide crystal. The THF was subsequently evaporated using an electric thermal fan (HP8110), after which all samples underwent scanning.

2.4.2 Thermal Analysis

The thermal weight test condition is set as: sample quality control is

between 3 to 6 mg; heating temperature range is 30-800℃, temperature rise 10℃/min, with gas carrier for N2 atmosphere.

2.4.3 GPC Analysis

The cover glue was dissolved using chromatographic-grade tetrahydrofuran (THF), with the concentration adjusted to a range of 1.0 to 1.5 mg/ml. Subsequently, a specified volume of this solution was introduced into the machine via an injection needle. The pre-established treatment method was then subjected to analysis.

2.4.4 Viscosity Measurement

Using a digital viscosity gauge (SNB-2 type), select the appropriate rotor model, adjust the rotation speed, and determine the viscosity at different temperatures.

2.4.5 Measurement of Stripping Intensity

Put film coating on paper / aluminum foil, paper / paper, paper / PE film, aluminum foil / PE film, cooked in 60℃ electrothermal constant temperature blast drying box for 48 hours, and determine 180 peel strength with tensile material tester (HD-B617-S).

3. Results and Discussion

3.1 FITR characterization

Component A represents the expansion vibration absorption peak of the hydrogen-bonded OH group at 3450 cm-1, while Component B emerges at 3335 cm-1. Both these peaks are discernible in the complex sample, with 1100 cm-1 marking the expansion vibration peak in C—O—C. Notably, Component B corresponds to the stretching vibration peak of the —NCO group at 2270 cm-1, which is present albeit weakened in the complex sample, suggesting the involvement of the —NCO group in the coated glue. Additionally, 1100 cm-1 signifies the stretching vibration peak in the amino ester of C—O—C, further underlining the formation of crosslinks between the acrylic ester segment and the polyurethane chain segment. As depicted in Fig. 4.

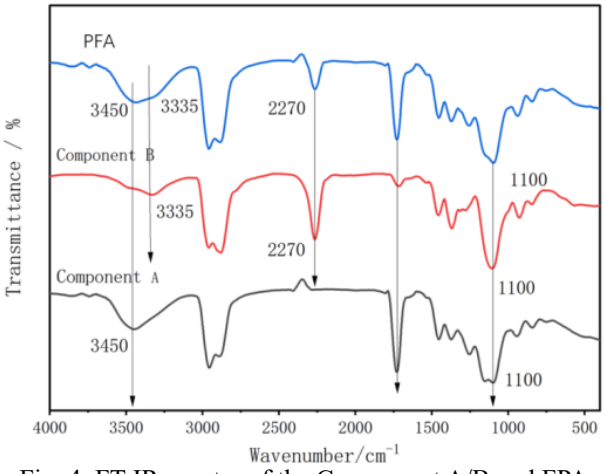

Fig. 4. FT-IR spectra of the Component A/B and FPA

3.2 Thermal analysis

As shown in Fig. 5, the film covering glue 200℃ began to lose weight, the temperature is stable at 339.73℃, and the weight loss is 24.5%, indicating that the polymer may break the chain or melt at this time, and after the temperature increases, the weight drops sharply at 448.91℃. The adhesive exhibits excellent thermal resistance and stability.

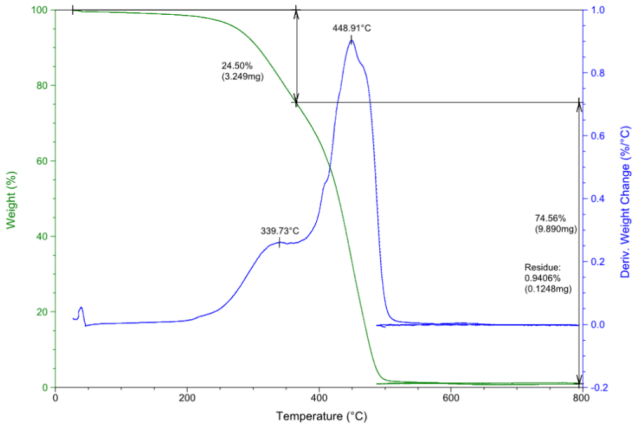

Fig. 5. TGA curves of the FPA

3.3 Gel Permeation Chromatography

The molecular weight of the FPA was precisely measured via gel chromatography, yielding both the weight-average (Mw) and number-average (Mn) molecular weight data, as illustrated in Fig. 6. The adhesive boasts a weight-average molecular weight of approximately 5600, and a number-average molecular weight hovering around 4890. This indicates that components A and B have successfully undergone polymerization, resulting in the formation of a polymer with a notably

high molecular weight.

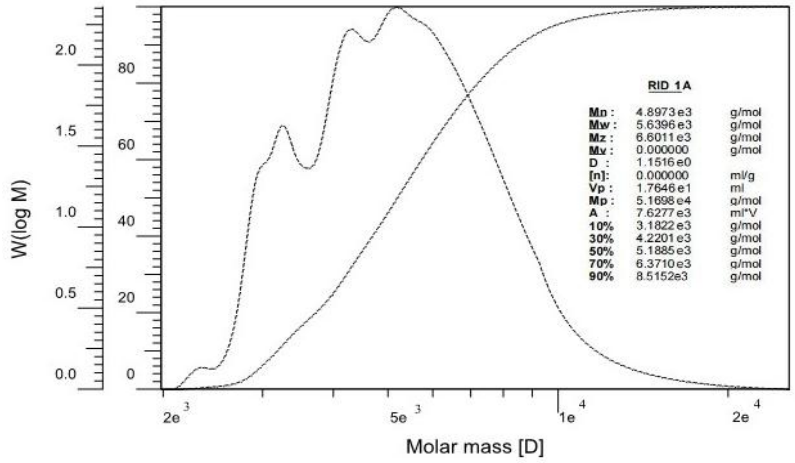

Fig. 6. GPC curves of the FPA

3.4 Adhesive viscosity determination

The temperature-viscosity curves of the component A and B, obtained for the three schemes are shown in Fig. 7. Among them, the viscosity of component A decreases with the temperature is 55℃, the inflection point appears, the viscosity change is not obvious, and the intermolecular friction force tends to equilibrium, as shown in Fig. 7 (a). Component B is analyzed according to Scheme 1 and 2, adding catalyst to promote the reaction and increasing the viscosity at the same temperature; According to Scheme 1 and 3, polyether diol (PPG) with different molecular weights can also affect the viscosity of the adhesive under the same temperature conditions, as shown in Fig. 7 (b).

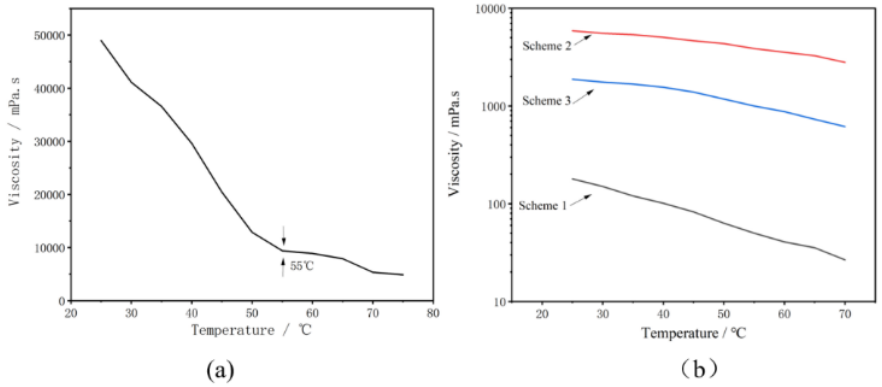

Fig. 7. Viscosity curves of the (a) component A and(b) component B

According to Fig. 8, temperature-viscosity curve analysis of Scheme 1-3 and

components A (acrylate); under the same temperature conditions, the viscosity of the adhesive. Under the same A content, the viscosity decreases as the temperature increases. This is because the viscosity depends on the internal friction force between molecules, the internal friction force of the liquid is contingent upon the attractive force existing between its molecules. When temperatures rise, the distance separating molecules diminishes, When the temperature attains a specific level, the attractive forces and internal friction forces tend to equilibrate, resulting in a negligible change in viscosity. Among the three schemes of component B, the production system of Scheme 2 has the largest viscosity; followed by scheme 3, and the minimum viscosity is Scheme 1. The fraction B (polyurethane) has a large viscosity component, mixed with the same volume of fraction A (acrylate), and the system viscosity of the two components is also significantly high.

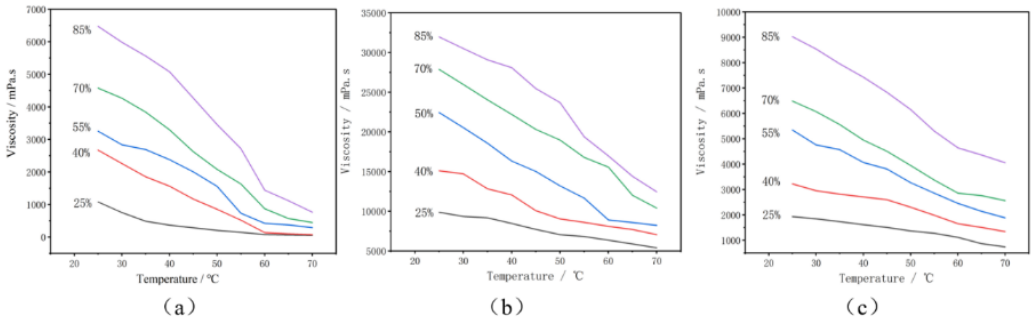

Fig. 8. Temperature - viscosity curve of the FPA with different content ratio
(a) scheme 1, (b) scheme 2, (c) scheme 3.

3.5 Peeling strength

Compactions A and B were FPA to different volume ratios, and the adhesive was evenly applied on paper / aluminum foil, paper / paper, paper / PE film, aluminum foil / PE film for peel strength test. The test results are shown in Fig. 9 (a) and Fig. 9 (b). When scheme 2 is adopted, and the volume ratio of component A is 40%, the stripping strength of paper / aluminum foil and paper / paper is the highest, which can reach 2.971 N / 15mm and 3.567 N / 15mm respectively. As shown in Fig. 9 (c) and Fig. 9 (d), when using Scheme 3, component A is 70%, the stripping strength of paper / PE film and aluminum foil / PE film is the highest, which can reach 1.068 N / 15mm and 0.803 N / 15mm respectively.

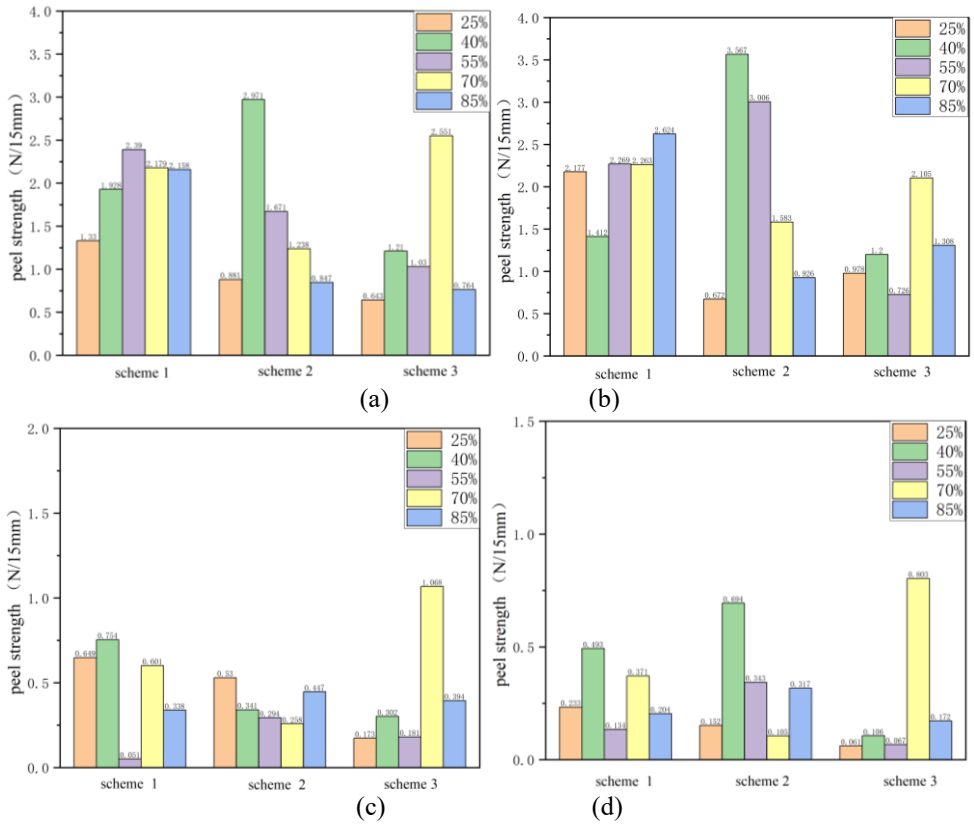

Fig. 9. Comparison of stripping intensity of (a)Paper/aluminum foil(b)Paper/paper(c)Paper/PE (d)Aluminum foil/PE

4. Conclusion

In this article, hybrid polyurethane-acrylate solvent-free flexible packaging adhesives were successfully synthesized to represent the structure, thermal properties and polymerization molecular weight of adhesive by FTIR, TGA and GPC, respectively, and to investigate the influence of group allocation ratio and different synthesis conditions on adhesive viscosity and peel strength. The results show that by increasing the proportion of component A, the use PPG-1000 and dibutyltin DBTDL, the viscosity and peel stripping can be significantly improved. The peel strength of paper / aluminum foil and paper / paper can reach 1.068 N / 15mm and 0.803 N / 15mm respectively, and the highest peel stripping strength of paper / PE film and aluminum foil / PE film can reach 1.068 N / 15mm and 0.803 N / 15mm respectively.

Of the three preparation schemes of component B, the overall integrated adhesive of protocol 2 was optimal. When Scheme 1 and Scheme 3 are used, along with certain proportions of component A, the adhesive performance is poor for

some substrates. Compared with Scheme 2, the adhesive performance is inferior. Comprehensive consideration, the use of Scheme 2 for production is relatively cost-effective.

Traditional solvent-based adhesives possess the advantages of favorable water resistance and high viscosity. However, the volatilization and leaching of organic solvents such as benzene and esters give rise to toxicity risks. Additionally, the requirement for drying to remove both water and organic solvents during production imposes substantial technical challenges on equipment and leads to significant production costs. Production is anticipated to diminish energy usage, lower production expenses, and enhance the product quality ratio based on this study, thereby advancing the objectives of carbon peaking and carbon neutrality.

Acknowledgments

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