Preparation and Properties of Thermally Expandable Microspheres for Leather Foam Coating

by

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Abstract

A type of thermally expandable microspheres (TEMs) for foam coating was prepared by suspension polymerization with acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VAC) as shell polymer monomers and i-pentane as core foaming agent. The effects of an aqueous additive (Sodium Chloride, NaCl) on the size and distribution of TEMs, and the effects of crosslinking degree, i-pentane dosage and monomer mass ratio on the expansion property, expansion temperature and solvent-resistance of TEMs were investigated. The results showed that when the dosage of NaCl was close to the saturation solubility (30%), the dosage of crosslinking agent and alkane were about 0.09% and 7.4%, and the mass ratio of AN/MMA/VAC w rm distribution and good solvent resistance, the expansion diameter ratio was 5 times under 110~120°C, which meets the application requirements for foam coating of leather or synthetic leather.

Introduction

Thermally expandable microspheres (TEMs) are polymer particles at micrometrical scale, prepared by microencapsulation technology.[1] TEMs are composed of a polymer shell with good gas tightness and an inner core of an alkane which has a low boiling point. Figure 1 demonstrates its expansion process: when heating, the internal alkanes create vapor pressure as the temperature rises. As it comes to the correct temperature to soften the polymer shell, TEMs begin to expand; once the temperature decreases, the polymer shell is in a rigid state, and expansion of TEMs remains, which exhibits a foaming effect.[2-3] Because of these characteristics, TEMs have been widely used in many industrial fields, such as plastic foaming,[4-5] adhesives,[6] ink printing,[7] etc. For example, TEMs are added to crystalline polymers, such as polyethylene, to make low density and high heat-resistant foaming composites. When TEMs were blended with adhesives and expanded after fabric and paper being coated and heated, the treated substrates were found to have the advantage of being skid resistant and easy to color. In leather manufacture, TEMs can also be used to prepare foam coating for split leather. Specifically, TEMs are blended with water based polyurethane resin firstly, then followed by a coating process on the corresponding substrate, and accompanied with the procedure of pre-drying and foaming, a foam coating layer can be achieved. The split leather products made by this method not only have a fluffy effect of high quality, an exquisite feel and a tender lustre[8-9] but also possess enhanced fullness, air-permeability and moisture-penetrability.[10] In addition, TEMs can be used as matting and mending materials for grain damaged leather.[11] The damaged grain repaired by this foaming coating shows obvious matting effect, excellent fullness, and polishing performance which will greatly improve the grade of inferior leather products.[12]

Currently, great efforts have been done to investigate the TEMs. Hou et al.[2] used vinylidene chloride (VDC), AN, and MMA as the shell polymer monomers, and isobutane as the internal alkane to prepare such TEMs with the diameter approximately 20μm, the temperature of expansion was 110°C-120°C, and the greatest ratio of expansion was 3 times. Even though VDC is a cryogenic monomer, equipped with the advantage of heat and corrosion resistance, and good gas tightness,[13] it is an extremely toxic substance, in the process of decomposing, it produces harmful substances. Up to now, there are few reports about TEMs on their application in foam coating of leathers, synthetic leathers and textiles.

As a foam coating for leather or synthetic leather, TEMs should meet the technical requirements as below: (1) the polymer shell must be of good gas tightness, pliable, and tough (with proper cross-linking) to avoid the volatilization of the internal alkanes at a low boiling point and assure the morphological stability of TEMs during the expansion process instead of untimely breaking; (2) the internal alkanes of low boiling point should generate enough vapor pressure and should not penetrate the polymer shell during the heating process;[14] (3) because TEMs are blended with resin, which often contains organic solvents, [15] such as *N,N*-dimethylformamide(DMF) and acetone, the polymer shell should be solvent and chemical corrosion resistant; (4) the expansion temperature of TEMs should be higher than the pre-drying temperature (≈100°C) so as to evaporate the moisture and prevent the untimely breaking of microspheres.

Given the aforementioned requirements and taken the expansion performance and temperature, particle size and distribution as well as the solvent resistance of the TEMs into account, a type of TEMs were designed and prepared by optimizing the type of monomers,

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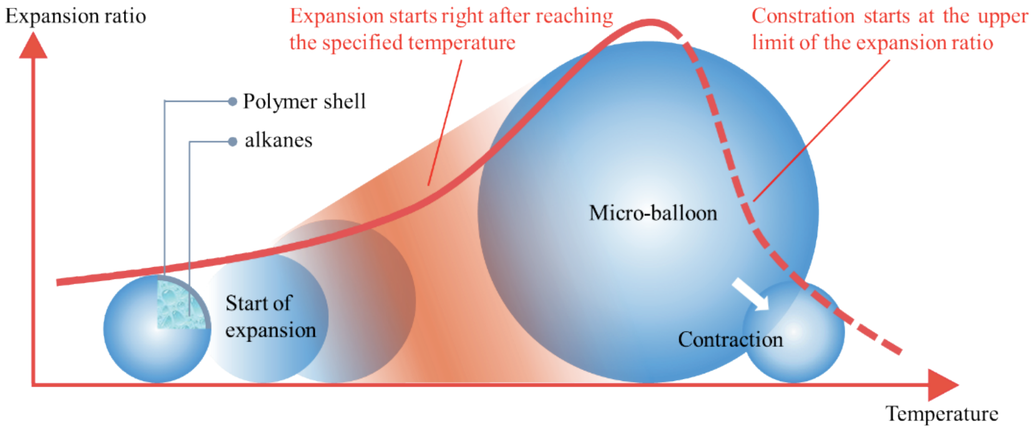

Figure 1. The foaming diagram of TEMs

aqueous additive (NaCl) concentration, cross-linking degree, alkane dosage together with the monomer mass ratio. Furthermore, the expansion ratio, temperature, and the solvent-resistance of resultant TEMs were investigated. The aim of this research is to provide a novel foaming agent and foam technology for leather, synthetic leather and textile coating.

Materials and Methods

Experimental materials

Acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VAC), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), isopentane (i-pentane) were all analytically pure and purchased from Shanghai Adamas Reagent Co., Ltd; Polyvinylpyrrolidone (PVP K30) was analytical pure and purchased from Aladdin China Chemical Reagent Co., Ltd.; sodium dodecyl sulfate (SDS), magnesium chloride hexahydrate($MgCl_2{\cdot}6H_2O$), sodium hydroxide(NaOH), sodium nitrite($NaNO_2$), sodium chloride(NaCl) were chemical purity and purchased from Chengdu Kelong Chemical Reagent Co., Ltd; deionized water was obtained by laboratory-self-made; Waterborne polyurethane(WPU) with 53% solid content was purchased from Liulian New Material Co., Ltd.

Preparation of TEMs

The basic formula for preparing TEMs is shown in Table1.

Table I

The basic formula for preparing TEMs

Phase state	Substance	Dosage/(%)[a]
Aqueous phase	Deionized water	100
	NaCl	0~30
	NaOH	3.70
	$MgCl_2{\cdot}6H_2O$	11.30
	SDS	1.50
	$NaNO_2$	0.03
	PVP K30	0.30
Oil phase	AN	21.5~26
	MMA	7.4~11.1
	VAC	1.9~6.3
	AIBN	0.29
	EGDMA	0~0.19
	i-pentane	3.7~14.8

a: The mass fraction of raw material in the aqueous phase and oil phase were based on the water content.

Aqueous phase preparation: a certain amount of NaOH and NaCl were fully dissolved in deionized water. The aqueous solution of $MgCl_2{\cdot}6H_2O$ containing SDS was first added slowly under stirring, and then stirred vigorously for 30 minutes to obtain the basic dispersion solution, then small amounts of $NaNO_2$ and PVP K30 were added to the mixture to obtain the final dispersion solution by dissolving the mixture evenly. The dispersion solution was put into a refrigerator to cool down.

Oil phase preparation: a certain amount of EGDMA, AIBN, i-pentane were dissolved in weighted mixed monomer (AN, MMA, VAC), and then placed in the refrigerator to cool down.

Emulsification and reaction: The cooled oil phase was mixed with the aqueous phase, and emulsified at 8000 rpm for 3 mins, then quickly poured into the reactor to seal, deoxygenated with nitrogen for 3 mins, and then pressurized to 0.4~0.6Mpa with nitrogen. The rotating speed of the agitator was adjusted to 300 rpm, and the reaction temperature was raised to 60°C. After 20 hours of reaction, the reactor was heated to 70°C for curing for 30 mins, then the temperature was cooled down, and the material discharged.

Post-treatment operation: The pH of the obtained product was adjusted to 2 by dilute hydrochloric acid to remove the magnesium hydroxide deposits on the surface of the microspheres, then washed, filtered and dried at 50°C for 24 hours, the TEMs were obtained.

Preparation of foaming coating

TEMs were added into WPU, and a certain amount of leveling agent, thickening agent and other additives were added under the stirring condition to prepare the coating slurry. The slurry with moderate viscosity was evenly coated on the leather, synthetic leather or textile substrate by roller coating method. The coated substrates were pre-dried in the oven at 100°C for 1 min, followed by a foaming process at 120°C for 1 min, finally, the foaming products were taken out and analyzed.

Finishing of split leather and damaged grain leather

Quantitative TEMs, WPU and other additives were mixed uniformly, and the viscosity of size was increased to a range of 3000~5000 cps, then the size was coated on the surface of split leather and damaged grain leather by roll coating, and pre-dried in the oven at 60°~80°C for 1 min, followed by a hot foaming process at 120°C for 3s, the foamed split leather or repaired leather was obtained.

Characteristics of TEMs

Determination of particle size and distribution

One to two grams of TEMs after the post-treatment were added to 20~30ml of deionized water and dispersed by ultrasonic wave for 2 minutes. The average particle size of TEMs was measured by laser particle size analyzer(LPS), and the size distribution of microspheres was calculated by the formula: $(D_{90}-D_{10})/D_{50}$, where D_{90}, D_{50}, and D_{10} represented the particle size of the sample when the percentage of cumulative particle size distribution reached 90%, 50%, and 10%, respectively, and their physical meaning indicated that the proportions of the number of particles inferior to this particle size out of the total number of particles were 90%, 50%, and 10%, respectively.

Observation on surface morphology

A small amount of dried TEMs were coated on the conductive adhesive, sprayed gold in a vacuum, and then was put under the scanning electron microscope to observe its surface morphology.

Determination of expansion property and temperature

The expansion property of the TEMs was measured by thermal mechanical analysis (TMA). The appropriate amount of the TEMs were placed in an aluminum crucible, being loaded with 0.06 N and heated to 250°C at 15 K/min in a nitrogen atmosphere. Observed the change of probe displacement (dimension change) with temperature to obtain the initial expansion temperature (T_{start}), the maximum expansion temperature (T_{max}), as well as the greatest expansion height (D_{max}).

The endothermic enthalpy(ΔH) of the microsphere in expansion process was measured by using the differential scanning calorimeter (DSC) as the temperature was increased from 20° to 200°C at a rate of 15 K/min under the protection of nitrogen to determine the amount of alkane contained in the TEMs.

Thermogravimetry (TG) analysis was carried out from 35° to 600°C at a heating rate of 15 K/min under the protection of nitrogen. The weight loss rate of TEMs during the expansion process was reflected by differential thermogravimetry (DTG) and used to analyze the change of the polymer shell during the expansion process.

Results and Discussion

Structure design of TEMs

As mentioned above, the polymer shells of TEMs for foam coating require good gas tightness and heat resistance, so the polymer shell of TEMs must be tough, tensile and solvent resistant. There are many available polar monomers with a double bond and heat resistance, such as acrylonitrile(AN), methyl acrylonitrile, methlacrylic acid, and vinylidene chloride, etc. among which AN has a strong interaction between molecules due to the presence of a strong polar cyanogen group in its structure, thus PAN has the advantage of high strength, good gas tightness, good solvent resistance, and high heat resistance.[16-17] Therefore, acrylonitrile was chosen as the main monomer for preparing TEMs. However, it is so susceptible to semi-crystalline that the polymer shell will become too rigid when AN is used as the polymer monomer alone, so the PAN must be modified by copolymerization so as to increase flexibility of the polymer shell.[15] Taken the heat-resistance into account, MMA was selected as a co-monomer. Copolymerization of AN and MMA will decrease the regularity of polymer molecular arrangement and thus decrease the crystallinity of polymer and increase the flexibility of polymer shell.[18] In the expansion process, the volume of microspheres will enlarge many times, so the polymer shell must have a certain of elasticity. On the other hand, the foaming temperature should not be too high, otherwise the grain leather will shrink. On this basis, VAC with a flexible side groups and low toxicity was chosen as the third copolymer monomer, its purpose was to improve the extensibility of the shell and control the expansion temperature.[19] Furthermore, a proper cross-linking can make the polymer shell form a network structure, which can further improve its heat resistance, gas tightness and strength. The alkane contained in TEMs requires a low boiling point, high vapor pressure generated at the expansion temperature, and low permeability from the polymer shell. According to the vapor pressure calculation formula proposed by Magnus Jonsson et al. [14] where vapor pressure (in Bar) = $\exp[C1 + (C2/T) + C3 * \ln(T) + C4 * TC5] * 10^{-5}$, the vapor pressure generated by i-pentane, iso-octane, n-heptane, n-octane and methylcyclohexane at different temperatures was investigated. It was found that the vapor pressure of i-pentane was 1.1 MPa at 122°C, and the temperature could just satisfy the ideal expansion temperature range of TEMs for foam coating of leather, synthetic leather and textiles and the vapor pressure was large enough to ensure the rapid expansion of TEMs. Moreover, the molecular structure of i-pentane is of a branched-chain type, it is difficult to penetrate the polymer shell, this steric hindrance is beneficial to the improvement of expansion performance, that is why the i-pentane was chosen as the inner core for TEMs in this experiment. Just as mentioned above, the particle size and distribution, surface morphology, expansion temperature, expansion ratio and solvent resistance of TEMs play a key role in its application performance in foaming leather-making. Therefore, the effect of parameters on the particle size and distribution, the surface topography, the expansion temperature, expansion ratio of TEMs and other performances of resultant leather were discussed in detail.

Effect of NaCl concentration on the size and distribution of TEMs

There are many aqueous phase additives in the synthesis of TEMs, such as NaCl, $NaNO_2$, PVP K30, SDS, etc. among them NaCl is the issue factor which affects the size and distribution of TEMs. During suspension polymerization, each monomer droplet contained three type polymeric monomers, AN, MMA and VAC, among them AN and MMA were slightly soluble in water, while VAC had a solubility of 20g/L. As the reaction proceeds, the water-soluble monomers will form secondary particles that cannot expand, and finally reducing the expansion properties of the TEMs. Fortunately, this tendency can be inhibited by addition of NaCl in the aqueous phase. Compared with monomers, NaCl has a stronger affinity with water, which will change the monomer-water chemical equilibrium due to the salting out effect, thus reducing the solubility of monomers in the aqueous phase.[20] Under the premise of fixed monomer ratio, the effect of NaCl concentration on the particle size, distribution and the surface morphology of TEMs is shown in Figure 2 and Figure 3, respectively. As can be seen from Figure 2, the prepared TEMs without NaCl show a small particle size and wide distribution. This is because, with the progress of the reaction, the monomers that dissolve in the aqueous phase undergo polymerization, generating fine particles with different sizes. Further observation through SEM indicated that these fine particles attached to the surface of TEMs, resulting in a non-smooth surface of TEMs (Figure 3a). When the concentration of NaCl is increased to 15%, the particle size of TEMs increase and the distribution becomes significantly narrower. When the concentration of NaCl is close to its saturation solubility (30%), there is no significant change in the particle size and distribution of the TEMs, but the surface morphology of TEMs become smoother and more regular (Figure 3c). This is because the increase in the dosage of NaCl breaks the chemical equilibrium of monomer-water, thus reducing the water solubility of AN, MMA, and VAC, which inhibits the polymerization of monomers in the aqueous phase.

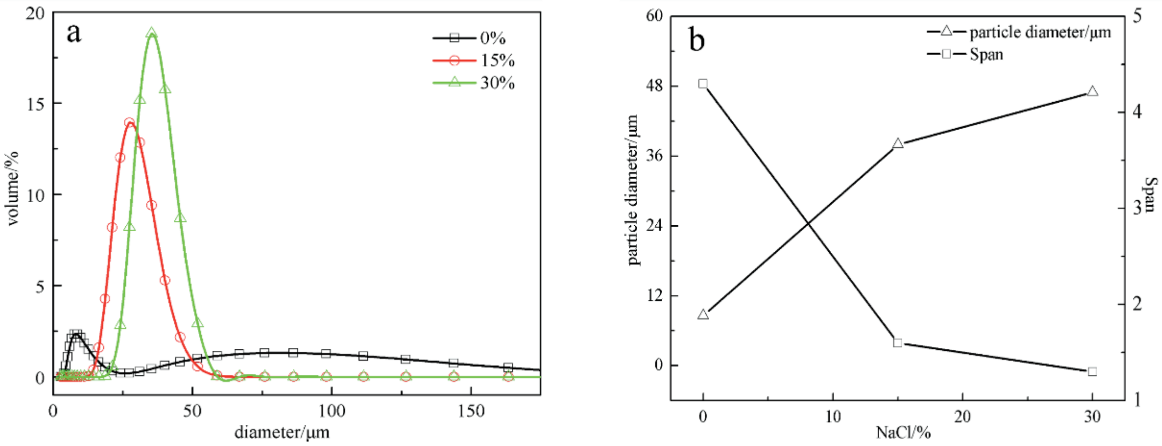

Figure 2. particle size distribution and mean particle size of TEMs with different content of NaCl: **(a)** Particle size distribution, **(b)** mean particle size.

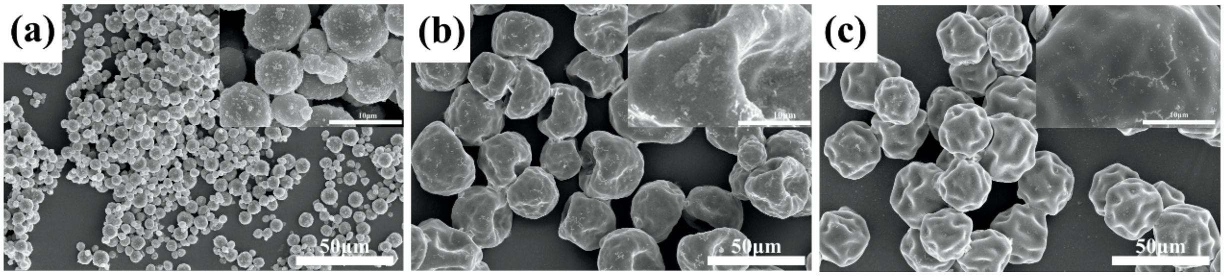

Figure 3. The SEM of the TEMs with different content of NaCl: **(a)** 0%, **(b)** 15%, **(c)** 30%.

Effect of crosslinking degree on the expansion property and temperature of TEMs

The addition of crosslinking agent was believed to increase of polymer flow viscosity at higher temperatures,[21-22] and a suitable crosslinking degree make the polymer shell more ductile to deform under the vapor pressure resulting from the evaporation of internal alkane as well as help TEMs change from their original core-shell structure into larger, hollow spheres. Herein, EGDMA was used as a crosslinking agent, and the effect of crosslinking degree on the expansion performance and expansion temperature of TEMs was investigated via the single variable method.

Table II shows the effect of the dosage of EGDMA on the expansion performance and expansion temperature of TEMs. As can be seen with the increase of cross-linking agent, the T_{start} of TEMs tend to increase slightly, while the T_{max} shows an obvious increase. Besides, the expansion ratio increases firstly and then decreases. According to the thermogravimetric (TG) curve in Figure 4a, no obvious weight loss has been observed in the low-temperature range for TEMs samples without crosslinking, which corresponds to the foaming height of 0μm in the static Thermomechanical Analysis (TMA, Figure 4b). The indicates that TEMs do not contain alkane in absence of crosslinking agent. When the dosages of crosslinking agent are 0.046%, 0.093% and 0.19%, the TG curve shows two stages of weight loss, the first weight loss corresponds the escape of alkanes. Moreover, the higher the degree of cross-linking, the more alkane it contains. Compared with the first weight loss curve of TEMs with 0.19% and 0.093% crosslinking agent, it was found that the slope is much steeper for the former than for the latter, which reveals that the release rate of alkane inside TEMs is rapid for 0.19% cross-linking agent than for 0.093% cross-linking agent in the process of expansion. Correspondingly, the greatest expansion height (D_{max}) also decreases from 1240μm to 857μm as shown in Table II. This is because too much higher crosslinking density increases the rigidity of the polymer shell whilst decreases its flexibility. As a result, even though more alkanes are enclosed inside, the excessive cross-linked shell limits the expansion of TEMs, and finally the TEMs rupture under the volatilization of alkanes, resulting in a low expansion ratio. On the contrary, when the shell is not cross-linked, the gas tightness of TEMs is too low to withstand the pressure generated by expansion.

Table II

Foaming properties and Foaming temperature of TEMs with different content of EGDMA

Crosslinker concentration/ (%)	T_{start}/ (°C)	T_{max}/ (°C)	Expansion ratio/ (d/d_0)	D_{max}/ (μm)
0	-	-	-	0
0.046	109	126	4.1	1021
0.093	110	127	5.0	1240
0.19	112	136	3.4	857

a: No expansion was observed during heating.

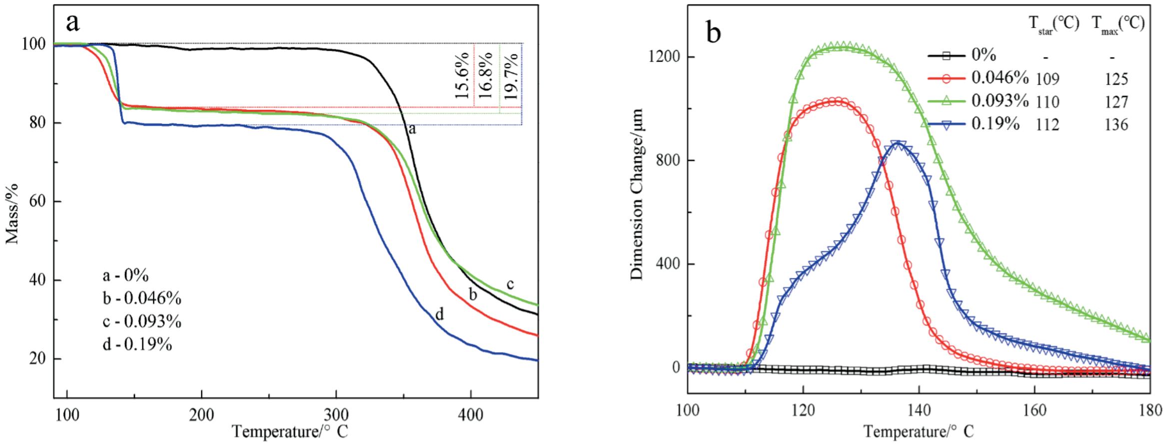

Figure 4. Thermodynamic analysis of TEMs with different dosage of EGDMA: **(a)** TG curve, **(b)** TMA curve.

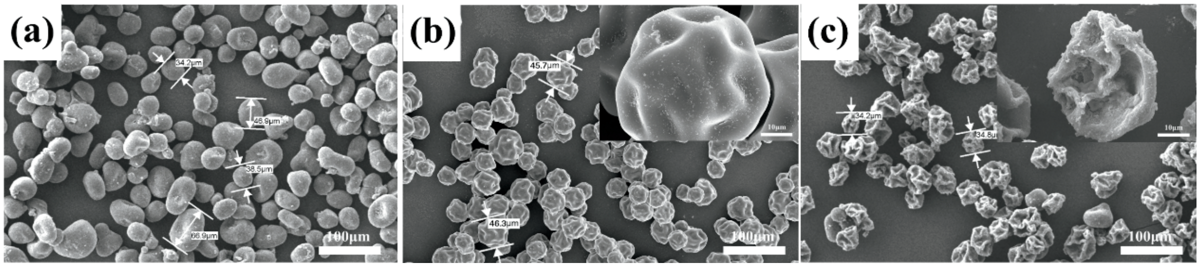

Figure 5. SEM of TEMs with different content of EGDMA: **(a)** 0%, **(b)** 0.093%, **(c)** 0.19%.

In addition, the cross-linking density also affects the surface morphology of the TEMs. As shown in Figure 5, with the increase of EGDMA, TEMs gradually transforms from regular spheres to irregular particles. This is because the shrinking force generated by the non-crosslinked polymer shell is smaller, and the internal pressure generated by the volatilization of i-pentane inside the microsphere is dominant, therefore, the TEMs show a smoother morphology and higher sphericity (Figure 5b). Further increase the crosslinking agent density, the shrinking force gets bigger, while the internal pressure is relatively small, so the surface morphology of the TEMs gets irregular gradually.

Effect of dosage of alkane on expansion property and temperature of TEMs

Keeping other parameters unchanged, the effect of i-pentane concentration on expansion property and temperature of TEMs was investigated. Figure 6a is the DSC curve of TEMs prepared with the concentration of 3.7%, 7.4%, 11.1%, and 14.8% i-pentane, and the endothermic enthalpy(ΔH) during the expansion of TEMs were listed in Table III. It can be seen that with the increase of i-pentane (3.7%, 7.4% and 11.1%), the ΔH increases, which means the content of i-pentane enclosed by TEMs increased. However, when the dosage of i-pentane reaches 14.8%, the content of i-pentane in TEMs decreases instead. This may be due to the excessive i-pentane with low boiling point leads to the excessive internal pressure in the polymerization process, which makes the microspheres unable to seal the i-pentane perfectly.

Dosage of alkane also influences the T_{start} and T_{max}. As shown in Table III, both the T_{start} and T_{max} decrease with the increase of i-pentane contained by the TEMs. This is because when the dosage of i-pentane contained inside TEMs was small, the polymer shell of TEMs was relatively thick. At the same temperature, the pressure inside TEMs containing less i-pentane is lower. In order to make TEMs expand, the temperature needs to be increased continuously. On the contrary, when TEMs contain more i-pentane, they would expand rapidly at a lower temperature, so the T_{start} and T_{max} shifts to the lower temperature range. Figure 6b reveals the relationship between expansion ratio and i-pentane concentration, when the dosages of i-pentane are 7.4% and 11.1%, TEMs show more high expansion heights, but TEMs with 11.1% dosage of i-pentane exhibits a very sharp expansion curve, which indicates that even though TEMs have achieved a satisfied expansion height, it could not withstand the high internal pressure and rupture prematurely at a lower temperature, reducing its foaming stabilization.

Table III

Effect of foaming agent dosage on the expansion property and foaming temperature of thermally expanded microspheres

Isopentane concentration/(wt%)	T_{start}/(°C)	T_{max}/(°C)	Expansion ratio/ (d/d_0)	D_{max}/(μm)	ΔH/(J/g)
3.7	114	138	2.3	253	12.76J/g
7.4	110	128	5.0	1240	47.8J/g
11.1	109	116	5.2	1341	51.32J/g
14.8	106	111	3.4	619	30J/g

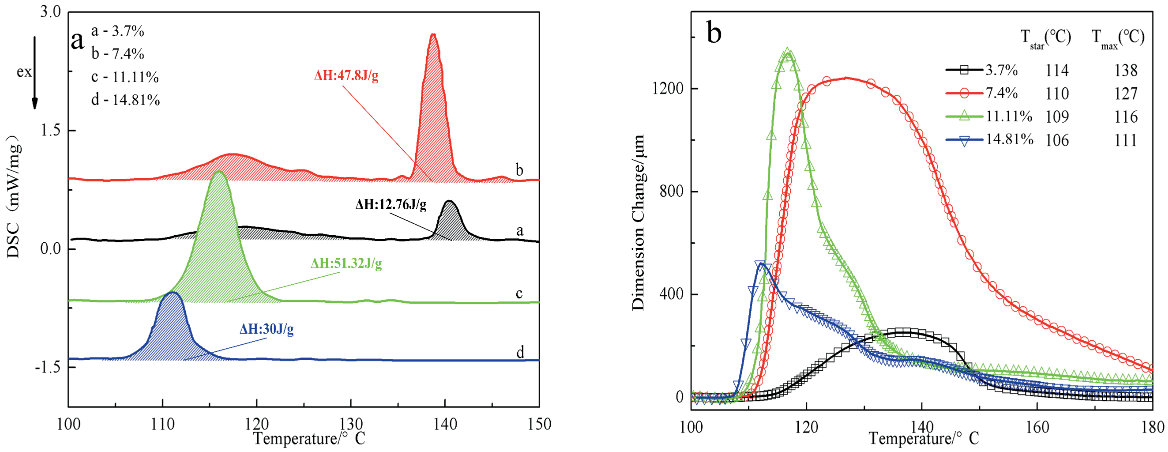

Figure 6. Thermo dynamic analysis of TEMs with different content of Isopentane: **(a)** DSC curve, **(b)** TMA curve.

Effect of monomer mass ratio on expansion property, temperature and solvent resistance of TEMs

As well known to all, each monomer has its own function, so the resultant properties such as gas tightness, heat-resistance, toughness, and solvent-resistance of TEMs are directly determined by the monomers in different proportions. The effects of AN, MMA and VAC mass ratio on the expansion properties and temperature of TEMs were shown in Table IV.

Table IV

Effect of monomer ratio on the expansion property and expansion temperature of thermally expanded microspheres

AN/MMA/VAC[a] (%)	T_{start}/(°C)	T_{max}/(°C)	Expansion ratio/ (d/d_0)	D_{max}/ (μm)
5/3/1	107	111	3.1	784
6/3/1	109	115	2.9	722
7/3/1	110	128	5.0	1240
8/3/1	111	129	4.8	1198
7/1/1	106	111	3.2	787
7/2/1	110	129	3.3	810
7/3/1	110	128	5.0	1240
7/4/1	111	117	2.3	549
7/3/0.5	112	116	1.6	402
7/3/1	110	128	5.0	1240
7/3/1.5	103	116	11	2730
7/3/2	98	118	3	752

a: AN/MMA/VAC is the mass ratio of the three monomers

Generally, for the heating process of the TEMs, the TG reflects two weight loss stages, the first is ascribed to the volatilization of alkane at low boiling point contained in the TEMs, with a temperature range of 100°~150°C, and the second is the weight-loss of the polymer shell, which usually occurs above 300°C. Here, the first stage corresponds to the expansion process of the TEMs. Differential thermogravimetry(DTG) can be used to reveal weight loss rate and fine structure of TEMs. It can be seen from the DTG in Figure 7b, with the increase of AN, the weight loss rate of TEMs decreases, and the peak of the maximum weight loss moves toward higher temperature, and meanwhile, the weight loss rate curve shows obvious double peaks for 5/3/1, 6/3/1, 7/3/1. This is because the lower content of AN results in the leakage of low boiling point alkanes at low temperature. In this case, TEMs have not fully expanded, so the weight loss rate curve becomes sharper and the corresponding D_{max} (Figure 7a) is very low. With the increase of AN, the weight loss rate exhibited a double-peak curve. This is because the increase of AN strengthens the gas tightness and the heat-resistance of polymer shell, resulting in more TEMs expand in the high-temperature region and relatively fewer TEMs expand in the low-temperature region. That is why the weight loss curve shows a double-peak in the DTG (Figure 7b) and the D_{max} in Figure 7a increases rapidly. However, when the mass ratio of three monomers reached 8/3/1, the polymer shell becomes too rigid and most of TEMs expand in the high-temperature region. Therefore, the weight loss rate curve (Figure 7b) changes again from a double-peak to a single-peak. Accordingly, the expansion ratio of TEMs decreases from 5.0 to 4.8 times (Table IV).

Keeping the proportion of AN and VAC constant, the effects of MMA concentration on T_{start} , T_{max} and D_{max} of TEMs were shown in Figure 8. It can be seen that the T_{start} of TEMs tends to rise gradually but the T_{max} of TEMs first increases and then decreases with the increase of MMA content until the mass fraction of MMA reaches

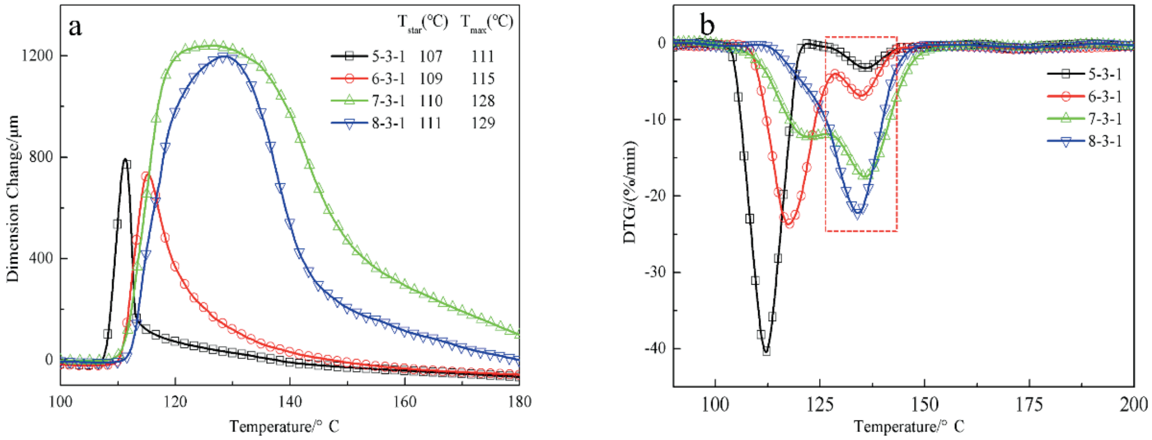

Figure 7. Thermo dynamic analysis of TEMs with different content of AN: **(a)** TMA curve, **(b)** DTG curve.

4, meanwhile, the maximum expansion height (D_{max}) of TEMs firstly increases and then decreases where the turning point occurs in the case of mass fraction of MMA increases to 3.When the mass fraction of MMA is 1, TEMs have poor expansion properties and the lowest expansion temperature. Because the mass ratio of AN is relatively higher in this case that the polymer shell of TEMs shows higher rigidity and lower flexibility, as a result, TEMs are easy to rupture during the expansion process. Correspondingly, a sharp weight loss peak can be observed in DTG in Figure 8b. With the increase of MMA mass fraction, the double-peak occurs and the second peak enlarged and the first peak weakened gradually in Figure 8b. Because copolymerization of MMA and AN can break the regularity of PAN, imparting the polymer shell of TEMs a certain of flexibility, therefore, the curve of the weight loss rate becomes flat and the D_{max} increases gradually. Besides the addition of MMA can also enhance the heat-resistance of the polymer shell, the T_{start} of TEMs show an increasing tendency (Figure 8a). But excessive MMA has a negative effect on the expansion property and temperature of TEMs, when the mass fraction of MMA increases to 4, a sharp weight loss peak occurs again in DTG, and the D_{max} shift to the lower temperature range. The reason is that the excessive MMA weaken the intermolecular force of the polymer shell, thereby reduces the gas tightness of the TEMs. This is not beneficial for the expansion of the TEMs, from the data in Table IV, the expansion ratio of TEMs is also reduced from 5 times to 2.3 times.

Similarly, the mass fraction of VAC also influences the T_{start} ,T_{max} and D_{max} of TEMs. It can be observed from TMA in Figure 9a that the T_{start} of TEMs shows a declining tendency with increasing in mass fraction of VAC; whilst the D_{max} and expansion ratio of TEMs increases (Table IV). Because the addition of VAC improves the ductility of the polymer shell, which means the polymer shell is easier to soften and deform during expansion. Therefore, a smoother curve of the weight loss rate in DTG (Figure 9b) and a greater expansion ratio are obtained. However, as the soft part of the polymer shell, excessive mass fraction of VAC will decrease the T_{start} of the TEMs, for example, when the mass fraction of VAC was up to 2, the T_{start} of TEMs is only 98°C (Figure 9a), which will cause the TEMs expansion ahead before pre-dried.

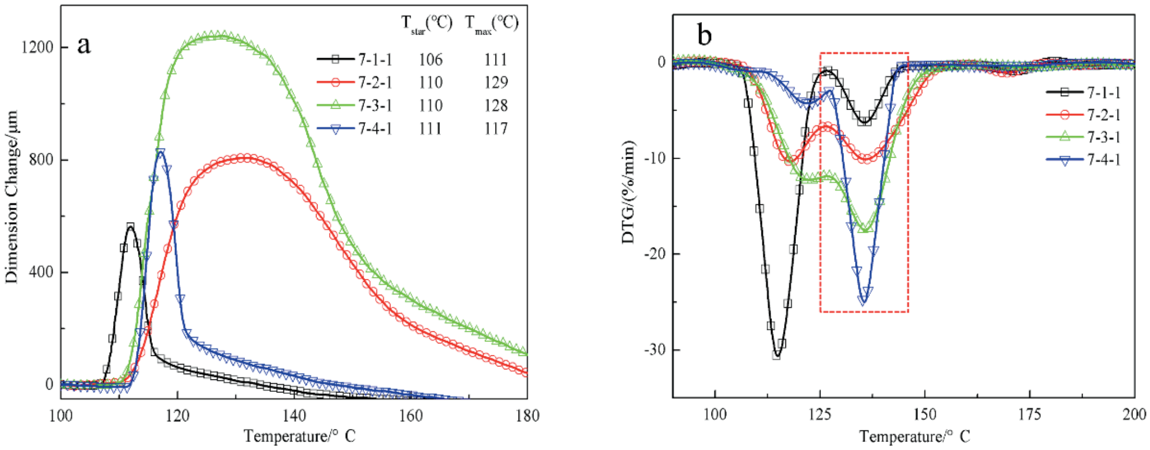

Figure 8. Thermo dynamic analysis of TEMs with different mass fraction of MMA: **(a)** TMA curve, **(b)** DTG curve

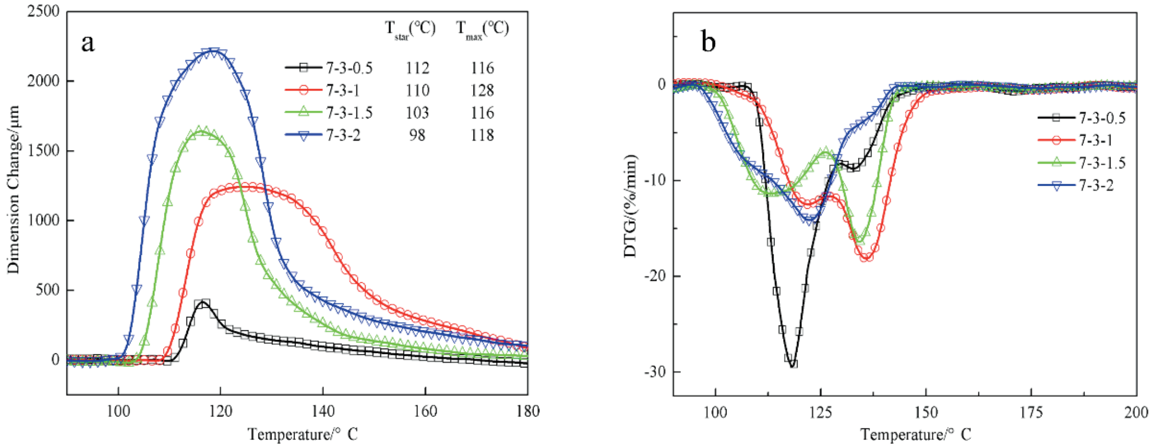

Figure 9. Thermo dynamic analysis of TEMs with different content of VAC: **(a)** TMA curve, **(b)** DTG curve.

In a real foam coating system, TEMs are frequently applied together with polyurethane or acrylic resin. The solvent-based resins always contain some solvents such as *N,N*-dimethylformamide (DMF), acetate esters, acetone and so on. Similarly, water-based resin sometimes also contain acetone and/or DMF. Therefore, the polymer shell of TEMs should have a resistance to solvents. In this experiment, 2wt% aqueous acetone, 2wt% aqueous DMF and 98wt% ethyl acetate were used to simulate water-base and solvent-base resins. TEMs with the mass fraction of AN/MMA/VAC of 7/3/1 were selected and soaked for 4 hours in these simulation systems, and then the expansion property of the corroded TEMs was tested by DSC and shown in Figure 10. It can be observed that all of the corroded TEMs shows endothermic peaks, indicating that TEMs have preferable solvent-resistance and expansion characteristics. Besides, the T_{start} of the corroded TEMs (the part in the red circle) decreases while the intensive expansion temperature (the part in the blue circle) increases slightly compared with control sample and the corresponded endothermic enthalpies also shows a declining trend, This revels that the polymer shell of TEMs are swelled to some degree by organic solvents so they cannot prevent the inner blowing agent from escaping before TEMs expand. From SEM in Figure 11, it is found that ethyl acetate has little effect on state of TEMs but DMF and acetone caused the soaked TEMs aggregating together and their surface become smoother (Figure 11c), indicating that the solvent resistance of TEMs is better for ethyl acetate than for DMF and acetone.

Morphology of split leather foam coating

The as-prepared TEMs were blended with WPU in proportion as well as other additives, and then the mixture was coated on split leather, pre-dried at 80°C for 1 min, and then foamed at 120°C to obtain foam coating layer. The SEM of the surface (Figure 12a) and

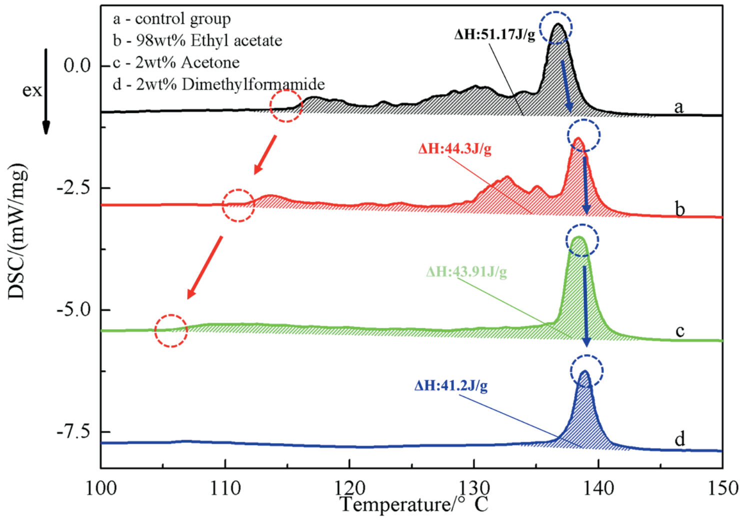

Figure 10. DSC curves of TEMs immersed in different solvent systems for 4h

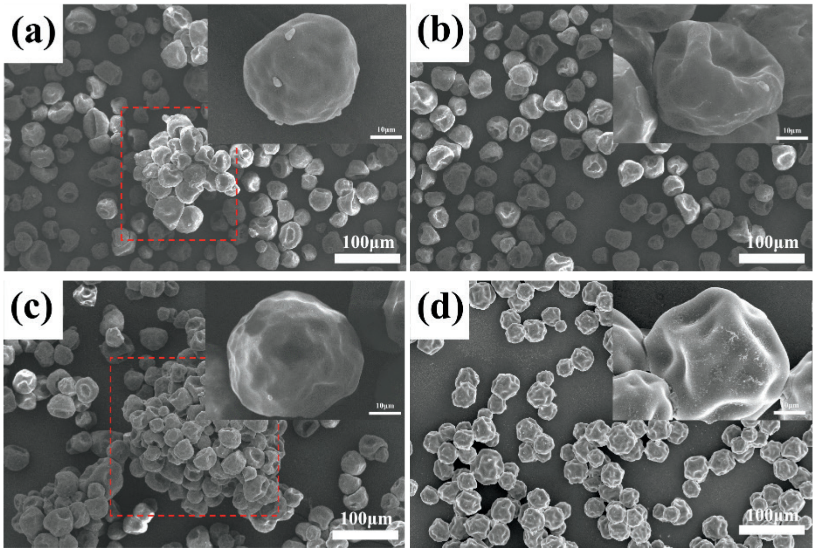

Figure 11. SEM of TEMs immersed in different solvents for 4h: **(a)** 2wt% acetone solution, **(b)** 98wt% ethyl acetate, **(c)** 2wt% DMF, **(d)** control group.

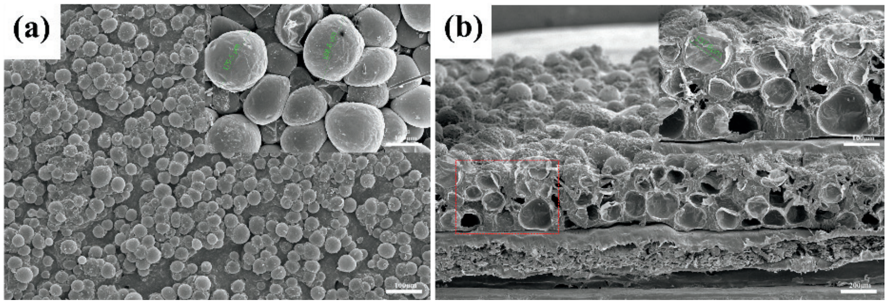

Figure 12. SEM of split leather foam coating: **(a)** surface, **(b)** cross section.

cross section (Figure 12b) of the foam coating are shown in Figure 12. It can be seen that the thickness of the foam coating is increased and hollow spheres with relatively uniform size are formed in the coating. Moreover, the cell walls are regular and compact, and few broken cells, combined cells, or large cells can be observed, which guarantees the resilience, fullness, air and moisture permeability of the coating layers.

Matting and mending effect of foaming coating

The as-prepared TEMs were mixed with WPU in proportion as well as other additives, and then the mixture was coated on the leather with scratches on the grain surface, pre-dried at 100°C for 1 min, and then foamed at 120°C for 3s to obtain the repaired leather. The leather surface before and after the repair is shown in Figure 13. It can be seen that the finished leather before foaming (Figure 13b) has obvious surface defects. After foaming (Figure 13c and Figure 13d), the coating basically covered all the original damages. Further study, found that the coating consists of two foaming layers (Figure 13d), showing a stronger covering performance. At the same time, the surface of the foamed leather is uniform and compact (Figure 13d), and good matting effect was also obtained

Conclusion

A kind of TEMs for foam coating was prepared and the effects of aqueous additive, crosslinking degree, alkane content, and mass fraction of comonomers on diameters and distribution, expansion ratio, expansion temperature and solvent-resistance of resultant TEMs were investigated. The conclusions are shown below:

(1) The additive NaCl can decrease the solubility of monomers in the water phase and then affect the diameter distribution and size of microspheres. At saturation concentration, the diameter of prepared TEMs is up to 47 μm with uniform distribution and more regular shapes.

(2) A proper crosslinking degree can improve the expansion properties and expansion temperature of microspheres, but the excessive crosslinking degree will restrain the expansion of TEMs. Appropriate expansion temperature (120°C) and maximum expansion ratio (5.0) can be obtained simultaneously for TEMs with 0.09% crosslinking agent.

(3) The i-pentane amount influences the expansion temperature and expansion ratio. Too low amount of i-pentane increased the expansion temperature but decreased the expansion ratio. Whilst too much i-pentane will result in the decrease of expansion temperature and break ahead of TEMs, the suitable foamability and expansion temperature occurred in a case of alkane amount was up to 7.4%.

(4) The mass fraction of co-monomers (AN/MMA/VAC) was controlled to 7/3/1, the resultant TEMs show designable T_{start}, T_{max} and expansion ratio together with good solvent resistance.

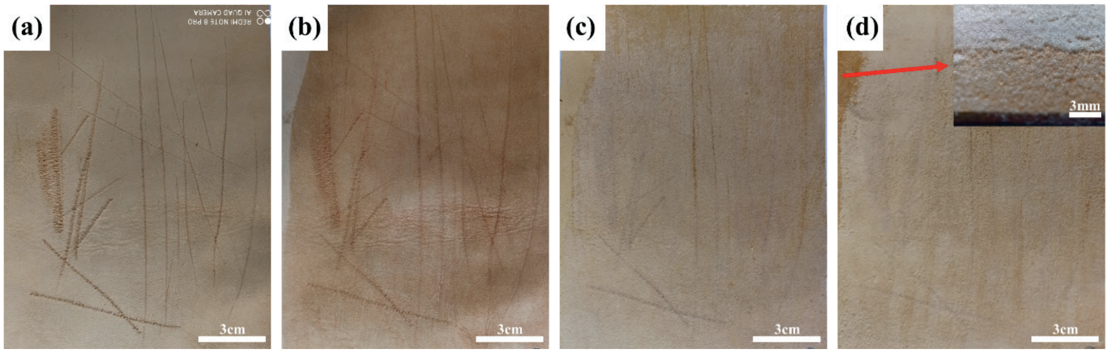

Figure 13. Surface of the finished leather: **(a)** control sample, **(b)** Before foaming, **(c)** One layer foaming, **(d)** Two layers foaming.

(5) TEMs can be used make foaming layer of split leather and matting and mending layer of damaged grain leather. The former can improve the resilience, fullness, air and moisture permeability of split leathers, and the latter can cover the damage of leather and impart the repaired leather suitable matting and mending effect.

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