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Novel ceramic processing method for substitution of toxic plasticizers

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ABSTRACT

A systematic screening of plasticisers for a polyvinyl butyral based binder system revealed that dibutyl maleate, dibutyl adipate and Pycal 94 are promising and less toxic alternatives to the very harmful but frequently used dibutyl phthalate. Pycal 94 seems especially promising as it unlike the two other candidates did not require a co-plasticiser, such as a polyethylene glycol, thus simplifying the system and reducing the risk of unwanted cross-interactions.

An effective and systematic procedure for substitution of the plasticiser, while maintaining chemical compatibility and mechanical properties, was also demonstrated. Incompatible systems were discarded in an initial broad screening while primary systems were further evaluated based on debinding properties, mechanical properties, flow behavior as well as sintering properties of ceramic tapes. The thermomechanical characterization performed on dried drops of binder and their corresponding tapes show strong similarities in the strain/stress profiles, validating the qualitative method used.

1. Introduction

For non-aqueous binder systems for tape casting, polyvinyl butyral (PVB) is a common binder [1–5], and it forms a network based on hydrogen bonding which acts as a matrix for the ceramic particles [3,4]. A PVB based system is ascribed a number of beneficial properties including high green strength, good flow properties, solubility in many common non-aqueous solvents, compatibility with other additives as well as a stabilizing effect on ceramic suspensions [4]. The length of the PVB chain determines the mechanical properties in the green state and it has been shown that an increased molecular weight of the PVB binder will result in increased green strength at the expense of plasticity [1].

In order to add an adequate plasticity to a PVB based binder system, an *ortho*-phthalate plasticizer is the common choice for non-aqueous processing [5]. The plasticizer acts by reducing the attractive forces between nearby binder chains and prevents the formation of stiff and brittle green ceramics [3]. The plasticizer will in general reduce the strength while improving the flexibility and decreasing the elastic modulus, internal stresses and the glass transition temperature in the green state [3–6]. The properties are often enhanced with increasing amounts and Pradhan et al. [10] has shown a decreased transition temperature with increasing plasticizer amounts.

The efficiency of the plasticizer will in general depend on the size and the active groups, and a plasticizer with a low molecular weight and few active groups is in general more efficient. This effect is achieved through a high mobility [3,4] though the effect can be lost if the plasticizer is too small compared to the binder [6]. The effect will also be lost if the active groups cross-link with the binder, causing stiffening and strengthening of the binder network [6].

Ortho-phthalates have been shown to be very efficient, when compared to aliphatic linear structures for PVB based binder systems, and this is ascribed to the aromatic unit [3]. *ortho*-Phthalates have however recently become unwanted as some of them exhibit a number of unwanted health effects including possible damage to unborn children, high toxicity to aquatic life as well as suspected damages to fertility. Dihexyl phthalate, dipentyl phthalate (DPP), N-pentyl-isopentyl phthalate, diisopentyl phthalate, bis(2-methoxyethyl) phthalate, diisobutyl phthalate (DIBP), Benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) have all been included on the European Chemicals Agency's "Candidate List of substances of very high concern for authorisation" with the reason "Toxic for reproduction" [7]. The latter four also appears on the "Authorization List" [8] while dihexyl phthalate is on the "Recommendation for inclusion in the Authorisation List" [9]. It is hence desirable to replace *ortho*-phthalates with other components even though it may affect lamination properties and microstructure [4,10,11].

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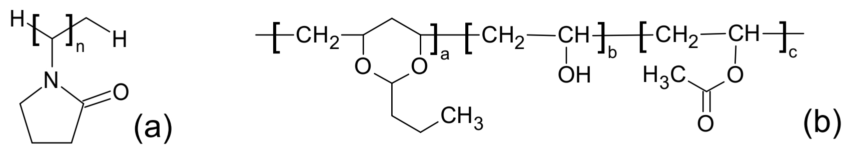

Fig. 1. Chemical structures, names and additional specifications for (a) polyvinyl pyrrolidone and (b) the binder. For the binder a = 78.0 ± 3.0 mol%, b = 19.5 ± 1.5 mol% and c = 2.5 ± 1.5 mol%.

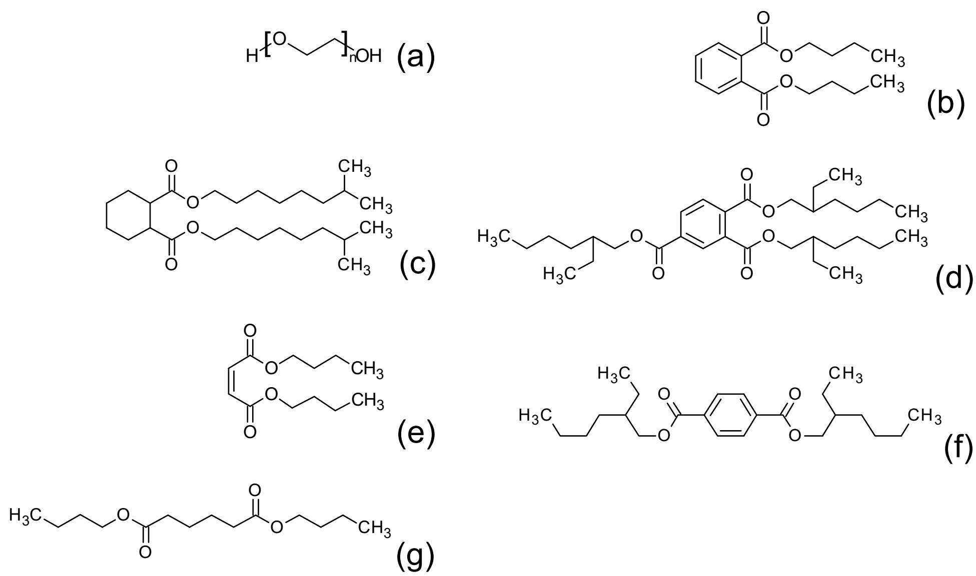

Fig. 2. Chemical structures and names of (a) polyethylene glycol, (b) dibutyl phthalate, (c) 1,2-cyclohexane-dicarboxylic acid diisonyl ester, (d) tris(2-ethylhexyl)trimellitate, (e) dibutyl maleate, (f) bis(2-ethylhexyl) terephthalate and (g) dibutyl adipate.

Typically azeotropic solvent mixtures such as toluene-ethanol, xylene-ethanol or 2-butanone-ethanol are investigated for binder systems and tape casting slurries [12] due to beneficial properties such as solubility, dielectric constant and evaporation rate [13,14]. Pure ethanol is however much more desirable from a handling and health perspective.

Recent investigations have shown viable alternatives to *ortho*-phthalates such as a modified castor oil [15] and triethylene glycol di-2-ethylhexanoate (S-2075) [16]. The present work aims at identifying additional plasticizers which are compatible with a PVB based binder system with ethanol as the sole solvent. Specifically dibutyl maleate, dibutyl adipate, Pycal 94, Hexamoll Dinch, tris(2-ethylhexyl) trimellitate and bis(2-ethylhexyl) terephthalate (a *para*-phthalate) was investigated both with and without a polyethylene glycol (PEG) as a co-plasticizer.

Incompatible systems were discarded in an initial broad screening while primary candidate systems were evaluated based on debinding properties, mechanical properties, flow behaviour as well as on sintering properties. The applicability of the systems, and thereby also of the more general substitution methodology, was demonstrated on a tape cast 8YSZ (8 mol% Y_2O_3 stabilized ZrO_2) electrolyte layer for use in an electrolyte supported solid oxide fuel cell.

2. Experimental procedure

2.1. Materials

The powder used was TZ8Y from TOSOH while the solvent was 99.9% ethanol from CCS Healthcare.

For the binder and dispersant a PVB and polyvinyl pyrrolidone (PVP) polymer were used respectively [17]. Fig. 1 gives structures and additional specifications.

As plasticisers the following were obtained from Sigma-Aldrich: Polyethylene glycol (PEG 600), tris(2-ethylhexyl) trimellitate (99%), bis(2-ethylhexyl) terephthalate (≥96%), dibutyl adipate (96%), dibutyl maleate (96%). Additionally 1,2 cyclohexane dicarboxylic acid diisonyl ester (Hexamoll Dinch) from BASF, Pycal 94 from Tape Casting Warehouse and dibutyl phthalate (for synthesis) from Merck were used. The dibutyl phthalate is included as a reference. The structures of all plasticisers but Pycal 94 were given by the supplier and can be seen in Fig. 2.

Pycal 94 has previously been identified as a polyoxyethylene aryl ether [18] but the specific structure has not been disclosed.

2.2. Selection and preparation of plasticizer systems

The variety of plasticisers was chosen in order to screen a broad spectrum of alternatives to DBP including different positions and lengths of the functional groups as well as different rigidities of the overall molecules. The dibutyl adipate is a small molecule with free rotation around all carbon bonds and with small functional groups, while tris(2-ethylhexyl) trimellitate is a much more rigid molecule, due to the stiff aromatic ring, with much bigger functional groups.

The total amount of plasticisers as well as the number of possible combinations made some initial rough screenings of suitable systems necessary.

It was decided to use a two component plasticizer system with a PEG as co-plasticiser. The use of a co-plasticiser can be desirable as different classes of plasticisers acts differently and induce slightly different behaviours to the final green tape [19,20].