Effect of 2,2-Dimethyl Malonate on the Volume Shrinkage Control of the CaCO₃/Unsaturated Polyester Resin Composites

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ABSTRACT: Shrinkage is critical to the unsaturated polyester resin (UPR) composite materials. Shrinkage influences the surface appearance, thus leading to warpage, internal cracks, and depression on the surface of the composite materials' products. Some studies and technologies have been conducted to controll the shrinkage. In this study, we presented 2,2-dimethyl malonate as an anti-shrinkage agent, which was different from the previous thermoplastic macromolecular agents. The shrinkage level of the CaCO₃/UPR matrix dropped to zero with 12% 2,2-dimethyl malonate by mass of UPR. The bending strength of CaCO₃/UPR matrix with 2,2-dimethyl malonate was also higher than that with the same adding amount of commercial thermoplastic agents at the low-shrinkage level (below 0.25%) and the micro-shrinkage level (below 0.08%). A reaction including two stages was proposed on the supporting of DSC and FTIR investigations. From the analysis results, we deduced that the first stage of the reaction was the esterification between 2,2-dimethyl malonate and UPR, which did not occur in the UPR containing general thermoplastic anti-shrinkage agent, and the second stage was restraining the cross polymerization of UPR, same to the reaction processes of general macromolecular anti-shrinkage agents. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4606–4611, 2012

Key words: shrinkage; unsaturated polyester resin; 2,2-dimethyl malonate; CaCO₃; DSC; FTIR

INTRODUCTION

Shrinkage is critical to the unsaturated polyester resin (UPR) composite materials, although the composite materials are widely used in automotive component, mechanical or electrical complex, marine, petrol-chemical, and chemical industries for their excellent mechanical and chemical properties. Recently, as the application of low shrinkage products is considerably increasing in industry, severe shrinkage of composite products becomes a challenge to all of us. There are three technologies to control the volume shrinkage now. The first one is adding low-profile additive (LPA) as an anti-shrinkage agent,[1–6] the second one is modifying polymer resin properties,[7] and the last one is redetermining the manufacturing parameters.[8,9] LPA is the most effective approach in the controlling of the shrinkage among the anti-shrinkage technologies. Thermoplastic macromolecules, like polyurethane (PU), polyvinyl acetate (PVAc), poly-methyl methacrylate (PMMA), and polystyrene (PS), are all attributed to LPA.[10] LPA has been found to be highly effective in eliminating the polymerization shrinkage of UPR in high-temperature molding processes.[5,11] Researchers have paid great attention to the fundamental mechanism of LPA. The proposed hypothesis or explanations include controlling of LPA content at high temperature to obtain thermal expansion of resin and LPA phase separation,[12] and at low temperature to compensate shrinkage through co-promoter and secondary monomer.[12] Microvoid and microcrack formation during curing,[7,10,13–17] addition of comonomer,[18] the surplus styrene nucleation and expansion during the curing process,[10,17] thermal expansion of LPA,[10] nanoscale filler,[9] and semicrystalline polymer[19] were also considered the anti-shrinkage factors. The previous fundamental principles of anti-shrinkage generally tended to the formation of microvoid and microcrack during curing.[8,12–14,17]

As to LPAs, there are some deficiencies for the LPAs in the composite materials' manufacturing process. For example, it is difficult to control the addition of LPA accurately for its high viscosity. In addition, the mixing between LPA and resin is just a physical process, which means that the compatibility between LPA and resin has a great impact on the properties (such as shrinkage) of the composite product. To cope with those deficiencies, we suggest that 2,2-dimethyl malonate, as a powder and small molecular anti-shrinkage agent, is easy for weighing and adding to resin matrix, covering the shortage of LPA. Moreover, it will be a new idea that the
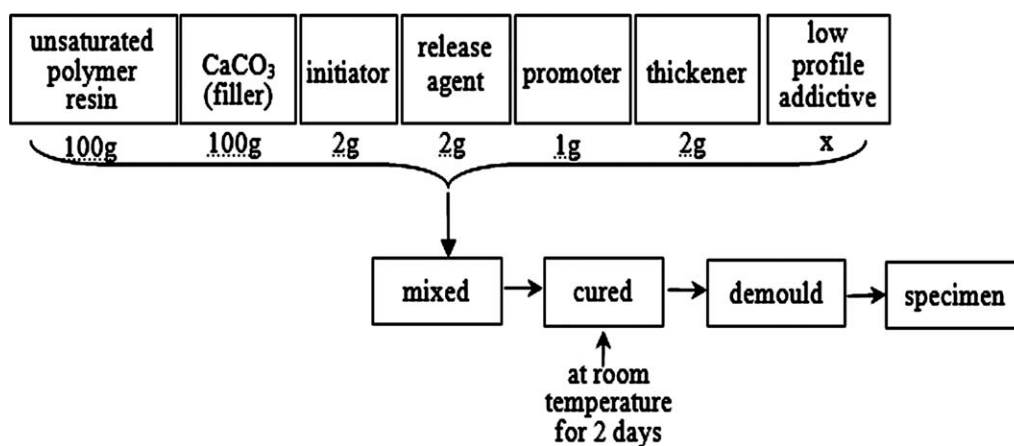
Figure 1 The scheme of treatment of resin.

thermoplastic polymer, which is formed in the chemical reaction between the carboxyl groups introduced by 2,2-dimethyl malonate and the diols remained in unsaturated polyester resin polymerization, is available to control the shrinkage of resin matrix.

In this study, a monomer of 2,2-dimethyl malonate, used as a new anti-shrinkage agent, which differs from the previous thermoplastic agents, was presented to explore a new method to decrease the shrinkage of UPR composite materials. Differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and Fourier-transfer infrared (FTIR) were used for reaction exotherm measurement, morphology observation and function groups change in the investigation of minimizing volume shrinkage or the characterization of the reaction mechanism.

EXPERIMENTAL

Materials

The unsaturated polyester resin (UPR) used in this work was P17-902 (obtained from Jinling DSM Resin in China). It is appropriate for sheet molding compounds. The initiator was a commercial product containing more than 97 wt % *tert*-butyl peroxide caprylate. The promoter used in this study was cobalt octoate, containing about 7.8–8.2 wt % cobalt. Thickener used in this study was MgO, containing more than 98 wt % MgO. Monomer anti-shrinkage additive used in this study was 2,2-dimethyl malonate (produced by Nanjing King-Pharm in China), containing more than 95% 2,2-dimethyl malonate. The filler of the resin was $CaCO_3$ (from Omiya Chemical in China), containing more than 98 wt % $CaCO_3$. The release agent was ZnSt from Shanghai Experimental Reagent.

All the specimens being tested were prepared according to a SMC production formula with a quantity ratio of 100 g resin: 100 g filler: 2 g initiator: 1 g promoter: 2 g release agent: 2 g thickener, but the content of the four kinds of anti-shrinkage agents varied from 0% to 18% at three interval by the weight of UPR. The specimen was cured at room temperature for 2 days in a size of $120 \times 15 \times 6$ mm^3 loader. In addition, the scheme of treatment of resin was illustrated by Figure 1.

Shrinkage measurement

The density of the cured specimen was determined by weighing the specimen before cured and after cured, respectively. The volume shrinkage of the cured specimen could be calculated by the following equations:

$$\text{Volume shrinkage} = (\rho_s - \rho_m)/\rho_s$$

in which ρ_m is the density of the resin mxiture before being cured and ρ_s is the density of the resin mixture after being cured at 25°C, according to the international ISO3521 shrinkage testing method.

Characterization

Differential scanning calorimetry experiment

An instrument NETZSCH DSC204 differential scanning calorimeter was used for measuring the reaction exotherm of the specimen. The specimen was sealed in a volatile aluminum sample pan. Non-isothermal scans were carried out from room temperature to 200°C at a heating rate of 10°C/min under the nitrogen condition. The total reaction exotherm could be calculated from the area under the isothermal and scanning DSC curves. The exotherm value could be converted to the reaction rate and conversion as a function of time, by assuming that the total reaction exotherm was equal to 100% conversion.

TABLE I
The Shrinkage of CaCO₃/UPR Specimens with Different Kinds and Adding Amounts of Antishrinkage Agents

| Adding amount g/ (100 g UPR) | Shrinkage | | | |
	With 2,2-dimethyl malonate	With H870-901	With H851-02	With H814-902
0	9.2	9.2	9.2	9.2
3	5.3	4.5	4.0	5.2
6	0.21	1.5	2.4	2.7
9	0.06	0.93	1.2	1.8
12	0.00	0.22	0.72	1.0
15	0.00	0.14	0.29	0.58
18	/	0.07	0.13	0.19

The modulation of temperature for DSC was ±0.1°C. Mass of prepreg specimen in the experiment was about 20 mg and sensitivity of the DSC is 0.1 μg.

Fourier-transfer infrared experiment

Fourier-Transfer Infrared instrument Nexus 670 (produced by Nicolet) was used to characterize group's specialty of the resin mixture before cured and after cured. Specimen was grinded with KBr and pressed to a piece in thickness less than 2 mm. The FTIR scanning range was from 4000 cm⁻¹ to 375 cm⁻¹ in the resolution of 0.09 cm⁻¹.

Scanning electron microscopy experiment

The morphological changes were obtained by means of Scanning Electron Microscope (JEOL JSM5900) at 10,000×.

RESULTS AND DISCUSSION

The influences of 2,2-dimethyl malonate and macromolecular anti-shrinkage agents on the shrinkage of CaCO₃/UPR specimen

The effects of the adding amount 2,2-dimethyl malonate on the 100 g CaCO₃ to 100 g UPR are listed in the second column of Table I, and their corresponding curves are shown in Figure 2. In Figure 2, the shrinkage of CaCO₃/UPR specimen decreases obviously with the adding amount of 2,2-dimethyl malonate increasing. The shrinkage level of the specimen is 0.21% when the adding amount of 2,2-dimethyl malonate is 6% by mass of UPR. This value is close to the low-shrinkage level of thermosetting plastic. The shrinkage of the specimen is 0.06% when the adding amount of 2,2-dimethyl malonate is up to 9% by mass of UPR, the result of which is in accordance with the micro-shrinkage level of thermosetting plastic, that is, lower than 0.06%. Furthermore, the

shrinkage is consistent with zero till the adding amount of 2,2-dimethyl malonate is more than 12% by mass of UPR.

The influence of H870-901, which is used as a polar macromolecular anti-shrinkage agent on the 100 g CaCO₃ to 100 g UPR specimen, is listed in the third column of Table I. The shrinkage of the specimen is close to the low-shrinkage level of the thermosetting plastic when the adding amount of H870-901 is 12% by mass of UPR. And this shrinkage value matches microshrinkage of thermosetting plastic as the adding amount of H870-901 is 18% by mass of UPR. The aforementioned experimental results demonstrate that the anti-shrinkage effect of the 2,2-dimethyl malonate is better than that of H870-901 with the same amount in the CaCO₃/UPR specimen.

H851-02 is a weak polar macromolecular anti-shrinkage agent, whose influence on the 100 g CaCO₃ to 100 g UPR system is listed in the forth column of Table I. The anti-shrinkage efficiency of H851-02 is weaker than that of 2,2-dimethyl malonate and H870-901, only approaching the low-shrinkage level of thermosetting plastic when its adding amount is 18% by mass of UPR. By comparison with four anti-shrinkage agents in Table I, the non-polar anti-shrinkage agent H814-902 performs the lowest anti-shrinkage effect among them.

In general, the more content of the anti-shrinkage agent is, the more excellent mechanical properties of the resin composite matrix are. Table II shows that the bending strength of the specimen with 2,2-dimethyl malonate is higher than that of the specimens with thermoplastic agents at the low-shrinkage and the micro-shrinkage level. Therefore, 2,2-dimethyl malonate, as a crystal and low weight molecule, might be a new kind of anti-shrinkage agent for CaCO₃/UPR composite materials.
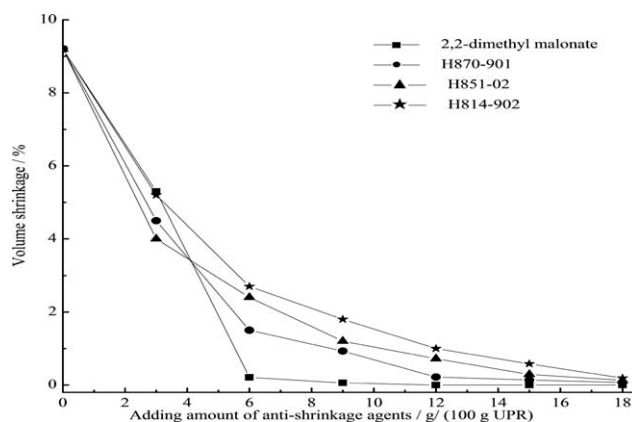
**Figure 2** The effects of four kinds of LPAs on the shrinkage of CaCO₃/UPR specimens.

Volume shrinkage (%)	Bending strength (MPa)			
	With 2,2-dimethyl malonate	With H870-901	With H851-02	With H814-902
0.25	24.8	22.6	21.8	20.3
0.08	24.3	21.4	19.6	18.7

## Analysis of anti-shrinkage mechanism for four anti-shrinkage agents

In two main anti-shrinkage reaction stages, a polar macromolecular anti-shrinkage agent H870-901 formed porous structure and later produced resin microgel particles [Fig. 3(a)] in the thermosetting resin polymerization. The porous structure and microgel particles reduced the shrinkage of thermosetting resin system. H851-02, as a weak polar macromolecular anti-shrinkage agent, formed flakes to fill some pores and to reduce its anti-shrinkage effect [Fig. 3(b)]. As a non-polar macromolecule, H814-902 fabricated less porous structure [Fig. 3(c)], performing a weak spur in anti-shrinkage. In particular, these three kinds of macromolecular anti-shrinkage agents reduced the UPR polymerization degree. The total reaction exotherm of the specimen with H870-901 was the smallest, showing the strongest polymerization resistance among the four of them, but H814-902 had the opposite effect on H870-901.

Figure 4 illustrates the DSC curves of CaCO$_3$/UPR specimens with H870-901, H851-02, H814-902, and 2,2-dimethyl malonate approaching to the low-shrinkage level. Different from the DSC exotherm adding with macromolecular anti-shrinkage agents, a small reaction exotherm peak at 117°C arises from the specimen adding with 2,2-dimethyl malonate before the main polymerization exotherm peak appears at 134°C. We deduce that it is the first stage of UPR reacting with 2,2-dimethyl malonate at 117°C. At this temperature, the carboxyl of the 2,2-dimethyl malonate, more reactive than that of the UPR, esterifies with hydroxide in the saturated diol crossing to form thermoplastic macromolecule with long chain. We suggest that this pre-reaction is the first solidification of the specimen with 2,2-dimethyl malonate. Some saturated diol groups of the UPR are reacted in the first reaction, and the polymerization of UPR goes with smaller amount of diol groups in the later reaction. The lower reaction
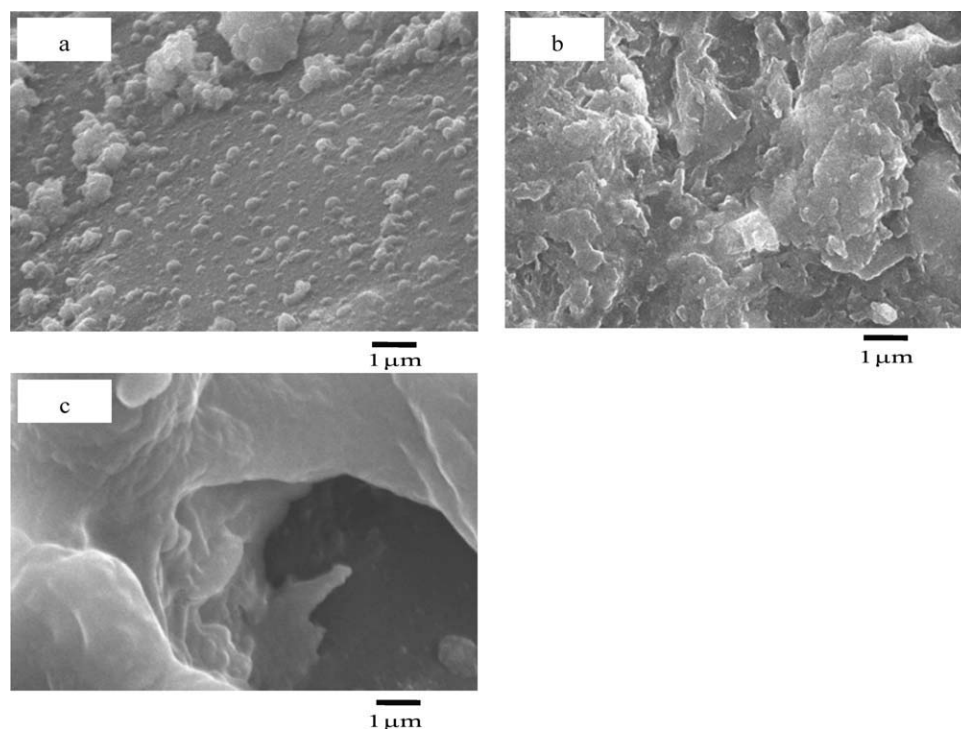
**Figure 3** SEM micrographs of the CaCO$_3$/UPR specimens with different LPAs.
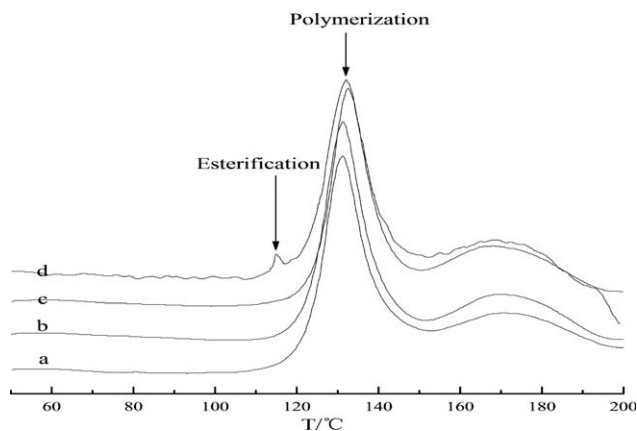
Figure 4 Thermograms of CaCO$_3$/UPR specimens with different LPAs approaching to 0.25% low-shrinkage level.

exotherm peak corresponds to lower polymerization of the UPR. 2,2-dimethyl malonate reduces the polymerization and decrees the shrinkage of the resin matrix. And this result is also demonstrated in Table III that with the decreasing of the adding amount of 2,2-dimethyl malonate, the polymerization exotherm reaches the lower polymerization degree. Both H870-901 and 2,2-dimethyl malonate release 55 J/g polymerization exotherm. So this value means that 2,2-dimethyl malonate performs the same anti-polymerization action with H870-901 in its so-called second reaction stage.

Figure 5 shows the DSC extherm of CaCO$_3$/UPR specimens in various amounts of 2,2-dimethyl malonate. The first reaction exotherm of DSC changes from 0.23 to 0.92 J/g with the adding amount of 2,2-dimethyl malonate from 3% up to 6% by mass of UPR. In contrast, the next polymerization reaction exotherm of DSC decreases from 63.62 to 54.01 J/g, due to the molecular anti-shrinkage agent with the small adding amount and ester in short chains. As the amount of 2,2-dimethyl malonate increases, the esterification becomes efficient. Meanwhile, more UPR reacts with 2,2-dimethyl malonate to form more thermoplastic macromolecules. Because a certain amount of UPR has reacted in the first reaction stage, the second cross polymerization reaction is restrained in the following stage, which is available

TABLE III
The DSC Exotherm of CaCO$_3$/UPR Specimens with Different Kinds of Antishrinkage Agents

Anti-shrinkage agent	Adding amount (g)	exotherm (J/g)
/	/	96.67
H814-902	18	56.09
H851-02	15	66.96
H870-901	12	57.85
2,2-dimethyl malonate	6	54.01
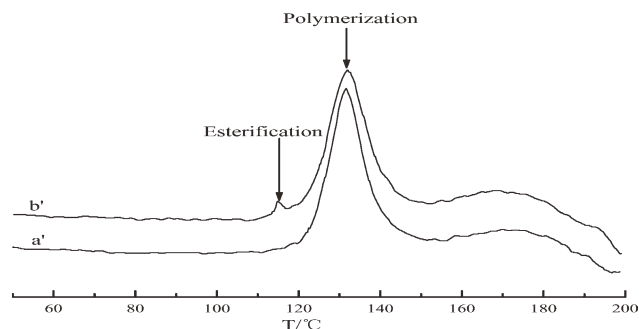
Figure 5 Thermograms of CaCO$_3$/UPR specimens with different adding amounts of 2,2-dimethyl malonate.

for reducing the shrinkage of the CaCO$_3$/UPR matrix.

The FTIR spectra of UPR specimens mixed with and without 6 g 2,2-dimethyl malonate are shown in Figure 6. Figure 6 illustrates that the absorption of carboxyl group at 1724 cm^{-1} is invariant, however the absorption of alkyl at 2982 cm^{-1}, the absorption of hydroxyl at 3623 cm^{-1} and the absorption of hydroxyl at 3460 cm^{-1} are all enhanced with 2,2-dimethyl malonate existing. As more carboxyl groups are introduced by 2,2-dimethyl malonate, the proton from the decomposition of the carboxyl groups breaks the balance between carboxyl and hydroxyl in the UPR matrix, causes a new esterification, however, a new balance is obtained later in the matrix. The esterification, between 2,2-dimethyl malonate and UPR, not only consumes a little of UPR but also forms a new thermoplastic anti-shrinkage compound which exerts influence on the shrinkage of the matrix on the second stage, same to the general macromolecular anti-shrinkage agents. The first reaction stage we propose is illustrated in Figure 7. Because of the quite small adding amount of 2,2-dimethyl malonate, compared with the amount of UPR, 2,2-dimethyl malonate results in small reaction exotherm of the esterification and the total content of carboxyl does not change obviously, coinciding with the inconspicuous changes of carboxyl absorption. Together with the hydroxyl group obtained in the reaction, the alkyl group introduced by 2,2-dimethyl malonate and obtained in the reaction becomes apparent at the absorption of 2982, 3623, and 3460 cm^{-1}. The above reaction mechanism with the existing 2,2-dimethyl malonate can be summarized as two reactions: the first reaction stage is the esterification, and the second is the restraint of ester formed in the above reaction on the cross polymerization of UPR.

CONCLUSIONS

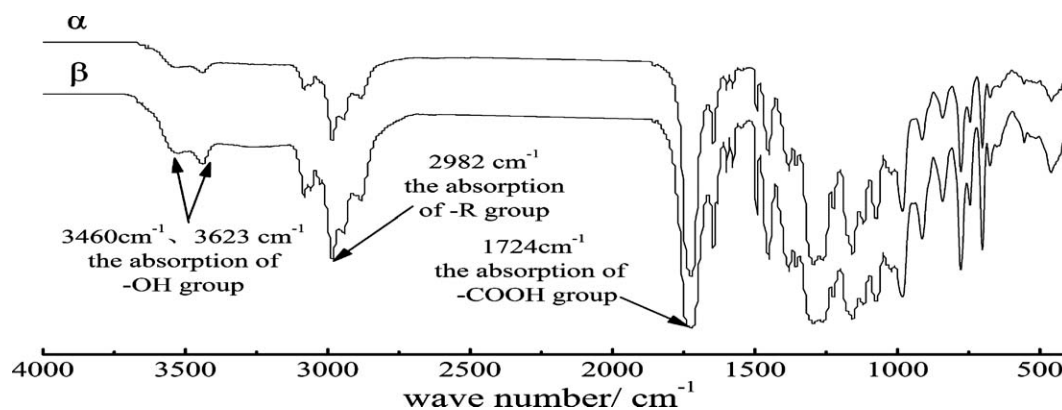2,2-dimethyl malonate was applied as a monomer anti-shrinkage agent in this study. DSC combined

Figure 6 FTIR spectra of CaCO$_3$/UPR specimens with and without 2,2-dimethyl malonate.
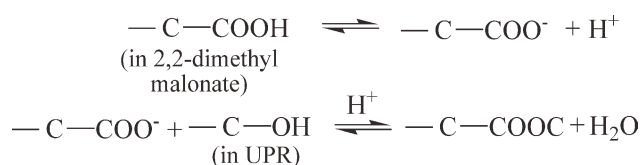

Figure 7 The scheme of esterification between carboxyl group in 2,2-dimethyl malonate and hydroxyl group in UPR.

with SEM and FTIR were used in the characterization of the process which 2,2-dimethyl malonate acted on UPR. The experiments showed that the small molecule could also perform an excellent anti-shrinkage function in the UPR cross polymerization, thus leading to zero shrinkage of the UPR matrix. The adding amount of the small molecule was less than that of macromolecular anti-shrinkage agents but more effective than the macromolecular anti-shrinkage agents, which brought out a new improvement for composite materials size and surface quality.

The DSC and FTIR experiments proved our finding that small molecule performance included two stages. The first stage is the esterifiable macromolecular anti-shrinkage compound formed in the esterification as a result of 2,2-dimethyl malonate which did not emerge in the general thermoplastic anti-shrinkage agent, and the second is the restraining of the cross polymerization of UPR, the same to the action processes of general macromolecular anti-shrinkage agents.

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