Article

Mixed solvents in multi-layer ceramic capacitors (MLCC) electronic paste and their effects on the properties of organic vehicle

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Abstract: The copper end paste used in multilayer ceramic capacitors sintered in nitrogen atmosphere will lead to carbon residue of organic vehicle, which will lead to the reduction of electrode conductivity and high scrap rate. With an attempt to leave no residue in the sintering, the compatibility of solvents and thickeners should be improved because it has an important influence on the hierarchical volatilization and carbon residue of organic vehicles. In this work, the volatility of different solvents was compared and several solvents were mixed in a definite proportion to prepare an organic vehicle with polyacrylate resins. The hierarchical volatility and solubility parameters of mixed solvents were adjusted effectively by changing proportions of different components, the thermogravimetric curves of resins and organic vehicles were measured by thermogravimetric analyzer, the effect of solubility parameter on the dissolvability of resins in the solvent and the residual of organic vehicles were studied. Results showed that the hierarchical volatilization of solvents can be obtained by mixing different solvents; the intrinsic viscosity of the organic vehicle is higher and the thermal decomposition residue of polyacrylate resins is lower when the solubility parameters of mixed solvents and polyacrylate resins are closer. The low residual sintering of organic vehicles can be achieved by using the mixed solvent with hierarchical volatility and approximate solubility parameters as resins.

Keywords: electronic paste; organic vehicle; mixed-solvents; solubility parameter; low residual rate

1. Introduction

With the increasing demand for multi-layer ceramic capacitors (MLCC) in the market, the requirements of electronic information products for MLCC tend to be high frequency, low power consumption, miniaturization, superior energy storage and low cost [1]. It is worth mentioning that the copper end electronic paste is composed of three main components including conductive phase (copper), bonding phase (glass or oxide crystals) and organic vehicle. The organic vehicle consists of organic solvent and thickener, in which the organic solvent accounts for 65-98%. In addition, polyacrylate resin is commonly used as the thickener in the organic carrier and the sintering residue of the organic vehicle mainly depends on the thermal degradation of the polyacrylate resin thickener in the solvent. At present, Cu electrode with better conductivity has replaced precious metal electrode as the mainstream electrode material [2], however, due to the oxidation characteristics of Cu, sintering can only be performed in nitrogen. Carbon residue caused by sintering Cu end slurry in nitrogen atmosphere poses a great challenge to the selection of organic vehicle composition of base metal inner electrode multilayer ceramic capacitor (BME-MLCC) [3]. The residual rate of thickener in organic vehicles is the key factor to determine the conductivity of electrodes [4]. The carbon remaining in the conductive film will greatly affect the electroconductibility of the film. There are copious studies on the effects of sintering atmosphere, temperature, rate, and time on electroconductibility [5–

10], but there is still not clear to our knowledge on the effect of thermal degradation characteristics of thickener on carbon residue, and thickener is the main component of the organic vehicle that applied in MLCC. Therefore, it has practical significance to develop the methods to select the mixed solvent with hierarchical volatility and to prepare organic vehicles with extremely low residue, on the basis of the relationship between the mutual solubility of mixed solvents and thickeners.

The organic vehicle is generally composed of solvent, thickener, surfactant, thixotropic agent, and other additives. The organic solvent is the primary component of the organic vehicle, with about 65% – 98% of the total mass of the organic vehicle. It should dissolve the thickener quickly with excellent solubility and have a high boiling point to avoid volatilization in preparing the organic vehicle. The organic vehicle with mixed solvent can adjust the volatilization characteristics and achieve non-volatilization at low temperature, whereas hierarchical volatilization at drying temperature [11]. Meanwhile, it can improve the viscosity and fluidity of slurry, and enhance its stability and printability. In addition, the reasonable selection of mixed solvents can also enhance the solubility of thickener and the wettability of copper, which greatly improves the performance of electronic paste in MLCC.

In this paper, according to the volatilization characterizes of different solvents, the mixed solvents with different components were prepared and the key factors of hierarchical volatilization of organic vehicles were explored. In order to investigate the wettability of copper powder and glass powder to mixed solvents, the contact angle data were measured by a contact angle tester. According to the solubility parameter close principle, solubility parameters of mixed solvents and polyacrylate resins were calculated and compared, meanwhile, the intrinsic viscosity of polyacrylate resins in the mixed solvents was measured, the relationship between solubility parameters and intrinsic viscosity of the organic vehicles was clarified in the end. Furthermore, thermal properties and residual rate of organic vehicles were characterized by TG, the effect of compatibility between the mixed solvent and polyacrylate resins on the residue of organic vehicle was analyzed.

2. Experimental

2.1. Materials

Terpineol (T) and N, N-dimethylformamide (DMF) were purchased from Tianjin Damao Chemical Reagent Factory, China. Diethylene glycol butyl ether (DGBE), Diethylene glycol butyl ether acetate (DBAC) and Ethylene glycol ethyl ether acetate (CAC) were purchased from MACKLIN, China. All reagents are analytical grade without further treatment before use. Copper powder and glass powder were provided by Guangdong Fenghua High Tech Co., Ltd., China. Polyacrylate resins A (DEGALAN®LP65/11, Mw≈30000 g/mol), polyacrylate resins B (DEGALAN®LP65/12, Mw≈44000 g/mol) were purchased from Degussa, Germany. Monomers of polyacrylate resin are methyl methacrylate (MMA) and butyl methacrylate (BMA).

2.2. Characterization

2.2.1. Constant temperature volatility of solvent

The constant temperature volatilization test of solvent was carried out on a collector-type magnetic heating agitator (DF-101S, Shandong Kecheng Scientific Instrument Co., Ltd., Shandong, China). 20 g each of five pure solvents or mixed solvents were weighed into a 50 mL beaker and marked as m_1. When the oil bath reached 70℃, 90℃, 110℃, 130℃, 150℃, 170℃, 190℃, respectively, the beaker was put into it and kept the temperature constant for 15 min. Then, the breaker was taken out and cooled to indoor temperature, it was weighed and marked as m_2. The volatilization was calculated according to formula (1), and the results were calculated by averaging the three repeated experiments. T was used as the main solvent to prepare the mixed solvent with the other four solvents at a mass ratio of 50:50, mark as T-XX, which T represents terpineol and XX is the abbreviation

of another solvent. For example, T-DMF represents the mixed solvent prepared with ter-pineol and DMF at the mass ratio of 50:50.

$$\text{Volatilization} = \frac{m_1 - m_2}{m_0} \times 100\%, \quad \text{where } m_0 \text{ is the actual weight of the solvent} \tag{1}$$

2.2.2. The wettability of copper powder and glass powder to mixed solvents

After the copper powder or glass powder was pressed into a sheet by a desktop electric tablet press (FYD-20, SCJS, Tianjin, China), the wettability of the copper or glass powder sheet to the mixed solvent was tested by a contact angle tester (Attentions Theta Flex, Biolin Scentific, Swenden).

2.2.3. Intrinsic viscosity of polyacrylate resins in the mixed solvents

The diluted Ubbelohde viscometer (1834B, ZONWON, Hangzhou, China) was placed vertically in a high precision thermostatic bath (VT2, ZONWON, Hangzhou, China) at $30 \pm 0.01°C$, the outflow time of solvent was marked as t_0, and t_1 of 1.00% poly-acrylate resins A or B solution (10 mL); 5 mL of solvent was added into the viscometer for dilution each time, the concentration of the solution decreased to 0.67%, 0.50%, 0.40%, 0.33% and the outflow time of the diluted solution were recorded as t_2, t_3, t_4 and t_5 respectively. The measurement was repeated for three times, to get the average. The intrinsic viscosity $[\eta]$ was obtained by extrapolation.

2.2.4. Thermogravimetric analysis (TGA)

TGA was carried out on a thermogravimetry analyzer (TG209F1, Netzsch, Germany). Terpineol, DMF and polyacrylate resins A were weighed according to the mass ratio (at 35:35:30) to prepare the organic vehicle, recorded as PA-T-DMF, which PA represents polyacrylate resins A and T represent terpineol. In the same way, the sample number of organic vehicles composed of mixed solvents and polyacrylate resins B mark as PB-T-XX. 10 mg of the organic vehicles was carried out by thermogravimetry in nitrogen atmosphere with a temperature range of 40 – 600°C, heating rate of 20°C /min, then the mass change ($\Delta m\%$) was recorded in the decomposition stage of polyacrylate resins in the thermal decomposition curve.

3. Results and discussion

3.1. Constant temperature volatility of solvent

The volatilization characteristics of organic vehicles are closely related to the manufacturing process of thick film electronic components, which play an important role in the printability, drying and sintering process of electronic pastes [11]. The organic vehicle should not be volatile at room temperature, which is conducive to the storage stability of the slurry. In the drying temperature period, the slurry should volatilize rapidly, which can shorten the processing time. Therefore, the organic vehicle should have a hierarchical volatilization curve [12]. The organic solvent is an important part of preparing organic vehicles, which is to dissolve thickener and adjust slurry. In the sintering process, if the organic vehicle volatilizes too slowly, it will result in sagging at the edge of the end electrode because of the decrease of slurry viscosity at high temperature, if the organic vehicle volatilizes too fast, it will lead to holes in the film because of a large amount of escaped gas. The electrical properties of MLCC are closely linked to the film quality. Therefore, a variety of solvents with different boiling points are often used to form a mixed solvent with a hierarchical volatilization curve. The thickener should have commendable solubility in mixed solvents, which has the characteristics of non-volatile at low temperature and rapid hierarchical volatilization during drying.
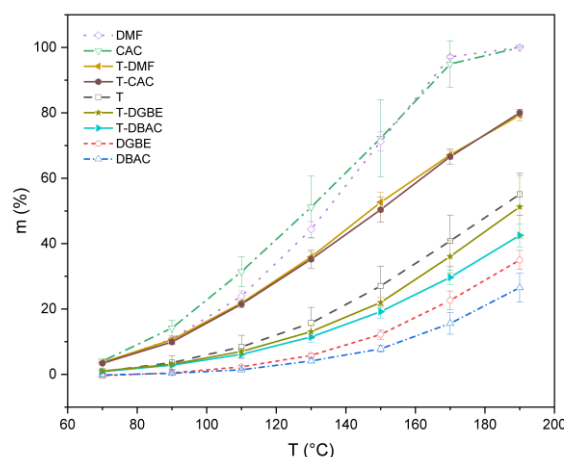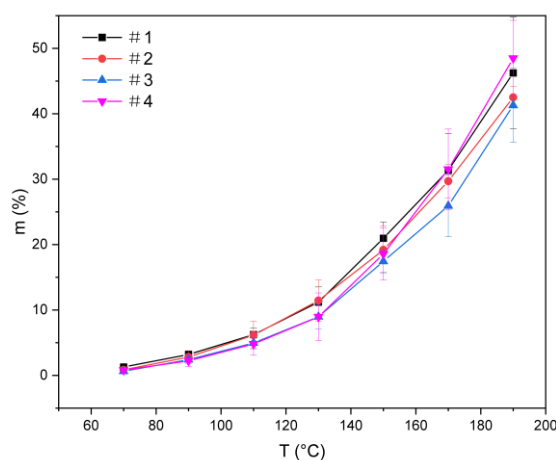
Figure 1. Volatilization curve of pure solvents and mixed solvents, mean values are plotted with error bars representing standard deviation.

The volatilization properties of pure solvents and mixed solvents with a mass ratio of 50:50 are shown in Figure **Figure 1**. The volatilization amount of all solvents increases continuously with the increase of temperature in the overall trend. The evaporation rates of pure solvents from high to low are DMF, CAC, T, DGBE and DBAC which are corresponded to their boiling points at 152.8°C, 156°C, 217°C, 227°C and 246.4°C respectively. It is in line with the law of easy volatilization with a low boiling point. The volatilization amounts of DMF and CAC with low boiling point are more than half at 150°C and they are almost completely volatilized at 190°C. The volatilizations of DGBE and DBAC with high boiling points are indubitably small at 150°C; although the volatilizations are increased to 3 times at 190°C, the volatilizations below 40% are too small to meet the satisfactory sintering process of organic vehicles. In contrast, T volatilizes slowly at low temperature and rapidly at 150 – 190°C, the volatilization at 190°C is nearly twice that at 150°C, which shows the excellent characteristics of not easy volatilization at low temperature and rapid volatilization at high temperature. Therefore, the use of T as one main component in the mixed solvents can effectively avoid the problems such as cavities and sagging of the film after sintering. The volatilizations of T-DMF and T-CAC are lower than those of DMF and CAC because of the relatively lower volatilization ability of T in the mixed solvents. On the contrary, T has better volatilization ability than DGBE and DBAC, which leads to a higher volatilization amount of T-DGBE and T-DBAC.

It is an effective method to adjust volatilization by combining solvents with different boiling points. This can be attributed to the partial pressure of the mixed solvent. According to Henry's law [13], under a certain temperature and equilibrium state, the relative content of the mixed solvent determines the relative ratio of vapor pressure. The ratios of the four mixed solvents are consistent before the thermal volatilization. In the process of thermal volatilization of T-DMF and T-CAC, the two solvents with low boiling points (DMF and CAC) will volatilize preferentially at low temperatures, however, T has less volatilization at low temperatures. Different volatilization rates result in the increased relative ratio of T to DMF and CAC after volatilization for a period, the partial pressure of T increases while the partial pressure of DMF and CAC decreases, which will cause more volatilization of T. For T-DGBE and T-DBAC, T is the component with a low boiling point and volatilizes mainly at the beginning. With the change of partial pressure, the volatilization of DGBE and DBAC will be increased. Therefore, mixed solvents with proper proportions can achieve hierarchical volatilization in order to avoid volatilization unevenly.

Based on the volatilization results of solvents, CAC shows the rapidest volatilization and the largest standard deviation due to its low boiling point. In order to reduce the error of solvent volatilization, a small amount of CAC is utilized to prepare mixed solvent for adjusting volatilization in relative low temperatures. At the same time, T and DBAC have better volatilization stability, which is suitable as the primary components of mixed

solvents to investigate the effects of different ratios on the volatilization characteristics of mixed solvents. The volatilization characteristics of mixed solvents composed of T, DBAC and CAC in different proportions were studied, the mass fraction, volatilization curves and amounts are shown in Figure **Figure 2** and Table **Table 1**. From the volatilization curves, the mixed solvents added with CAC showed better hierarchical volatilization, furthermore, #4 showed the most obvious hierarchical volatilization characteristics. In the range of 40 – 130°C, the rising range of volatilization curve was small, showing the first level of the curve. In the range of 130 – 170°C, the solvent began to volatilize rapidly, and the rising range of volatilization curve increased, showing the second level of the curve compared with the previous stage; After 170°C, the rise of volatilization curve is more obvious than that of the previous stage, showing the third level of the curve. In summary, the mixed solvent shows multi-level volatilization with slow volatilization at low temperature and rapid volatilization at high temperature.

Figure 2. Volatilization curve of mixed solvents with various mass ratio, mean values are plotted with error bars representing standard deviation.

Table 1. Composition of mixed solvents and their volatilization amount at different temperatures

Sample	T (wt/%)	DBAC (wt/%)	CAC (wt/%)	Vol (%)	
				150°C	190°C
#1	50	40	10	20.96	46.24
#2	50	50	0	19.20	42.51
#3	30	60	10	17.44	41.28
#4	60	30	10	18.56	48.48

From Table **Table 1**, the volatilization amount of the four mixed solvents at 190°C is more than twice that at 150°C, moreover, volatilization amount of #4 at 190°C is the highest, showing commendable volatilization performance.

It is mainly due to the difference in boiling points of the three components. According to Figure **Figure 1**, the volatilization of the three solvents is small at low temperature, and DBAC with a high boiling point is basically nonvolatile. The partial pressure of the mixed solvent is mainly concentrated in the relative content of T and DBAC, the volatilization curve rises gently. With the temperature being close to the boiling point of CAC, CAC begins to volatilize a large amount, the volatilization curves increase rapidly. As the temperature rises to 170°C, CAC has been volatilized completely due to its small relative content, the volatilization of solvent is mainly concentrated in the co-volatilization of T and DBAC. Compared with CAC, T and DBAC have greater relative content, so the volatilization curve shows a greater increase range. Furthermore, the relative content of T in #4 is

greater than that of DBAC, and the volatilization capacity of T is better than that of DBAC, so the rising range of volatilization curve is greater and the hierarchy is the most obvious. The volatilization ability of #3 is the worst because of the highest content of DBAC in the mixed solvent. It can be concluded that the hierarchical volatilization of the mixed solvents can be adjusted effectively by adjusting the proportion of solvent components [11,14,15]. Therefore, the slurry prepared with the organic vehicle with hierarchical volatilization can achieve satisfactory discharge and sintering [16].

3.2. Wettability of mixed solvents to glass powder and glass powder

As a base metal with excellent conductivity, Cu has gradually attracted much attention in the field of electronic paste in recent years. Da Costa et al. stated that the dispersion of copper plays the most important role in sintering, and it is the main agent responsible for the densification both in solid and liquid states [17]. The wettability of mixed solvent to copper powder sheet is shown in Figure **Figure 3**. It can be observed in the figure that the four mixed solvents have satisfactory wettability to the copper powder sheet. Contact angles are all below 10°, which is close to complete wetting. Moreover, the wettability of the four mixed solvents to the glass powder is complete wetting (see the supporting for detailed data). According to the contact angle data of solvent on metal particles and glass powder, the four mixed solvents with the mass ratio of 50:50 meet the requirements of commendable wettability to bonding phase and conductive phase. Better wettability of mixed solvents to copper and glass powders is beneficial to the dispersibility of particles in the slurry and uniformity of sintering products. When the slurry is sintered, the glass powder softens, and the liquid organic vehicle can freely contact the adjacent copper conductive phase. With the increase in temperature, the metal particles rearrange and tend to be close. During the cooling process, the glass powder shrinks and the metal particles are in close contact, finally, a satisfactory conductive path is formed [18,19].
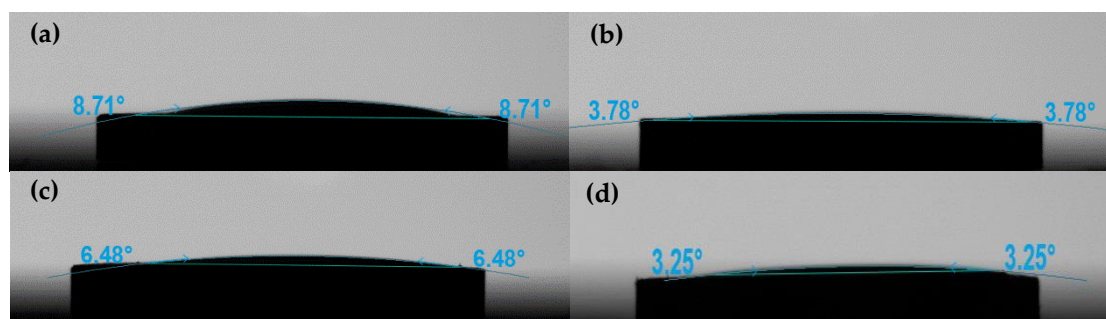
Figure 3. Contact angles of the mixed solvents on copper powder sheet (**a**) T-DMF; (**b**)T-DBAC; (**c**) T-CAC; (**d**) T-DGBE

3.3. Solubility of polyacrylate resins in mixed solvents

Polyacrylate resin is often used as thickener in electronic paste, the solubility of solvent to thickener is genuinely important for film-forming quality, it not only has an important impact on the rheology of organic vehicle, but also plays a certain role in the thermal degradation of polyacrylate resin, better solubility can effectively reduce the thermal degradation residue of thickener. When the solubility parameters of solvent and thickener are closer, it is generally considered that the thickener has stronger solubility in solvent. According to Hansen's dissolution parameter theory, the group contribution method is often used to calculate the solubility parameters δ of polymers [20,21]. Hansen et al proposed to divide the cohesive energy into three parts, i.e., $E = F_d + F_p + F_h$, which F_d, F_p and F_h are the contribution values of dispersion forces, dipole force and hydrogen bonding respectively. Therefore, the solubility parameters can be calculated as following:

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2 \tag{2}$$

δ_d is the dispersion solubility parameter; δ_p is the polar solubility parameter; δ_h is the hydrogen bond solubility parameter.

The three-dimensional solubility parameters of copolymers such as polyacrylate resins can be calculated by the mole fraction weighted average of homopolymer solubility parameters [22]:

$$\delta = \sum \delta_i \phi_i (\phi_i \text{ is the mole fraction of component i}) \tag{3}$$

Due to the limitations of the classical model for calculating the solubility parameters of mixed solvents, Yang long et al. [23] proposed a new nonlinear mathematical model calculation method to accurately calculate the solubility parameters of mixed solvents and introduced the volume component of solvents as the calculation parameters. Calculate the solubility parameters of mixed solvents:

$$\delta^2_{t,m} = \psi_1 \delta_{t,1}{}^2 + \psi_2 \delta_{t,2}{}^2 + \dots + \psi_n \delta_{t,n}{}^2 \tag{4}$$

ψ_i represents the volume component of component j, $\delta^2_{t,m}$ represents the square of solubility parameters in each dimension.

According to the three-dimensional solubility parameters of solvents and monomers of resins in Table S1, the solubility parameters of polyacrylate resins and mixed solvents are calculated according to formula 3 and formula 4, as shown in Table **Table 2**. The solubility parameters and the intrinsic viscosity of the organic vehicles with polyacrylate resin A are shown in Figure **Figure 4**.

Table 2. Three-dimensional solubility parameters of solvents, and resins

Sample	δ_d (J$^{1/2}$*cm$^{-3/2}$)	δ_p (J$^{1/2}$*cm$^{-3/2}$)	δ_h (J$^{1/2}$*cm$^{-3/2}$)	δ (J$^{1/2}$*cm$^{-3/2}$)
A and B	16.59	4.20	7.71	18.77
T-DMF	17.25	10.41	11.30	23.10
T-DBAC	16.56	4.87	9.93	19.91
T-CAC	16.56	5.13	11.01	20.54
T-DGBE	16.56	6.26	11.01	20.85
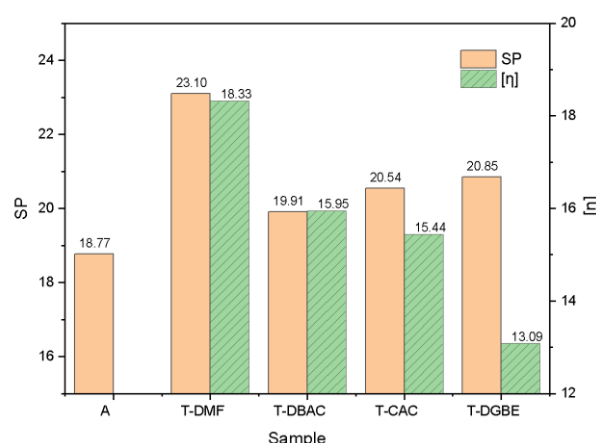
Figure 4.. Solubility parameters (SP) and intrinsic viscosity of organic vehicles with polyacrylate resin A

The solubility parameters of polyacrylate resins A and B are 18.77, because their monomer compositions are the same. The solubility parameters of the four mixed solvents T-DMF, T-DBAC, T-CAC and T-DGBE are 23.10, 19.91, 20.54 and 20.85 respectively. Among them, the solubility parameter of T-DBAC is the closest to those of resins, and the difference between solubility parameters of T-DMF and resins is the largest, especially for the polar solubility parameter (δ_p). When the solubility parameters of polymers are equal to

the solubility parameters of solvents, the intrinsic viscosity of their solutions will be maximized [24] because of the commendable thermodynamic properties. However, As shown in Figure **Figure 4**, the organic vehicle of T-DMF, which has the largest difference in solubility parameters from polyacrylate resin A, shows the highest intrinsic viscosity, while the organic vehicles of T-DBAC, T-CAC and T-DGBE conform to the rules that the smaller the difference in solubility parameters from polyacrylate resin A, the greater the intrinsic viscosity of organic vehicle.

It is noted that DMF is a strongly polar organic solvent with a high polar solubility parameter component. Therefore, the chain stretching process of polyacrylate resin A in T-DMF is mainly controlled by the component of polar solubility parameter. High polarity makes the molecular chain completely stretch, so it has larger hydrodynamic volume and greater intrinsic viscosity. Eom and Kim studied the dissolution process of polyacrylonitrile (PAN) in DMF and DMSO [25], and found that the solubility parameter of DMF (δ = 24.8) is closer to PAN (δ = 25.3) than DMSO (δ = 26.6), however, the experimental results showed that the hydrodynamic diameter of PAN and intrinsic viscosity of solution in DMSO are higher than those in DMF. It is believed that this is mainly caused by the higher polar solubility parameter component of DMSO than DMF. Similarly, it also provides an explanation for the behavior of the intrinsic viscosity of the organic vehicle with A dissolved in T-DMF in this paper.

For the other three mixed solvents with similar three-dimensional solubility parameters as polyacrylate resin A, the hydrodynamic volume of the polymer in the solvent is determined by the solvent. In the solvent which has a high affinity (good solvent) for the polymer, it is easy to be dissolved, and the molecular chain will be stretched, which will result in has a large hydrodynamic volume. On the contrary, if the polymer is dissolved in a solvent with low affinity (inferior solvent), the polymer molecular chain will be curled up and thus have a relatively small hydrodynamic volume [26,27]. The intrinsic viscosity refers to the contribution of a single molecule to the solution viscosity. Since the hydrodynamic volume of the polymer is directly proportional to the viscosity of the polymer solution, the intrinsic viscosity of the polymer solution dissolved in a good solvent will be greater than inferior solvent [26–28].

3.4. Analysis of thermogravimetric results

3.4.1. Thermogravimetric analysis of polyacrylate resins

In order to prevent the poor conductivity caused by oxidation when the copper end is sintered in oxygen atmosphere, at present, the copper electrode MLCC is mostly sintered in nitrogen atmosphere. In the copper end slurry in MLCC, incomplete thermal decomposition of thickener in nitrogen atmosphere will cause carbon residue on the surface of copper powder. Therefore, the selected thickener should have low residue in nitrogen atmosphere. The thermogravimetric analysis results of A and B are shown in Figure **Figure 5**.
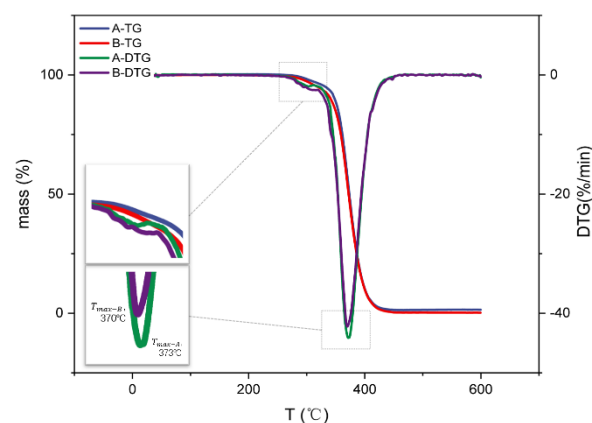
Figure 5. Thermogravimetric curves of polyacrylate resins A and B

The initial decomposition temperature of the sample is about 260°C, and it is completely decomposed at about 460°C, with the final residue rates as 1.46% and 0.21% respectively. Comparing resin A and B, resin B shows a lower initial decomposition temperature and lower maximum decomposition rate temperature, T_{max}, is about 3°C lower than A. With the same monomer compositions, the thermal decomposition stability of polymers is mainly influenced by the molecular weight. The higher the molecular weight, the worse the thermal stability, because the activation energy of polymer degradation decreases with the increase of molecular weight [29]. Meanwhile, the enhanced extraction of intermolecular hydrogen at high temperatures will result in chain scission and increased thermal decomposition [30]. The longer chains showed a great tendency to form tight curves. The resulting bond angular strain will lead to a higher C-C scission rate [31]. In general, the increase of molecular weight will increase the contribution of random fracture, resulting in different end group structures.

The thermogravimetric curve showed two thermal decomposition peaks, of which the thermal decomposition peak of near 370°C was the most obvious. The thermal decomposition process of A and B in nitrogen atmosphere can be divided into two stages: the first stage is 260 – 320°C, the weight loss in this stage is not obvious, mainly the volatile decomposition of residual solvents and small molecular components in the polymer [32]. The second stage is 320 – 460°C, the weight loss is the most notable, and the weight loss rate reaches 95%. The second degradation stage represents the degradation of A and B into small monomer molecules. The resin produces alkyl methacrylate monomer and a small amount of other decomposition products, such as carbon monoxide, carbon dioxide, ethane, methanol, ethanol, and 1-propanol [33,34]. With the continuous fracture of end group structure and the decomposition products volatilize, the weight loss gradually increases.

3.4.2. Thermogravimetric analysis of organic vehicles

The organic vehicle is the key of the electronic slurry in MLCC, which plays a role in dispersing all phases and adjusting the performance of the slurry. The organic vehicle should have commendable thermal degradation performance and low residue to ensure the normal discharge process of the slurry. The TGA of organic vehicles prepared by different mixed solvents and resins were tested, and the results are shown in Figure**Figure 6**.


(a)   (b)
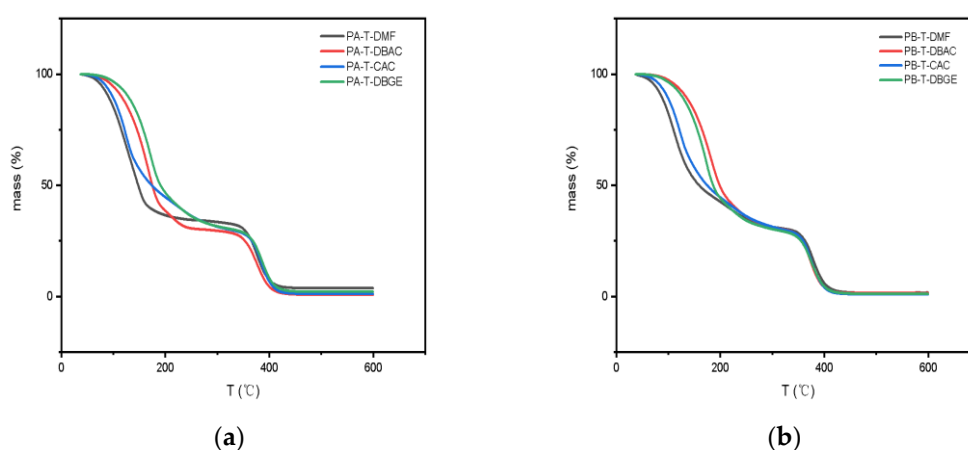
Figure 6. Thermogravimetric curve of the organic vehicles：(**a**) organic vehicles with resin A; (b) organic vehicles with resin B

The thermal decomposition curve of the organic vehicle can be divided into two stages, the first stage is 40 – 320°C, and the weight loss rate is close to 70%. The weight loss in this stage is mainly caused by the thermal volatilization of the mixed solvents in the organic vehicles. Among them, the weight loss is also associated with the volatilization

of the solvents. For both organic vehicles, the weight loss with mixed solvents of T-DMF and T-CAC are started at lower temperatures because of the low boiling points of DMF and CAC. In the second stage of 320 – 460°C, the mixed solvents have been volatilized completely and the polyacrylate resins undergo thermal decomposition. Therefore, the weight loss rate is about 30% which is the proportion of resins in the organic vehicles.

Comparing the thermogravimetric curves of different organic vehicles, it is found that the thermal decomposition of resin in PA-T-CAC and PA-T-DGBE begins at 320°C, the polyacrylate resins in PA-T-DMF and PA-T-DBAC has lower thermal decomposition starting temperature, which is 10 – 20°C lower than PA-T-CAC and PA-T-DGBE. The result indicates that T-DMF and T-DBAC reduce the thermal stability of resin A and B, that is because the curled chain structure of the polymer is stretched, and the hydrodynamic volume and free volume increases more in good solvent [26,27], resulting in the reduction of the distance between molecular chains, the decreased energy to destroy the chemical bond in the molecular chain, therefore, the thermal decomposition temperature decreases to a certain extent. This shows that the intrinsic viscosity of the organic vehicle is qualified as a reasonable indicator for the thermal decomposition of resin, as the intrinsic viscosity of resin A in T-DMF and T-DBAC is greater than that in T-CAC and T-DGBE. However, the solvent has no effect on the thermal stability of B. on the one hand, the solvent has a more obvious effect on the low molecular weight resin, on the other hand, the thermal decomposition of high molecular weight polymer is faster than that of low molecular weight polymer.

In order to further verify the relationship between intrinsic viscosity [η] and residual mass of resin A and B, the intrinsic viscosity, and the mass changes $\Delta m\%$ of organic vehicle in the range of 320 – 460°C were summarized in Figure **Figure 7**. It can be seen that the intrinsic viscosity is directly proportional to the thermal decomposition degree of resin A and B. With the highest intrinsic viscosity, PA-T-DMF and PB-T-DMF show the greatest degree of thermal decomposition and the mass change rate $\Delta m\%$ is 29.58%, 29.10% (the mass ratio of A and B in organic vehicle is 30%), the thermal decomposition rate is 98.6% and 97.0% respectively; On the contrary, PA-T-DGBE and PB-T-DGBE have the lowest intrinsic viscosity, which shows the lowest degree of thermal decomposition with the mass change $\Delta m\%$ as 28.46%, and the thermal decomposition rate as 94.87%. It can be concluded that the greater the intrinsic viscosity of organic vehicles, the more completed the thermal decomposition with less residue.
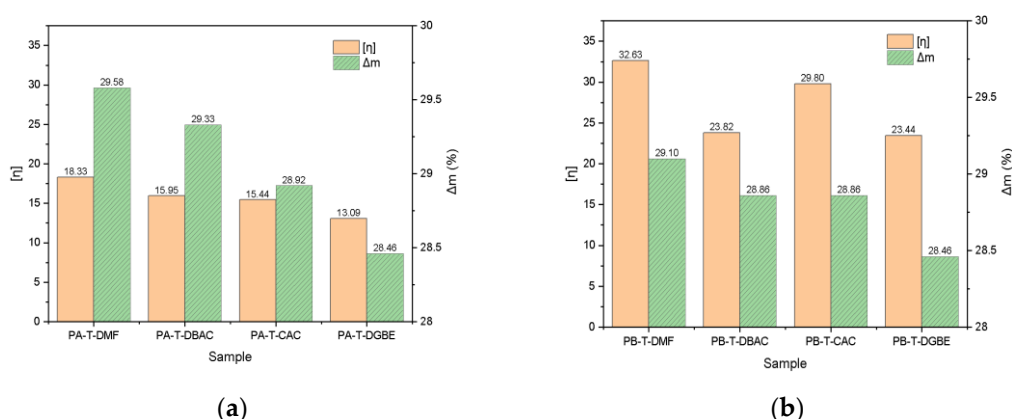
Figure 7. Intrinsic viscosity [η] and mass changes Δm of organic vehicles: (**a**) organic vehicles with resin A; (**b**) organic vehicles with resin B

4. Conclusions

It is an effective method to prepare mixed solvents with differential boiling points and proportions in order to realize the hierarchical volatilization of organic used in MLCC. Terpineol can volatilize slowly at low temperature and rapidly at high temperature, which is a commendable main component in the mixed solvents.

The solubility parameters can be used as the theoretical basis for the selection of mixed solvents for electronic pastes, and the intrinsic viscosity can directly characterize the degree of dissolution of polymers in solvents. The closer the solubility parameters of the mixed solvent and polymer are, the greater the intrinsic viscosity of the organic vehicle is. Furthermore, intrinsic viscosity is a reasonable indicator for the thermal decomposition of resins, the thermal decomposition residue rate of organic vehicle decreases gradually with the increase of intrinsic viscosity, the thermal decomposition residue rate of organic vehicles decreases gradually, and the maximum thermal decomposition rate can reach 98.6%. When preparing the organic vehicle for MLCC electronic slurry, the mixed solvent with similar solubility to the used polymer can be preferentially selected in order to achieve low carbon residue of organic vehicles in the sintering process.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1：Contact angles of the mixed solvents on glass powder sheet (a) T-DMF; (b)T-DBAC; (c) T-CAC; (d) T-DGBE; Video S1-S4: Wetting processes of the mixed solvents on glass powder sheet; Table S1: Three-dimensional solubility parameters of solvents and monomers of resins.

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