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# Improvement on the mechanical properties of zinc oxide green sheets by aqueous acrylamide gel tape casting

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**Abstract**

Various organic constituents were used to improve the mechanical properties of green sheets prepared by a novel aqueous gel tape casting. Two deadly problems of green sheets: brittle and surface exfoliation were settled and mechanical properties were estimated. Compared with poly(ethylene glycol) (PEG400 (Mw ≈ 400)), poly(propylene glycol) (PPG400 (Mw ≈ 400)) and di-ethylic phthalate (DEP), glycerol was the most efficient plasticizer to improve the flexibility of the green sheet. The addition of PEG2000 eliminated the surface-exfoliation phenomenon of green sheets in air and had no distinct deterioration in mechanical properties. The flexible and lubricous green sheets were obtained. The solid loading of the suspension reached 73.5 wt.% and the relative green density was 58%.

*Keywords:* A. Suspensions; A. Tape casting; C. Toughness and toughening; C. Mechanical properties

## 1. Introduction

ZnO varistors have been used widely to protect electrical circuits due to their excellent non-linearity and their very large surge-withstanding capabilities [1,2]. In 1981 Shohata et al. developed a ZnO-based multilayer chip varistor by applying the same manufacturing process as to a multilayer ceramic chip capacitor [3]. High performance multilayer ZnO varistors become more and more important in industrial applications [4].

Tape casting is the most widely used technique for large-scale fabrication of green sheets in multilayer ceramic packaging technology [5–7]. The tape cast green sheet forms the basic building block and needs to meet several requirements during fabrication to enable final high quality and reliable produces. More specifically, the green tapes must possess dimensional stability and mechanical integrity during punching and thick film paste screening. These conditions are usually better achieved by using organic-based systems, but it has disadvantages such as health problems, environmental hazards and high cost. Aqueous solvents, which have the advantages of incombustibility, non-toxicity and low cost, are the substitute of non-aqueous solvents [8–10]. But it also has the disadvantages such as slower drying rate and higher crack sensitivity. Therefore, producing suitable green tapes strongly depends on a strict control of all these variables, making the slurries' formulation for aqueous tape casting process much more problematic than when the solvent is an organic liquid [11].

Derived from gelcasting brought forward by the researchers of the Oak Ridge National Laboratory [12], gel tape casting was invented by Tshinghua University in 2001 [13–15].

In this process, ceramic slurries can be solidified by the polymerization of monomers to form green bodies. There are many advantages of this process, such as high solid loading, instant solidification and uniform green microstructure. However, the anti-polymerizing effect of oxygen during gel casting is easily produced, which results in a shell off from the green body surface contacting air [16]. In addition, the green body is too brittle to be rolled and shaped. To overcome these obstacles, additives are added in ceramic slurry to improve the flexibility and inhibit the oxygen anti-polymerization. Therefore, green sheets can be successfully produced to possess the mechanical properties which the tape casting needed to produce multilayer ceramics.

The present work aims to evaluate the mechanical properties of ZnO green tapes obtained by aqueous gel tape casting. The effect of structure and quantity of plasticizer and the oxygen

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anti-polymerization inhibitor on intensity, plasticity and toughness of green sheets are investigated. Such an investigation will help to obtain a green sheet with higher maneuverability in aqueous gel tape casting.

## 2. Experiment

### 2.1. Materials and chemicals

The doped ZnO powder (96 mol% ZnO and 4 mol% dopants including $Bi_2O_3$, $Sb_2O_3$, $Co_3O4$, $Mn_3O_4$ and $Cr_2O_3$) used in this study was chemically synthesized by the solid reaction method. The average particle size of the powder was about 1 μm. Deionized water and ammonium polyacrylate (PAA) were used as solvent and dispersant, respectively. The binder used in gel tape casting was a proportional mixed monomer acrylamide (AM) and cross-linker N,N′-methylenebisacrylamide (MBAM). The initiator of polymerization used was 3 wt.% ammonium persulfate (APS) aqueous solution. The catalyst used was N,N,N′,N′-tetramethyl ethylenediamine (TEMED). Glycerol, PEG400, PPG400 and DEP were selected as plasticizer to impart the plasticity and flexibility of green tape. PEG 2000 was used to inhibit the oxygen anti-polymerization.

### 2.2. Sample preparation

The flow chart of gel tape casting is presented in Fig. 1. The solution of AM and MBAM in water which was called binder solvent was prepared. The concentration of the binder solvent was 15 wt.% and the ratio of AM and MBAM is 48:1. Then doped ZnO powder and dispersant (0.45 wt.% based on dry weight powder) were added into the premix solvent to make slurry with solids loading 50 vol.%. The pH was adjusted to 8–10 according to Ref. [17]. After 10 h of ball milling, different amounts of plasticizer and oxygen anti-polymerization inhibitor were added in and ball milled for a further 4 h. The suspension was deaired for 5 min using ultrasonic method. Then, approximately 0.1 g per 1 g AM of both APS and TEMED was used to initiate gelation. The suspension was tape cast with a stationary casting head at a casting rate of 1.5 cm $s^{-1}$ immediately in the conventional tape casting equipment. A gap of 180 μm and a silicon-coated Mylar carrier film under the blade was selected for all the casting tests. After drying, the thickness of the tapes was about 100 μm. Tape drying was carried out at room temperature and in the open air.

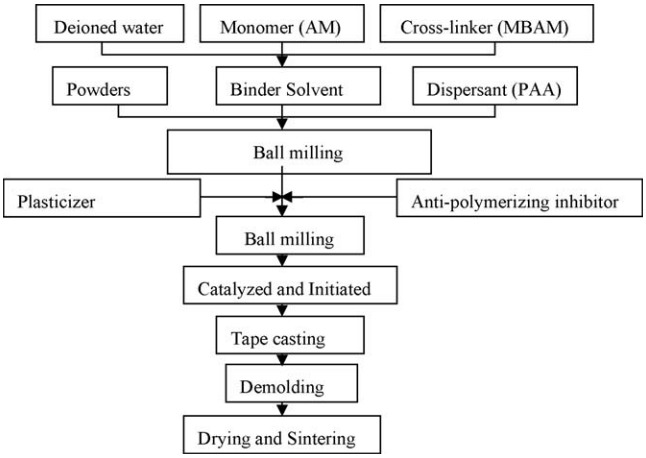

Fig. 1. The flow chart of aqueous gel tape casting.

### 2.3. Characterization

In order to investigate the effect of chemical structure and quantity of plasticizer on the mechanical properties of green sheets, the process was first carried out in $N_2$ ambience. The suspension was then prepared without plasticizer, the tape casting was implemented in air to discuss the effect of oxygen anti-polymerization inhibitor.

The tensile testing of green tapes was accomplished using an Electron universal testing machine with a 100 N load cell. Tensile measurements were done at room temperature (24 °C) and humidity of 50 ± 5%. Dog bone shape tensile specimens with 9-mm tensile width and 32-mm gauge length were cut in parallel to the casting direction with a razor blade. The cell sensibility was 0.1 N and the traverse speed was set to 1 mm $min^{-1}$. The stress and strain values obtained correspond to the average of at least 10 measurements. Tensile strength, elastic modulus and elongation at break were calculated as below:

$$\text{Tensile strength(MPa)} = \frac{\text{maximum force applied during the test(N)}}{\text{initial cross-sectional area of the sample(mm}^2)}$$

$$\text{Elastic modulus(MPa)} = \frac{\text{force at corresponding strain(N)}}{\text{cross-sectional area(mm}^2)} \times \frac{1}{\text{corresponding strain}}$$

$$\text{Elongation at break(\%)} = \frac{\text{increase in length(mm)}}{\text{original length(mm)}} \times 100$$

Rowe [18] hypothesized that data from tensile testing of free films could be used not only comparatively during film formulation development, but also to predict the incidence of defects during processing. In particular, the ratio of tensile strength to elastic modulus (*T*/*E*) was a valuable tool with high values preferable for film formulations as these were indicative of fewer process related problems. In this paper, *T*/*E* was used to evaluate the mechanical properties of green tape.

## 3. Results and discussion

### 3.1. Improving the flexibility of green sheets

In terms of mechanical properties, an ideal green sheet of tape casting should have a high tensile strength, a large elongation to break and a high elastic modulus. Such green sheets will be hard and tough without being brittle. Fig. 2 shows the stress–strain curves of green tapes prepared with various plasticizers. The addition of all plasticizers is 50 wt.% of binder

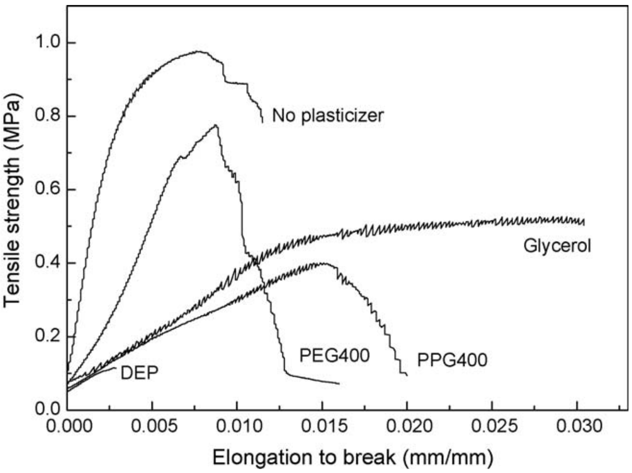

Fig. 2. Elongation–tensile strength curves of green sheets prepared with ZnO suspensions with various plasticizers.

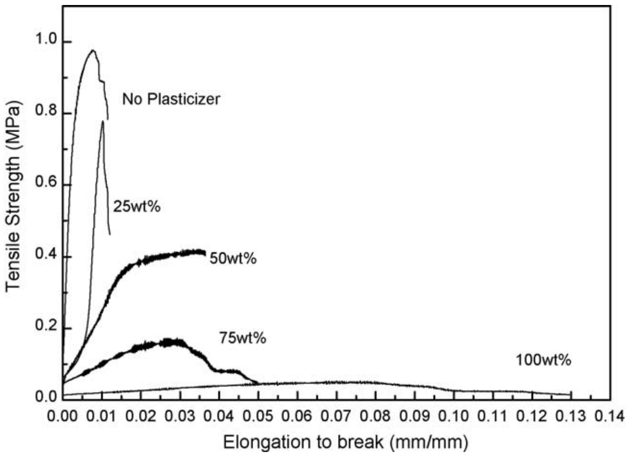

Fig. 3. Elongation–tensile strength curves of green sheets with different amounts of glycerol.

solvent. The green tape without plasticizer exhibits the typical brittle behavior. In general, the physical properties of polymer products are strongly dependent on the interaction between polymer chains. In case of PAM macromolecule network, which is made up by polymerization and cross-link of AM, interaction between polymer chains can be formed during gelation due to the strong C–N and C–C bonding [14]. It is very brittle in room temperature because of the cross-linker structure.

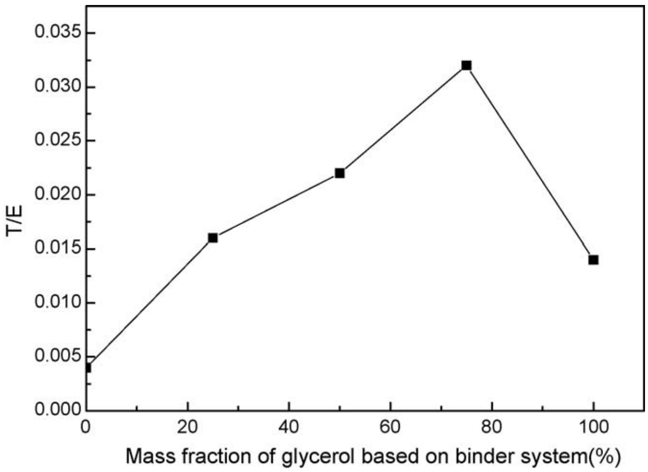

Fig. 4. The influence of glycerol amount on tensile strength to elastic modulus ratio (*T*/*E*).

As shown in Fig. 2, the ductile behavior become noticeable with the additive of plasticizer except DEP. Referring to the mechanism of plasticizer, glycerol, PEG400 and PPG400, which are well dissolved in the PAM chains, increase the distance of the polymer chain as accessibility and penetration of plasticizer to PAM chains. The DEP plasticizer makes the tensile strength declined tremendously indicating that the DEP inhibits the polymerization of AM. Thus DEP is inefficiency to cross-linked PAM binder. The tensile modulus, tensile strength and elongation of green tapes prepared with various plasticizers are represented in Table 1. It is recognized that green tapes prepared with plasticizer show lower elastic modulus, lower tensile strength and larger elongation than that without plasticizer, indicating that plasticizers affect flexibility of the green tape. Also, glycerol yielded the highest *T*/*E* value is the most efficient plasticizer in cross-linked PAM binder. Fig. 3 shows mechanical properties of green tapes with different amount of glycerol. As the glycerol increasing, the tensile strength declines and the elongation increases. Fig. 4 shows the influence of glycerol amount on *T*/*E* value. As the addition of glycerol is 75 wt.% based on binder solvent, the *T*/*E* value reaches highest, the green sheets with appropriate mechanical properties possess higher maneuverability in next working procedure.

### *3.2. Eliminating the surface exfoliation*

PEG2000 is selected in order to eliminate the surface-exfoliation phenomenon of green bodies cast in air. To study the effect of PEG2000 on the surface exfoliation and mechanical properties of green sheets, the suspensions with various amounts of PEG2000 are tape cast. The amount of PEG2000, the degree of surface exfoliation and the corresponding mechanical

Table 1
The tensile modulus, tensile strength, and elongation of green sheets prepared with various plasticizers.

| | Tensile strength (*T*) (MPa) | Engineering strain (%) | Tensile modulus (*E*) (MPa) | *T*/*E* |
|---|---|---|---|---|
| No plasticizer | 0.98 ± 0.13 | 1.15 ± 0.32 | 242 ± 18 | 0.0040 |
| Glycerol | 0.53 ± 0.28 | 3.04 ± 0.58 | 24 ± 5 | 0.0221 |
| PPG400 | 0.40 ± 0.07 | 2.02 ± 0.68 | 29 ± 9 | 0.0138 |
| PEG400 | 0.61 ± 0.26 | 1.49 ± 0.35 | 67 ± 8 | 0.0091 |
| DEP | 0.12 ± 0.01 | 0.16 ± 0.05 | 24 ± 9 | 0.0050 |

Table 2
Influence of amount of PEG2000 on the surface of green sheets and mechanical properties.

| Amount of PEG2000 | Surface of samples | Tensile strength (MPa) | Engineering strain to failure (mm/mm) | Tensile modulus (*E*) (MPa) | *T*/*E* |
|---|---|---|---|---|---|
| 0 (in $N_2$) | No exfoliation | 0.98 ± 0.13 | 1.15 ± 0.32 | 242 ± 18 | 0.0040 |
| 0 (in air) | Obvious exfoliation | 0.77 ± 0.11 | 0.82 ± 0.19 | 308 ± 22 | 0.0025 |
| 5% (in air) | Obvious exfoliation | 0.74 ± 0.11 | 0.90 ± 0.20 | 270 ± 23 | 0.0027 |
| 10% (in air) | Partly exfoliation | 0.70 ± 0.14 | 1.21 ± 0.18 | 223 ± 20 | 0.0031 |
| 15% (in air) | No exfoliation | 0.69 ± 0.13 | 1.49 ± 0.19 | 187 ± 22 | 0.0037 |
| 20% (in air) | No exfoliation | 0.66 ± 0.09 | 1.76 ± 0.22 | 169 ± 17 | 0.0039 |
| 25% (in air) | No exfoliation | 0.65 ± 0.10 | 1.98 ± 0.20 | 156 ± 19 | 0.0042 |

properties are shown in Table 2. It is shown that the green sheets in air yield lower tensile strength and *T*/*E* value than in $N_2$. The surface exfoliation induces to the high inner stress in drying process that deteriorates the mechanical properties. As the increasing of PEG2000 amount, the tensile strength decreases, elastic modulus declines and the elongation increases. That is because the PEG2000 whose Mw is far smaller than that of cross-linked PAM acts as a plasticizer in some extent. The *T*/*E* values change slightly which illustrate that the addition of PEG2000 have not deteriorated the mechanical properties. Since PEG2000 would decrease the fluidity of the suspension, the suspension with 15 wt.% PEG based on binder solvent which has no surface exfoliation is adopted. Fig. 5 shows the surface of the ZnO green sheets without and with 15 wt.% of PEG2000.

Xie in Tsinghua University [19,20] has shown that some water-soluble macromolecule compound with high Mw such as PVP10000, PAM10000 and PEG10000 could eliminate the anti-polymerizing effect of oxygen. They hypothesize that the mechanism of macromolecule compound in eliminating the surface-exfoliation problem of green bodies is the thickening hydrogen bonding between the molecules which serve as a ceramic binder for the particles on the sample surface [21]. But the low Mw compound such as PEG2000 could also have the same effect. That might because PEG has a large number of $-CH_2-O-CH_2-$ ether units. The polyether units are easily oxygenated to become peroxide in air. The PEG consumes the oxygen before the free radical is died out by oxygen.

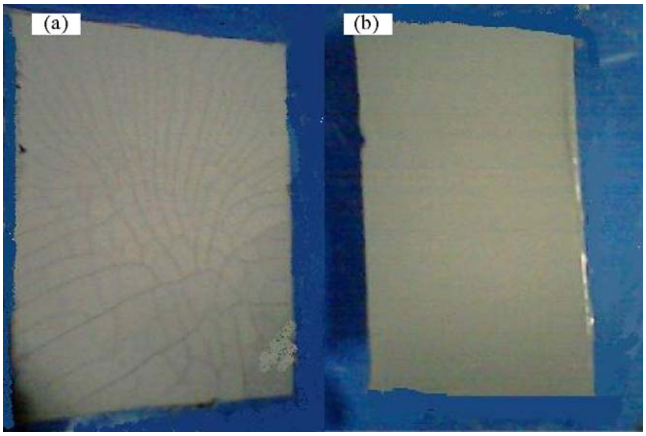

Fig. 5. The surface of the ZnO green sheets without (a) and with 15 wt.% of PEG2000 (b).

Table 3
The appropriate composition of doped ZnO aqueous gel tape casting slurry.

| Material | Content (%) |
|---|---|
| Powder (doped ZnO) | 73.5 |
| Solvent (water) | 11.73 |
| Monomer (acrylamide) | 2 |
| Cross-linker (N,N′-methylenebisacrylamide) | 0.04 |
| Plasticizer (glycerol) | 10 |
| Oxygen anti-polymerization inhibitor (PEG2000) | 2 |
| Initiator (ammonium persulfate) | 0.2 |
| Catalyst (N,N,N′,N′-tetramethyl ethylenediamine) | 0.2 |
| Dispersant | 0.33 |

Fig. 6. Photograph of a green sheet wound on a column showing its flexibility, along with a strip showing holes made by punching.

According to the discussion, the appropriate composition of ZnO suspension in aqueous acrylamide gel tape casting is listed in Table 3. Fig. 6 is the photograph of the green tape showing its flexibility, lubricity in surface along with a strip showing holes made by punching. The ultimate tensile strength of the tape is 0.16 MPa, the elastic modulus is 5 MPa and the elongation is 5.3%. These mechanical properties produce sufficient handing of the green tapes for further processing. Green tapes produce a high relative green density of 58% due to the high suspension solid loading 73.5 wt.%.

## 4. Conclusions

Compared with PEG400, PPG400 and DEP, glycerol is the most efficient plasticizer in cross-linked PAM binder. The suitable additive amount of glycerol is 75 wt.% based on binder solvent. The addition of 15 wt.% PEG2000 eliminates the surface exfoliation due to the oxygenation of ether units. The green sheets with high flexibility and lubricous surface are obtained. The solid loading of suspension reaches 73.5 wt.% and the relative green density approaches to 58% by gel tape casting.

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