

Original Research Paper

Preparation of Fluorine/Silicon Co-Modified Elastic Acrylate with Low Fluorine and High Performance

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Abstract: The methyl acrylate was modified with hexafluorobutyl methacrylate (G02) and vinyl triethoxy silane (A-151) as modified monomers, Methyl Methacrylate (MMA) as hard monomer and Butyl Acrylate (BA) as soft monomer. Pre-emulsification, seed emulsion and semi-continuous synthesis process were adopted to the effects of the preparation process, the ratio of G02 and A-151 modified monomers, the amount of soft monomer and hard monomer on product performances. The structure of the modified acrylate was characterized by infrared spectroscopy (FTIR). The thermal stability of the product was determined by the Thermo Gravimetric Differential Thermal Analyzer (TG-DTA). It was showed that the water absorption of the paint film prepared by using the optimized formula was 5.1%, the adhesion of the surface layer of the tinplate was grade 1, the tensile strength of the latex film layer was 2.13 MPa and the elongation of the high elastic resin was 736%. The organic fluorine-silicon and monomers were successfully grafted onto the acrylic polymer, the low fluorine high performance fluorine/silicon co-modified elastomeric acrylate was successfully prepared. Compared with other silicone and fluorine modified acrylate, the product has better thermal stability and tensile strength, improved cost-effectiveness of this type of exterior coating.

Keywords: Acrylate, Fluorine/Silicon Modification, Resin Properties, Tensile Strength, Breaking Elongation

Introduction

Acrylic resin was good in gloss retention and chemical resistance. The disadvantages of acrylic resin are hot sticky, cold brittle, poor light aging resistance, etc. Acrylic resin was susceptible to thermal expansion and contraction due to the influence of ambient temperature, causing cracks, ash absorption and resin denaturation. Fluororesin was excellent in temperature resistance and other characteristics (Merkel and Toy, 2006; Ebnesajjad and Morgan, 2012). It was an important material in various cutting-edge technologies and the defense industry. It was used to prepare elastic resin coatings with good stain resistance (Mastrapostoli *et al.*, 2014; McKeen, 2013). The silicone resin Si-O large bond energy was difficult to break chemical bonds and good aging resistance and chemical resistance (Rui and Haijun, 2016; Liao *et al.*, 2010). Different kinds of monomers modify the acrylate to make the resin certain

elasticity, resisting and covering the cracks generated in the base layer (Sun *et al.*, 2006, Yuan *et al.*, 2010). Zhu *et al.* (2007) prepared a silicone-acrylic emulsion with γ -methacryloxypropyltri methoxysilane as a silicon monomer. Using the above two different monomers, the acrylic resin can be modified to be elastic, resist and cover the cracks. Wang and Zhang (2008) prepared silicone-acrylic emulsion containing 9.1% organic siloxane monomer. Sui *et al.* (2016) prepared fluorine/silicon modified acrylate emulsion with G02 and A-171 as monomer. Li *et al.* (2016) modified acrylate with methacrylate Decafluoroheptyl Methacrylate (DFMA) and Vinyl Trimethoxysilane (VTMS). Lu *et al.* (2016) have prepared modified acrylate emulsion used 1, 3, 5-tris (3, 3, 3-trifluoropropyl), methylcyclotrisiloxane (D3F) and methacryloxy propyl trimethoxyl silane (KH-570). Borisova *et al.* (2019) used TGA and FTIR to study the application of asphalt and heavy oil in the polymer material industry. Arasaretnam and Kirudchayini (2019)

modified phenolic resin with lignin biomass. It's better due to their sustainability, environmental control, low production cost and their ability to adsorb heavy metals. Moon *et al.* (2012) studied the relationship between the self-cleaning ability of acrylic resins with different fluorine contents. Naghash *et al.* (2006) prepared a silicone-modified acrylic resin by emulsion copolymerization and verified the structure and thermal stability of the resin using FT-IR and TGA. Omrani *et al.* (2017) reported a comparison between moisture susceptibility of WMA and WPMA mixtures. The tensile strength of modified WMA under different conditions was compared. Shihab *et al.* (2018) discovered that applying initial duration time with different temperatures highly affect the mechanical properties of soft clay soil – fly ash based (Geopolymers. Jain and Hamedi 2018) found that adding dry resin polymer increases adhesion and bonding in the mixture.

Fluorine resins with high fluorine content are expensive. It was hard to degrade which cause environmental pollution. Therefore, acrylic resin with organic fluorine monomer G02 and silicon monomer A-151 were modified to reduce the amount of organic fluorine monomer with high value and serious pollution. The resins were also modified to properties of thermal stability, high tensile strength and elongation.

In this study, the methyl acrylate was modified with hexafluorobutyl methacrylate (G02) and vinyl triethoxy silane (A-151) as modified monomers, Methyl Methacrylate (MMA) as hard monomer and Butyl Acrylate (BA) as soft monomer. Pre-emulsification, seed emulsion and semi-continuous synthesis process were adopted to the effects of the preparation process, the ratio of G02 and A-151 modified monomers, the amount of soft monomer and hard monomer on product performances. The structure of the modified acrylate was characterized by infrared spectroscopy (FTIR). The thermal stability of the product was determined by the Thermo Gravimetric Differential Thermal Analyzer (TG-DTA). The results show that the resin has excellent thermal stability and other properties meet GBT 20623-2006 and JG/T172-2014.

Experimental Methods

Materials Preparation

Soft and hard monomer MMA, BA and silicone A-151, organic fluorine monomer G02, sodium lauryl sulfates SLS, ammonia water, OP-10; initiator Ammonium sulfate APS; NaHCO₃; deionized water. RG T-10 Microcomputer controlled electronic universal testing machine, VQF-410 FTIR Infrared Spectrometer; DTA-TG coupled Analyzer, were used to analysis.

Preparation of Fluorine/Silicon Modified Acrylic Emulsion

The monomer mass fraction was 30% for MMA and 70% for BA. The amounts of the modified monomers G02 and A-151 and the following reagents were calculated based on the total mass of the monomers. The sum of G02 and A-151 was 5% and the ratio of G02 to A-151 was 4:1. SLS: OP-10 was 1:1; accounting for 3% of the total monomer, pH regulator NaHCO₃ was 0.3% and initiator APS was 0.4%. The solid content was 45%.

Emulsified monomers with 1/2 complex emulsifier were prepared. The 20% pre-emulsified monomer, the 30% initiator solution and the pH regulator Na₂CO₃ solution were placed in a four-mouth flask. The reaction was initiated with heating up and the seed emulsion was obtained. After the blue phase appeared in the four-mouth bottle, the residual emulsified monomer was added, the dropping time was controlled and the temperature was preserved after reaction finished increasing the monomer conversion rate. After the reaction was over, the temperature was dropped, pH was adjusted to 7~8 with ammonia and the emulsion was filtered by 100 mesh screen. The solid content of emulsion, monomer conversion and gel rate were calculated. At last, the latex film was prepared for performance evaluation.

Results and Discussion

Determination of solid content X:

$$X = \frac{W_2 - W_1}{W} \times 100\% \quad (1)$$

W_1 indicates the quality of aluminum foil box, W_2 represents the mass of resin aluminum foil box after constant weight and W was the mass of emulsion added to aluminum foil box.

Determination of monomer conversion rate S:

$$S = \frac{\text{total emulsion} \times \text{solid content} - \text{nonvolatile content except resin}}{\text{monomer total}} \times 100\% \quad (2)$$

Determination of Gel rate G:

$$G = \frac{M_1}{M} \quad (3)$$

In this formula: G was gel rate; M_1 represents the mass of the polymer after drying; M was the total number of monomers.

Tensile Performance Test

According to the national standard of China GB 228-2002: Cutting a latex film with a length of 100 mm, a

width of 10 mm to 14 mm and a thickness of 1 mm, a test temperature of 10°C and a tensile rate of 50 mm/min.

FTIR Infrared Spectrometer Test

The resolution was 4.0, the scanning interval was 4000~400 cm⁻¹ and the scanning frequency was 32 times.

TG-DTA

Nitrogen protection, Temperature measurement from 0 to 800°C, Heating rate of 10°C/min

According to the national standard of China GB/T20623-2006 to determine the stability of emulsion Ca²⁺, GB/T1738-79 (89) to determine the water absorption rate of the membrane, GB GB/T9286-1998 to determine the adhesion.

The Ratio of Soft and Hard Monomers

According to the initial formulation soft and hard monomer ratio on the emulsion and film properties, the results were shown in Table 1. The experiment obtained a stable emulsion of blue-white with fluorescence as seen in Table 1. Calcium ion stability meted the requirements. As the amount of hard monomer increased, monomer conversion decreased. When the

MMA/BA was 0.4/0.6, the water absorption of the film was the smallest. It was illustrated in the experiment that when the proportion of hard monomer was small, the surface of the latex film was sticky and soft at room temperature and the formed film was not dense enough; when the proportion of hard monomer was increased to 0.7:0.3, there were tiny cracks in the film formation.

The elasticity of the prepared film was shown in Fig. 1. With the increasing of the ratio of hard monomer, the tensile strength of latex film increased and the elongation decreased. The resin was elastic because the glass Transition temperature (T_g) of the prepared resin was low. The polymer was in a high elastic state at room temperature. According to the Chinese National Standards, the index of elongation at break of elastic coatings on internal and external walls was ≥150; ≥200 and no elasticity was specified. Generally, the elongation was about 200%, the elasticity was low, 300% was medium elasticity and 400% or more was high elasticity. The results showed that the conversion rate was high, the film formation at room temperature was good, the water absorption rate of the film was low and the MMA/BA with high elasticity was 0.4/0.6. The following experiment was carried out to balance the resin properties.

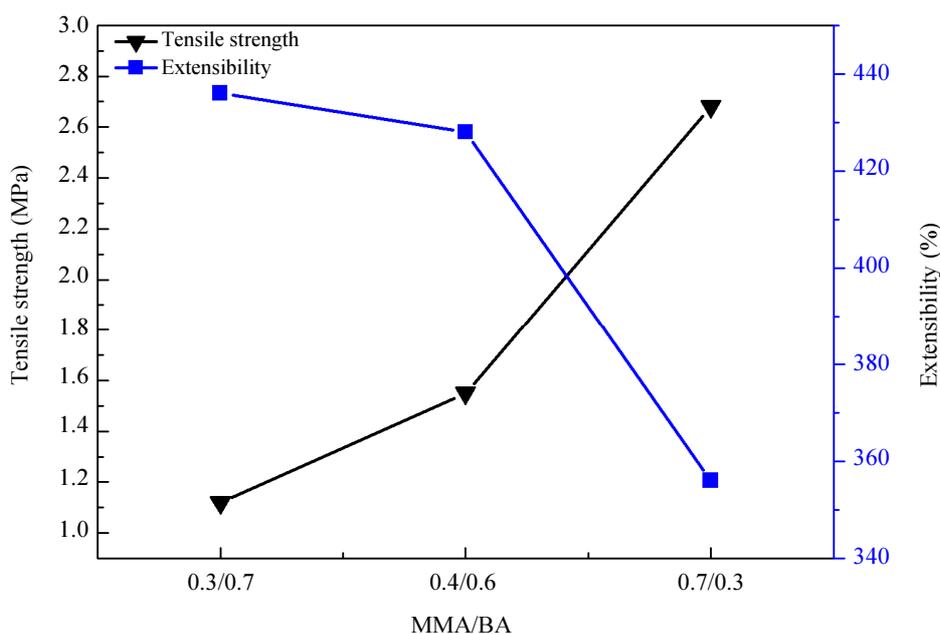


Fig. 1: The tensile and extensibility of the ratios of soft and hard Monomer

Table 1: The results of the ratio of soft to hard monomers

MMA/BA	Emulsion appearance	Gel rate %	Fractional Conversion [%]	Calcium ion stability	Water absorption [%]	Adhesion	Tensile Strength [MPa]	Extensibility [%]
0.3/0.7	Blue and white	3.1	96.8	Stable	9.5	1	1.12	436
0.4/0.6	Blue and white	1.2	96.5	Stable	7.1	0	1.55	428
0.7/0.3	Blue and white	2.2	93.2	Stable	11.9	0	2.68	356

Table 2: Effect of fluorine/silicon content on properties of acrylic emulsion

Total fluorine/ silicon content [%]	Gel rate [%]	Fractional conversion [%]	Tensile strength [MPa]	Extensibility [%]	Water absorption [%]
5	1.2	96.5	1.55	428	6.3
8	0.9	94.4	2.14	332	4.8
11	2.2	92.1	3.87	285	5.7

Effect of Total Fluorine Silicon on the Properties of Acrylic Emulsion

The results of the study on the effects of total fluorine and silicon monomers are shown in Table 2. As can be seen from Table 2, as the total amount of fluorine and silicon monomers increases, the tensile strength of the adhesive film increases, but the elongation decreases. The possible reason is that G02 and A-151 act similarly to hard monomers in the resin. The methyl group in G02 and the ethoxy group in A-151 also hinder the rotation of the carbon chain, improve its tensile strength and reduce film extension performance.

In the calcium ion stability test of the emulsion, calcium chloride was added to the emulsion and allowed to stand for 48 h. The three emulsions prepared were observed to have no delamination, gelation, flocculation and the like and the calcium ion stability was determined. As seen from Table 2, with the increasing of the total amount of G02 and A-151 fluorine/silicon monomers, the monomer conversion decreased the tensile strength of latex film increased and the elongation decreased. However, the membrane water absorption decreased and then increased, due to slight cracking of the membrane.

When the total amount of fluorine/silicon was 5%, the elongation of the film exceeded 400%, the film reached the requirement of high elasticity and the tensile strength still conformed to the requirement of not less than 1.0MPa stipulated by JGT/172-2005. But it still didn't conform the requirement of ≥ 2.0 in JG/T172-2014 "Elastic Coatings".

The Proportion of Fluorine/Silicon Monomer

The effects of G02 and A151 are similar, but the properties of the modified resin are different due to their different structures. The amounts of fluorine silicon were shown in Table 3.

As shown in Table 3, the fluorine to silicon ratio was increased, the tensile strength was increased and the elongation was highest at 2:3. As the amount of G02 organofluorohexafluorobutyl hexafluorobutylate increased, the water absorption of the coating film decreased, which was due to an increase in the content of the organic fluorine hydrophobic group. At the same time, it was seen in the calcium ion stability experiment that as the amount of G02 was increased to 4:1, calcium ions are added to the emulsion and a large amount of

precipitate was formed immediately and the stability of calcium ions was not satisfactory. Compared with the ratio of fluorine to silicon of 2:3 and 3:2, the calcium ion stability meets the requirements. Although the ratio of fluorine to silicon was 3:2, there was better tensile strength and the elongation rate meets the requirements of high elastic resin. When the ratio was 2:3, there was a better elongation and lower fluorine content, so the following experiment was carried out when the ratio of fluorine to silicon was 2:3.

The Effect of Seed Emulsion

The pre-emulsified monomer, water and an initiator were added to the reactor four-necked flask and the mixture was heated to carry out emulsion polymerization to produce a certain amount of latex particles with a small particle size as a seed. The amount of seeds prepared was changed and the effect on the modified resin was examined, as shown in Table 4.

As shown in Table 4, the preparation process affects the quality of the resin. The amount of the seed emulsion formed was different and the properties of the prepared emulsion and film are also different. This was because the reaction was based on the latex particles formed by the seed emulsion and the reaction proceeds on the surface and the latex particles grow. The larger the amount of the seed emulsion, the more latex particles are formed and the smaller the diameter of the latex particles formed by the polymerization of the remaining monomers on the latex particles. That was to increase the seed emulsion, the latex particle size was reduced and the seed emulsion was reduced, which can increase the particle size of the latex and affect the performance of the resin.

The experiment was carried out with 20% seed emulsion with lower monomer conversion, maximum elongation and lower water absorption. Furthermore, the properties of the resin were affected.

As seen in Table 4, the amount of seed emulsion affected the monomer conversion rate less and under the experimental conditions, there was a higher monomer conversion rate. The experiment was based on the Chinese standard GB T 20623-2006 "Coating emulsion" and the previous experimental results of all factors met the requirements. Adhesion was 3 only when the amount of seed emulsion was 10%. The effect of the amount of seed emulsion on the elasticity of the film was shown in Fig. 2.

Table 3: Effect of fluorine/silicone on emulsion

Fluorine/silicon ratio [%]	Gel rate [%]	Fractional conversion [%]	Tensile strength [MPa]	Extensibility [%]	Water absorption [%]
1:4	1.4	96.8	1.57	413	6.5
2:3	1.6	95.6	1.76	713	6.1
3:2	1.4	98.7	1.94	659	5.2
4:1	1.6	99.0	3.98	376	4.8

Table 4: Effect of seed emulsion content

Seed emulsion content [%]	Emulsion appearance	Gel rate [%]	Fractional conversion [%]	Water absorption [%]	Adhesion	Tensile strength [MPa]	Extensibility [%]
10	Transparent blue light	0.4	95.8	6.1	3	1.51	589
20	Ivory-white blue light	1.2	98.5	5.3	1	1.95	724
30	Ivory-white blue light	2.7	97.8	6.7	1	1.75	556
40	Ivory-white	0.8	98.0	8.9	1	2.21	453

Table 5: Effect of dropping time on pre-emulsified monomers

Dropping time [h]	Gel rate [%]	Fractional conversion [%]	Tensile strength [MPa]	Extensibility [%]	Water absorption [%]
1.5	2.1	87.9	1.80	237	11.5
2.0	1.2	98.3	2.13	736	5.1
2.5	2.7	97.8	2.76	588	4.9

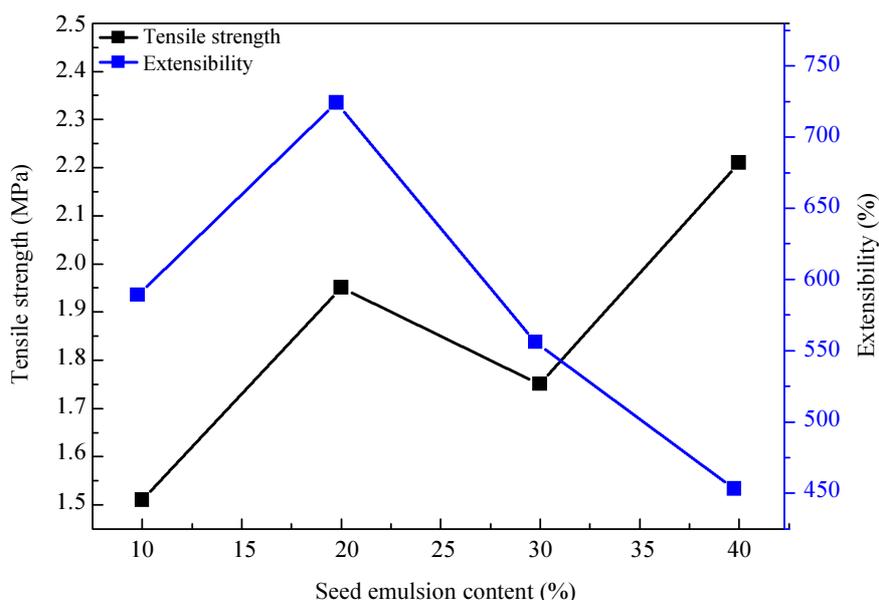


Fig. 2: The effect of the amount of seed emulsion on the elasticity of the film

As shown in Fig. 2, when the amount of the seed emulsion was 20%, the tensile strength and the elongation ratio were optimized. The following experiment was carried out with a 20% seed emulsion amount.

Relationship between Monomer Conversion Rate and Pre-Emulsified Monomer Dropping Time

Monomer pre-emulsification, seed emulsion and semi-continuous emulsion polymerization processes

were employed to explore the relationship between monomer conversion rate and pre-emulsified monomer dropping time. Based on the above formula optimization, the relationship was shown in Table 5.

As shown in Table 5, monomer conversion, gel fraction and film properties were affected by the time during which the pre-emulsified monomer was added. When the pre-emulsified monomer dropping addition time was too short, the polymerization reaction time was

also short and the polymerization time of the monomer was shortened as a whole, so that the monomer conversion rate was low at 1.5 hours. The tensile strength and elongation of the prepared modified resin were also small. At the same time, the water absorption of the prepared film was large. As the pre-emulsified monomer drop addition time increased, the tensile strength of the latex film increased and the elongation increased. However, as time went on, the tensile strength of the film increased and the elongation decreased. As shown in Table 5, when the dropping time were 2 hours, the water absorption of the film was low and the tensile strength and elongation meet with the Chinese national standard GBT 20623-2006 "Coating emulsion" and JG/T172-2014 "Elastic Coating"

Optimization and Characterization

Based on the above single-factor experiments, the optimized formula and process are as follows: The ratio of MMA to BA is 0.4: 0.6, the amount of G02 and A-151 is 5% of the total monomers. The dosage ratio of G02 and A-151 is 2: 3. The total amount of compound emulsifier OP-10/SLS is 3% of the mass of the total monomers and the ratio is 1: 1. The amount of initiator was 0.4% and the amount of buffer was 0.3%. The experiment uses monomer pre-emulsification and seed emulsion semi-continuous synthesis process. The seed emulsion is 20% of the pre-emulsified monomer and the remaining emulsified monomer dropping time is 2 h. The reaction temperature was 80°C. The conversion rate of the prepared emulsion was higher. The tensile strength and elongation of the modified resin were larger. The water absorption rate was lower. The adhesion was level

1. The infrared spectrum of the prepared modified resin was shown in Fig. 3.

As shown in Fig. 3, the stretching vibration peak of Si-O-C was 1163 cm^{-1} . Characteristic peaks of Si-C 752 cm^{-1} and 840 cm^{-1} C-F stretching vibration peak 1239 cm^{-1} . However, the characteristic peak of C = C was not seen, indicating that C = C in the soft and hard monomer and G02, A151 was completely involved in the copolymerization. The reaction was complete. 1732 cm^{-1} was the characteristic peak of ester carbonyl C = O in acrylate. 2876 cm^{-1} and 2958 cm^{-1} were the methyl and methylene C-H stretching vibration absorption peaks, respectively. The O-H stretching vibration peak at 3438 cm^{-1} and the hydroxyl absorption peak formed by hydrolysis of A151.

As shown in Fig. 4. The fluorine/Silicone co-modified acrylic resin TG-DTA, below 200°C, the weight loss rate of the modified resin was only 2.05%, which may be the unreacted monomer in the resin, or solvent water. The rate of weight loss was slow. As shown by the DTA curve, the curve was a downward trend between 0°C and 49.5°C, because the resin was heated and the small molecules were volatilized by heat. The weight loss rate of the latex film was mainly in the range of 301.6°C ~ 435.3°C. The rate of weight loss was the fastest at 399.76°C. The polymer as shown was thermally stable. It can be used below 400°C. As shown in the figure, the curve of DTA was expressed as an endothermic peak in the range of 311.4°C ~ 436.3°C, which may accelerate the weight loss of TG, which were C-Si, C-F bond energy, a fracture absorption peak in the polymer. The thermal stability of the modified resin was better and suitable for coatings.

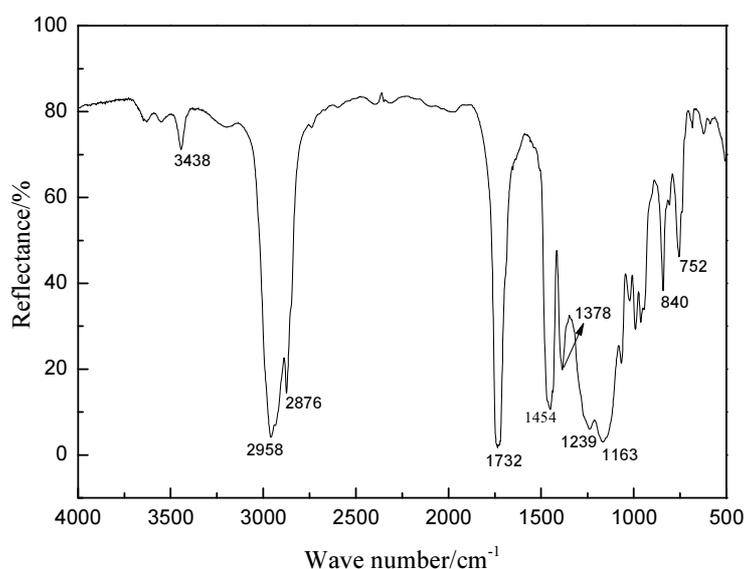


Fig. 3: Infrared spectra of fluorine/silicon co-modified acrylic emulsion

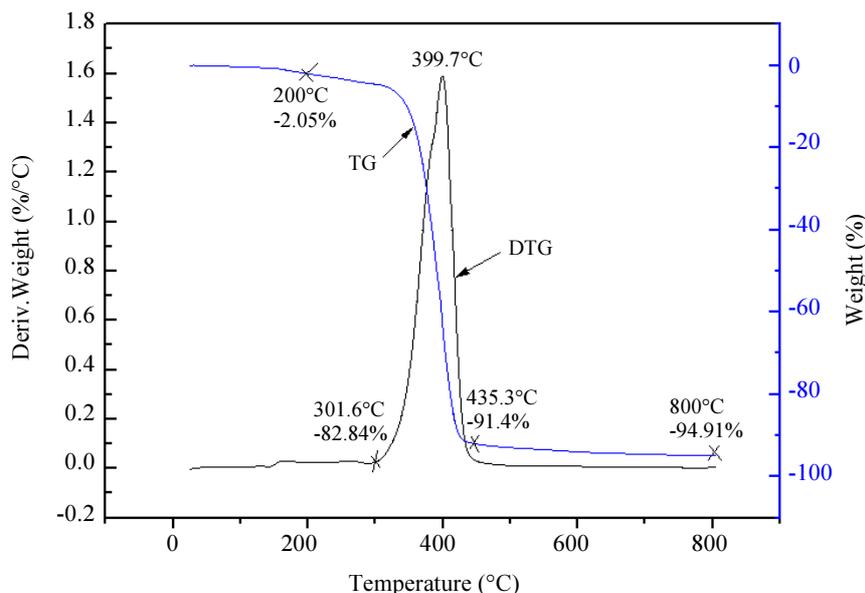


Fig. 4: TG-DTA Diagram of Fluorine/Silicon Co-Modified Acrylic Resin

Conclusion

From the above experiments and analysis, the amount and ratio of the modified monomers G02 and A-151 have a greater impact on the tensile strength and elongation of the acrylate. As the amount of the fluorine monomer increases, the tensile strength of the resin increases. When the fluorine/silicone is 2/3, the resin has the highest elongation. At the same time, the properties of the resin were affected by the preparation process. When the amount of seed emulsion is 20% and the drop time is 2h, the tensile strength and elongation are optimized. A fluorine silicone co-modified acrylate containing a lower fluorine monomer was prepared. And FT-IR verified that acrylic resin was successfully modified by G02 and A-151 because the characteristic peak of C = C was not seen. There was no C = C bond capable of photo aging in the modified resin and the light aging resistance was good. The weight loss rate before 200°C was only 2.05%. The rate of weight loss was the fastest at 399.76°C, this means that the use temperature of the paint film is below 400°C. The heat resistance was good. The tensile strength and elongation of the resin were better, meeting the requirements of the Chinese national standard GB/T 20623-2006 and JG/T 172-2014. The experiment obtained an elastic emulsion that satisfies the requirements and thermal stability, tensile strength and elongation of the prepared product are better than other modified acrylic resins.

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Author's Contributions

Yuan Zhihua and Xia Chunlei: Participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Geng Ziye, Zhao Hongzhi and Zhang Aili: Designed the reached plan and summarized the experimental data.

All authors read and approved the final manuscript.

Ethics

The authors declare their responsibility for any ethical issues that may arise after the publication of this manuscript.

Conflict of Interest

The authors declare that they have no competing interests. The corresponding author affirms that all of the authors have read and approved the manuscript.

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