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# Roles of Poly(propylene glycol) during Solvent-based Lamination of Ceramic Green Tapes

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## Abstract

Solvent lamination for alumina green tapes is readily accomplished using a mixture of ethanol, toluene and poly(propylene glycol) (PPG). After lamination, the PPG is clearly present as a discrete film at the interface between the laminated tapes. This condition, however, does not generate delamination during firing. Systematic sets of experiments are undertaken to determine the role of PPG in the lamination process and, specifically, the mechanism by which it is redistributed during subsequent processing. PPG slowly diffuses through the organic binder film at room temperature. The PPG diffusion rapidly increases as temperature is increased to 80°C. The key to the efficiency of adhesives during green-tape lamination is mutual solubility of the nonvolatile component of the glue and the base polymeric binder.

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## Introduction

Multilayer manufacturing processes allow easy fabrication of large or, more often, complex ceramic components. The most widespread use of this technology is in the fabrication of electronic substrates and capacitors.[1] Commonly in this process, a sheet-like powder-compact or "green tape" is first prepared. Then, the sheet materials are cut or punched into the desired shapes before joining together and sintering to obtain the final ceramic component with useful properties.

Joining is therefore important to the success or failure of the end ceramic component. Joining or lamination must preserve registration of assembled parts and generate local particle packing in the joint region such that complete defect-free bonding occurs during subsequent sintering. Indeed, it is preferable to join ceramics in the green state rather than after densification in order to obtain a microstructure during firing that does not reflect the joining history.[2] The joining technique employed for a particular substrate depends on the intended application and material composition.

In ceramic powder processes, shaping yields a green state in which the ceramic powder is held together by organic binders, which are often a plasticized thermoplastic. Thus, in principle, the joining techniques employed to assemble the thermoplastic composites[3-10] into structures, i.e., mechanical fastening, adhesive bonding, and welding can be utilized with green tapes.

Techniques used for green tape lamination are determined based on the nature of binder system. Thermomechanical compression is the joining technique that has been commonly used in multilayer processing. Temperature and pressure are selected depending on type and content of polymeric binder. Warm uniaxial pressing and isostatic pressing are simple and cost effective methods used in multilayer components when resulting strain is tolerable.[11,12] An approach similar to solvent welding of polymers[13,14] has been shown to produce green lamination with low permanent strain, i.e., preserving the specimen dimensions.

Wei has explored both thermocompression and solvent bonding, for geometrically complex stacks of porous poly(vinyl butyral)-based alumina green tape.[15] Thermocompression (warm isostatic, warm uniaxial and semi-isostatic) was an effective method to obtain good lamination. However, poor dimensional stability was observed due to significant shear strains, 5-10 %, that occurred during lamination. Softening the tape interface using a solvent mixture, in this case ethanol and toluene, gave good lamination of green tape with very small permanent strain, less than 1 %, but it proved to be a sensitive process. The solvents evaporated quickly or migrated throughout the tape volume. The engineering solution was to add a diluent, that is, a material that was nonvolatile and of relatively high viscosity. A mixture of ethanol, toluene and poly(propylene glycol) (2:1:2 by weight) proved to be a very stable and tolerant formulation that gave good, reproducible lamination in green state with no evidence of delamination after sintering, and with only a minimal dimensional change less than 0.5 % in the stacking direction.[15]

Although the distribution and the function of PPG in laminated green material were not really known, it was presumed that the adhesive underwent marked segregation upon contact with the tape. First, the solvents are absorbed into the tape, and then ultimately evaporate. In contrast, the nonvolatile PPG, which has low mobility, must be retained as a separate phase presumably near the original interface. This is consistent with the "glazing" effect that Wei observed when the free surface of a tape was painted with the mixture. Clearly, there must be a redistribution of material, specifically the PPG must migrate away from the interface in order to produce a defect-free dense part (as was regularly observed). The possible mechanisms for redistribution of PPG within the green tape are shown in Fig. 1. It is presumed that PPG penetrates into porosity of the green tape by capillary action then diffuses into the polymeric binder. The purpose of the work reported herein is to determine both the mechanism and kinetics of the PPG redistribution. It is expected that understanding the penetration mechanism and role(s) of PPG in laminated alumina tapes will lead to a general adhesive system which can be used to laminate various kinds of porous green parts.

## Experimental

→ what is the initial pore content in these tapes + is the porosity interconnected?

### *Materials and Chemicals*

The commercial green tapes used in this work were provided by the Coors Electronic Package Company, Chattanooga, Tennessee. The binder system in this tape is based on poly (vinyl butyral), PVB, with molecular weight ranges 90,000-120,000, (Monsanto Company, St.Louis, MO). In addition, two alkyl fatty acid ester based plasticizers, AFA1 and AFA2, are used, but the specific chemical formulations are proprietary. The adhesive mixture is composed of ethanol and toluene (Fisher Scientific Company, NJ) and poly(propylene glycol), Mw = 1,000 (Aldrich Chemical Company, Inc, Milwaukee, WI).

Mw distribution
?

*Procedures*

Adhesive Lamination of Green Ceramic Tapes ← subheading

Lamination experiments of green ceramic tape, with systematically varying combinations of solvents and PPG, were conducted using a procedure essentially identical to that of Wei's. Three different adhesive formulas are used; 1) a mixture of ethanol, toluene and PPG in ratio of 2:1:2 by weight following Wei[15], 2) an azeotropic solvent (ethanol:toluene = 2:3 by weight) with different fractions of PPG (0, 20, 40, 60, and 80 % of PPG by weight), and 3) pure PPG.

The same lamination procedure was used for each specimen as shown in Fig. 2. Ten layers of 2.5 x 2.5 x 0.06 cm green-tapes were laminated together to generate specimens for microstructural analysis. Fewer layers of different cross-section were used for mechanical tests as described below. The adhesive was applied to the free surface of the stack and a new tape was placed on top, and the most recently applied layer was rolled with a 0.45 kg polished aluminum cylinder. The final assembly was then pressed with uniaxial pressure at 0.5 kPa for 5 minutes. For the samples with pure PPG, the specimens were put under pressure 0.5 kPa using a dead load, heated and held at 80°C for 12 hours after assembly.

In the debinding process, specimens were heated at 0.5°C/min from room temperature to 800°C under air, and then the specimens were held at 800°C for 4 hours before cooling. In the sintering process, the specimens were heated at 2.5°C/min from 600°C to 1560°C and held for 30 minutes prior to cooling.

→ Not one of the adhesive systems used for lamination

## Fracture Surface Observation

Three sets of specimens were prepared using the 2:1:1 adhesive formula. The first set of specimens was kept at room temperature for 20 hours. For the second and the third, after the initial 20 hours at room temperature, the specimen were heated to 80°C and held for either 18 hours (second set) or 36 hours (third set). Both were then cooled to room temperature. To prepare specimens for microstructural examination, the green specimens were scribed, immersed in liquid nitrogen to make them brittle, and broken. Fracture surfaces of laminated green tapes in each condition were observed using a scanning electron microscope, SEM, (model S-4500, Hitachi). In preparation, each sample was coated with palladium as a conducting material.

## The Evaporation of Solvents after Lamination

? [illegible] used?

The weight loss pattern of each specimen laminated with adhesive formula 2 was determined using a microbalance (Mettler33340, Mettler Ins. Corp.). The weight change of solvents from the laminated specimens as a function of time was calculated using the following equation.

How do you know the initial solvent content in stack — is some evaporation likely occ during the coating process??

$$Weight(\%) = \frac{W_t - W_\infty}{W_0 - W_\infty} \quad X \quad 100$$

Where $W_t$ is weight of the specimen at time t, $W_\infty$ is the constant weight of the specimen after the solvents have completely evaporated, $W_0$ is the initial weight of specimen.

After the solvents were completely evaporated. Each specimen was debound and sintered by the procedures that were described in the previous section. After sintering, the parts were cut using a diamond saw to expose a cross section close to the center of the specimen that was perpendicular to the planes of joining. The surface of each specimen was observed under an optical microscope.

## Mechanical Properties

The penetration of PPG into green tapes, in principle, can affect mobility of the polymer chain in organic binder of the tape. The mechanical properties of the green tape under both dynamic and nominally static loading were used to track this as a function of adhesive formulation and post-lamination thermal history.

### Tensile Testing

→ Needs to be denoted as subheading

Tensile testing experiments were performed on an Instron universal testing machine (Model.1125, Instron Corp., MA) with a slow crosshead speed of 0.5 mm/min. Dog-bone shaped specimens of as-received tapes were prepared according to ASTM D5083-93a, i.e., 1.25 cm width and 5.70 cm gauge length. A load cell with sensitivity of 20 N/volt was used. The stress-strain behavior of single tapes and double tapes which were coated with the solvent mixture~~s~~ (ethanol: toluene = 2:1) or the adhesive (ethanol: toluene: PPG = 2:1:2) were observed and compared to the results obtained from as-received materials.

### Dynamic Mechanical Analysis

Needs to be denoted or subheading

Dynamic mechanical analysis (DMA) was used to observe the penetration of PPG into Coors alumina tape. The experiments were performed using temperature sweep mode from -120°C to 70°C in Dynamic Mechanical Spectrometer (RMS800, Rheometric Scientific Inc., NJ). The strain used was 0.03% after determining the linear viscoelastic range by a strain sweep experiment. The frequency employed was 6.28 rad/sec. For this test, specimens were cut into a rectangular shape, size 55.0 x 12.0 x 0.6 mm and coated with the adhesive solution (PPG:ethanol:toluene = 2:2:1 by weight). One set of adhesive-coated specimens was kept at room temperature for varying periods of time. The other set was kept at 80°C for varying periods of time, before cooling and testing. The changes of the resultant DMA spectra were compared as the function of time and temperature.

Need standard nomenclature

Check for tense match

## Results and Discussion

Alumina green tape is a porous sheet. When an adhesive mixture was applied on the surface of the tape, at least three phenomena take place; the evaporation of solvents through the porosity in the tape, migration of the liquids through the space by viscous flow, and interdiffusion between the constituents of the adhesive and the polymeric binder. The addition of the PPG appears to slow all three. Each will be discussed in turn.

Fig. 3 presents weight loss data collected from drying experiments conducted with the 10-layer green tape samples with different concentrations of PPG in ethanol-toluene mixture. The shapes of the weight loss curves show a similar trend for each specimen. However, the evaporation rates of solvents depend significantly on the amount of PPG in the adhesive mixture. The solvent weight loss slows down when the concentration of PPG in adhesive mixture is increased.

Secondly, without adding PPG, the azeotropic mixture of ethanol and toluene is quite aggressive. The organic binders at the surface of green tape are completely dissolved and alumina particles are observed to freely flow, i.e., transfer to the dropper surface was appreciable. Damage to the surface was reduced when the amount of PPG in the adhesive mixture was increased.

The cross-sections of ceramic materials laminated with this set of adhesive mixtures were observed using optical microscope. Delaminations were observed in the center of the samples laminated with pure azeotropic solvents. In contrast, very few delamination defects occurred in other samples with PPG 20%, 40%, 60% and 80%. (One implication of this observation is that PPG concentration as high as 80 % can give good lamination results.)

Lamination of the green tape with pure PPG was not possible at room temperature. Even attempts to induce lamination at 80°C under 0.5 kPa pressure were only partially success. ful Delamination defects were commonly observed in the cross-section of the specimen after sintering. An important aspect of the latter experiment is that this result suggests that PPG is dissolving and diffusing at 80°C.

→ NOT REALLY
IT MAY PREV
THE PVB
FROM
ADHERIN

Attention now turns to the presentation and discussion of results of direct microstructural observations. Fig. 4 shows the fracture surface of two-layer laminated green tapes joined by different mixtures. The ethanol-toluene mixture (2:1 by weight) gives good lamination results with essentially no defects. The mating surfaces conformed to produce intimate contact and the action of the solvent produced a seam that cannot be distinguished from the bulk tape. However, the fracture surface of specimen joined with the 2:1:2 ethanol-toluene-PPG mixture shows some gaps which remain at the interface between two surfaces. It also appears that during the fracture process to prepare the sample for SEM analysis the crack ran along the plane of the joint for some distance producing a step, see Fig. 4b. Both are consistent with a residual PPG film at the joint interface. Neither suggests local particle packing that is conducive to densification during subsequent firing. Despite the marked differences that are evident in the as-laminated state, both types of specimen routinely sinter to the equivalent high densities and in neither case show the evidence of residual defects. These results confirm the presumptions stated earlier: i) there is a discrete polymer film at the joint interface when using the 2:1:2 adhesive, and ii) PPG can and must migrate after lamination.

In order to confirm the latter changes of green microstructure, ten-layer laminated green samples prepared using the 2:1:2 adhesive were observed by SEM as a function of time and temperature. Results are shown in Fig. 5. Fracture surfaces of the adhesive-laminated multilayer green tapes show differing patterns for different conditions. After 24 hours at room temperature, a narrow stripe can be seen clearly at the interface between adjacent green tape layers. This pattern was observed even 5 days after lamination at room temperature. The contrast between interface and bulk regions was reduced after heating the specimen to 80 °C and holding for 18 hours. After holding for 36 hours at 80 °C, the contrast completely disappeared. This confirms that localized PPG migrates into the bulk organic phase of the green tape at the low temperatures compared to the onset of binder burnout. Therefore, the presumed homogenization is possible.

The evident transport behavior of PPG inside the alumina green tape was further studied at ambient temperature and the temperature higher than $T_g$ of the tape, 80°C, using a combination of tensile testing, and dynamic mechanical analysis.

Sentence should break into two sentences.

Tensile testing was used to determine changes in mechanical properties that occur when PPG is applied onto the surface of an alumina tape. For all test conditions used for studying multilayer samples, control experiments of a single tape or non-laminated set of two and three as-received tapes were included. As expected, stress-strain curves yielded identical results for all control specimens regardless of the number of tapes used.

Fig. 6 shows the stress-strain behaviors corresponding to different test conditions of laminated pairs of green tapes. The ethanol-toluene (2:1 by weight) laminated specimens dried at room temperature show stress-strain behavior that is

Figure 6 shows adhesive-laminated parts only. No solvent laminated parts are indicated.

indistinguishable from that of as-received tapes. This indicates that the action of the solvent is temporary, i.e. the solvent renders the binder tacky, but after drying the binder properties are fully recovered. The heated ethanol-toluene laminated specimens give the lower apparent yield point and the shallower slope after yield. These small changes in behavior are associated with equilibrating the distribution of phases within the binder, but not related to the lamination process. Single tapes subjected to the same history display the same stress-strain behavior.

Adhesive (ethanol: toluene: PPG = 2:1:2 by weight) laminated green tapes, which were left at room temperature for 24 hours before running the experiment, show the same apparent yield point as the ethanol-toluene laminated green tapes, but the slope of the curve after yield point is lower. The adhesive laminated specimens that were heated at 80°C show the lower apparent yield points and shallower slopes after yields. These phenomena are dependent on the treatment times at 80°C. The longer is the heating time, the lower is the yield point and the shallower is the slope after yield. The similar trends were also observed for single tapes which were coated with adhesive mixture, i.e., the changes are associated with the presence of PPG regardless of the geometry of the specimen.

Figure 6.

Elastic Modulus i.e., slope of stress/strain curve

Other work[16] has indicated that the slope after the apparent yield is indicative of the stiffness of the organic constituent. Thus, these results indicate that the presence of the PPG softens the binder even at room temperature, though much more markedly at elevated temperature.

DMA was also used to study the penetration of PPG in alumina tape after the lamination process. Although more rigorous analysis should use G″ to define the transition temperature, tan δ spectrum was more convenient to analyze for this complex system. The transitions at 30°C and –83°C refer to the transition temperature of plasticized PVB binder and free liquid plasticizer, respectively.[14] The free liquid plasticizer does not play any direct role in the tensile behavior. The slope of the stress-strain curve after yielding is correlated to the glass transition temperature of the plasticized PVB. In Fig. 7, the storage modulus (G′) of adhesive coated alumina tape in the low temperature regime (< 50°C) is slightly higher (≈ 1-2 GPa) than that of as-received green tape. This results from the filling of green tape porosity by PPG. After 6 hours at room temperature, the tan δ spectrum of the adhesive coated tape shows the appearance of a peak corresponding to that of expected for PPG glass transition around –60°C. This transition temperature corresponds to the mobility of the PPG in the porous space of the alumina tape. There are no changes in the transition temperatures associated with the as-received tape. Thus the viscoelasticity of green tape has not been changed by PPG in the pore space. However, after 2 days at room temperature, the transition temperature at –60°C becomes less distinct and a broader transition at 30°C is noticeable along with a shift in the position of peak to lower temperature, i.e., from 30°C to 20°C. The PVB transition was slowly moved to lower temperature as the function of aging time at room temperature. The spectrum continues to change until 17 days at room temperature. The presence of the PPG only affects the PVB, i.e., there is no change

This is in Figure 8. Need better correlation between text and Figures.

in the position or the amplitude of peak corresponding to the lower transition temperature (-83°C).

More marked shifts were observed for adhesive-coated tapes which were heated to 80 °C. All specimens were cooled and left at room temperature for 24 hours to ensure stability before running DMA experiments. As expected and visible in Fig. 8., when adhesive-coated tapes were kept at 80°C for 5 hours, the effects were qualitatively the same as for long time at room temperature, but the magnitude was greater. This annealing condition appears to lead to an equilibrium distribution as no change was observed after 6 days of heating at 80°C. The broad transition indicates the heterogeneity of the system is increasing due to the mobility of molecules of different molecular weight, i.e., some elements of the PVB structure are more susceptible to plasticization than other.

The migration of PPG into the organic binder system affects the properties of the green tape in whole. The approximate time used for PPG migration to go to equilibrium at room temperature or at 80°C can be estimated from DMA results. The alumina green density and the organic binder density are 2.40 g/cm$^3$ and 1.1 g/cm$^3$, respectively. The average diameter of the alumina particle is 4 μm and the alumina concentration is 91.5 % by weight. Assuming that the particle shape is round, the polymer thickness from alumina surface is approximately 0.13 μm. The diffusion rate of PPG into the PVB matrix can be approximated from:

$$D = \frac{a^2}{t}$$

I don't know if this is the appropriate length scale. Why did you select this? [illegible] diffusion [illegible] leads to very [illegible] where D is diffusion rate, a is polymer thickness and t is time that PPG adheres to the green tape surface and generates the change in transition temperature.

From DMA spectra of the green tapes after contacting with PPG, the peak position 17 days at room temperature leading to an estimated value for D of 1.15 x $10^{-16}$ $cm^2$/sec. Referring to Fig. 7 and Fig. 8, shifts in peak position at room temperature and 80°C require time of 2 days and 5 hours respectively. Inserting these values into the above expression yields the following estimates of D = 9.78 x $10^{-16}$ $cm^2$/sec at room temperature and 9.39 x $10^{-15}$ $cm^2$/sec at 80°C, respectively. That is, PPG slowly dissolve and diffuse at room temperature, but the process is greatly accelerated by warming the sample.

## Conclusion

The experimental evidences confirmed that there is redistribution of poly(propylene glycol), ~~PPG,~~ after depositing the adhesive mixture onto the green tape surface. PPG, as a constituent of the adhesive used for lamination, helps soften green tape surface, reduces aggressiveness of solvents, and slows solvent evaporation rates so prolongs the tackiness of the tape surfaces. PPG migrates into the green tape via capillary action. It then diffuses into the binder system and softens the green tape. The PPG diffusion can take place both at room temperature and 80°C.

? this seems highly unlikely!

## Acknowledgements

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## List of Figures

**Fig.1.** Schematic illustration of the presumed deposition of PPG at tape interfaces and the possible mechanisms of PPG redistribution during post-processing.

**Fig.2.** Steps of adhesive lamination (ethanol:toluene:PPG = 2:1:2 by weight)[15]

**Fig.3.** Normalized weight loss of solvents from 10-layer adhesive laminated tapes. The adhesives are the mixture of ethanol-toluene (2:3 by weight) combined with different amount of PPG. The normalized weight of of solvent is the weight after excluding the weight of green tape and PPG.

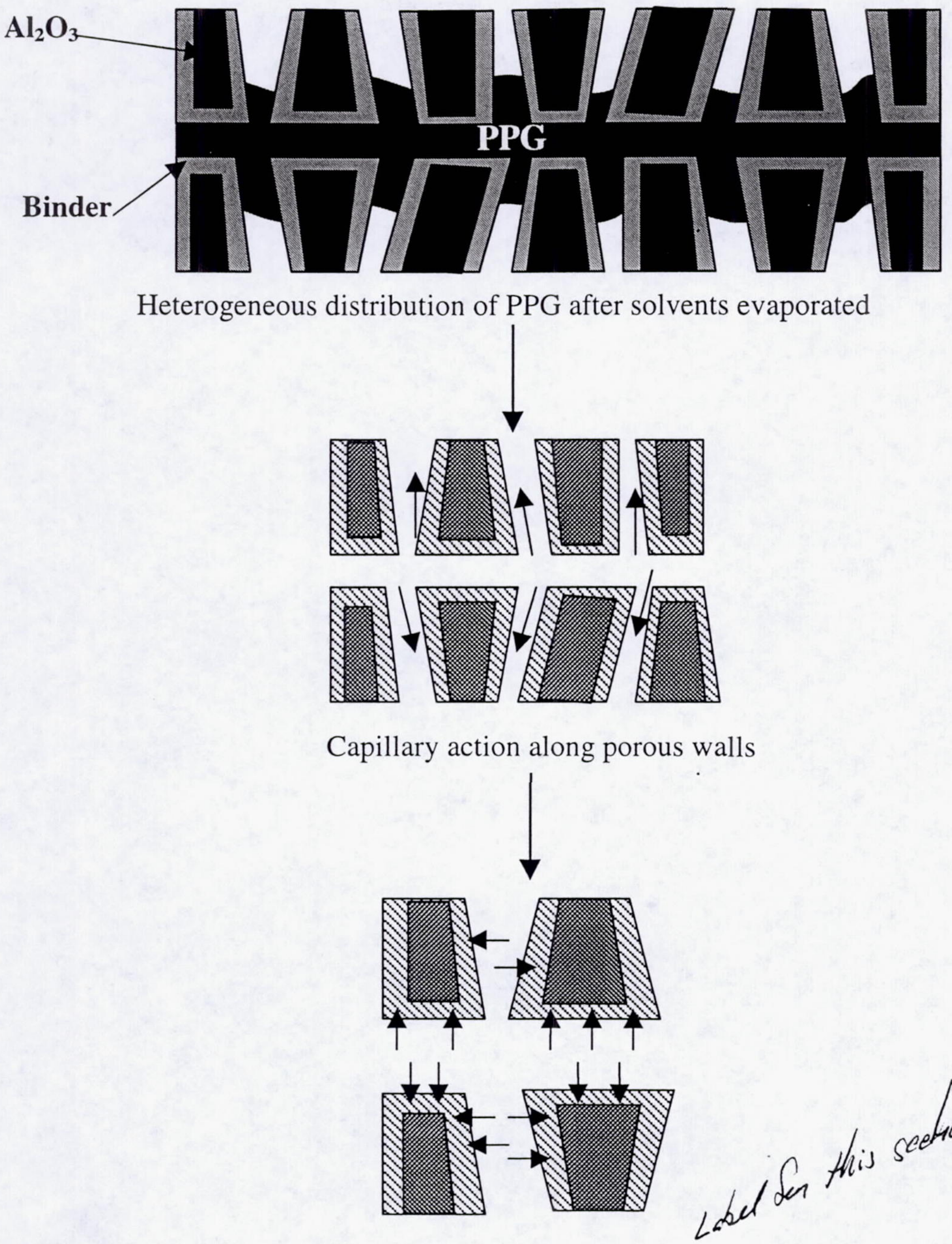
**Fig.4.** Fracture surafce of 2 layer laminated green specimens; (a) ethanol-toluene mixture (2:1 by weight), 24 h. at room temperature, (b) ethanol:toluene:PPG (2:1:2 by weight, 24 h. at room temperature (PPG = 0.002 g/cm$^2$)

**Fig.5.** Fracture surafce of ten-layer laminated green tape specimens (600 μm/layer) 0.002 g/cm2 of PPG. The differences of interfacial patterens can be be observed and compared; (a) after 20 hours at room temperature vs (b) after 18 hours at 80°C. The interfacial patterns disappear after 36 hours at 80°C.

**Fig.6.** Stress-strain curves of as-received tapes (a), adhesive-laminated two tapes aged at room temperature for 24 h. (b) and adhesive-laminated two tapes aged at 80 °C; for 0.5 h. (c), 1 h. (d), 3 h. (e) and 5 h. (f)

**Fig.7.** Dynamic mechanical spectra of as-receive green tape (——) vs adhesive-coated tape aged 6 hours at room temperature (- - - - ) and 2 days at room temperature (— - -), respectively. The peak at -60°C disappears and the PVB transition moves to lower temperature.

**Fig. 8.** Dynamic mechanical spectra of as-received green tape (—— ), PPF-coated tape at room temperature for 17 days (—+—), PPG -coated tape heat at 80°C for 6 days (— - · ). The PVB transitions move to lower temperature after long contact-taime at room temperature or heating to 80°C.



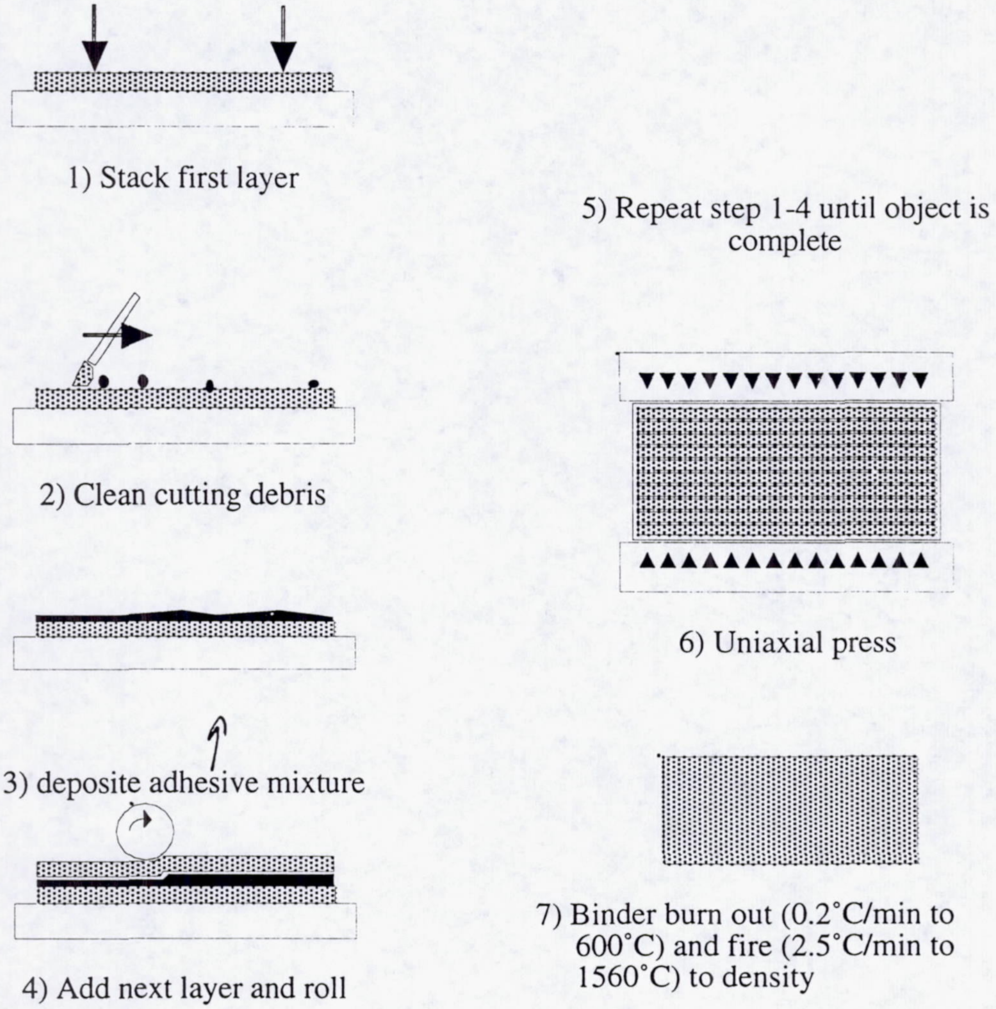
Heterogeneous distribution of PPG after solvents evaporated

Capillary action along porous walls

Are wetting angles correct for PPG on PVB?

Label for this section?

**Fig. 1.** Schematic illustration of the presumed deposition of PPG at tape interfaces and the possible mechanisms of PPG redistribution during post-processing.



1) Stack first layer

2) Clean cutting debris

3) deposite adhesive mixture

4) Add next layer and roll

5) Repeat step 1-4 until object is complete

6) Uniaxial press

7) Binder burn out (0.2°C/min to 600°C) and fire (2.5°C/min to 1560°C) to density

**Fig. 2.** Steps of adhesive lamination (ethanol:toluene:PPG= 2:1:2 by weight)[15]

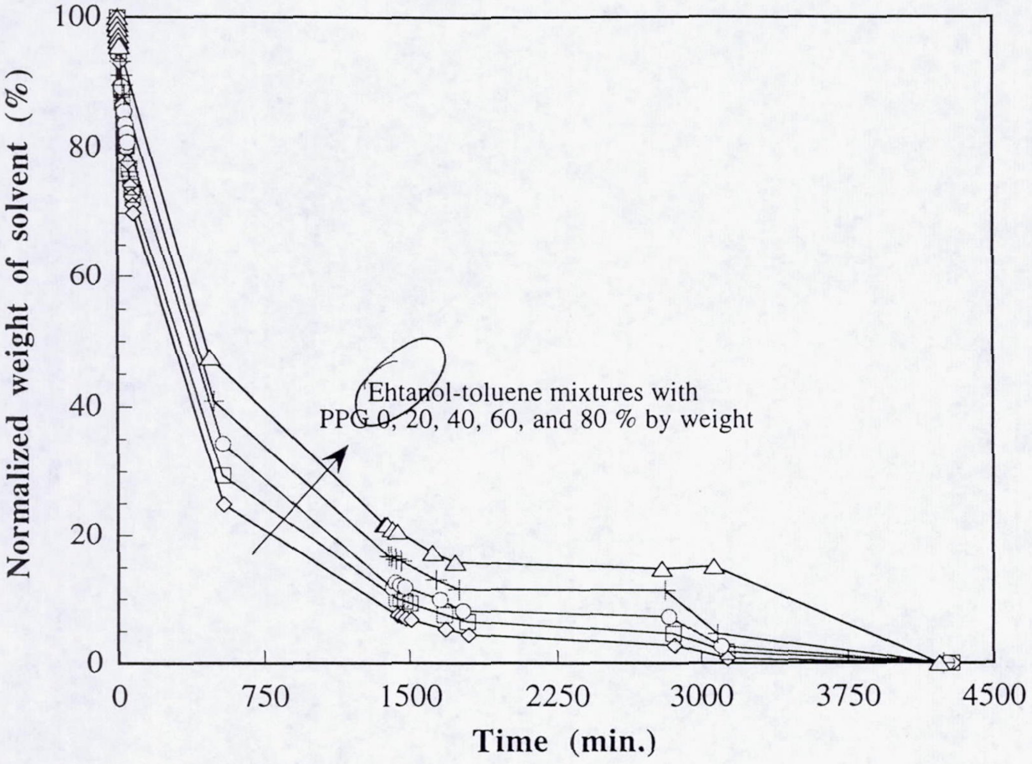
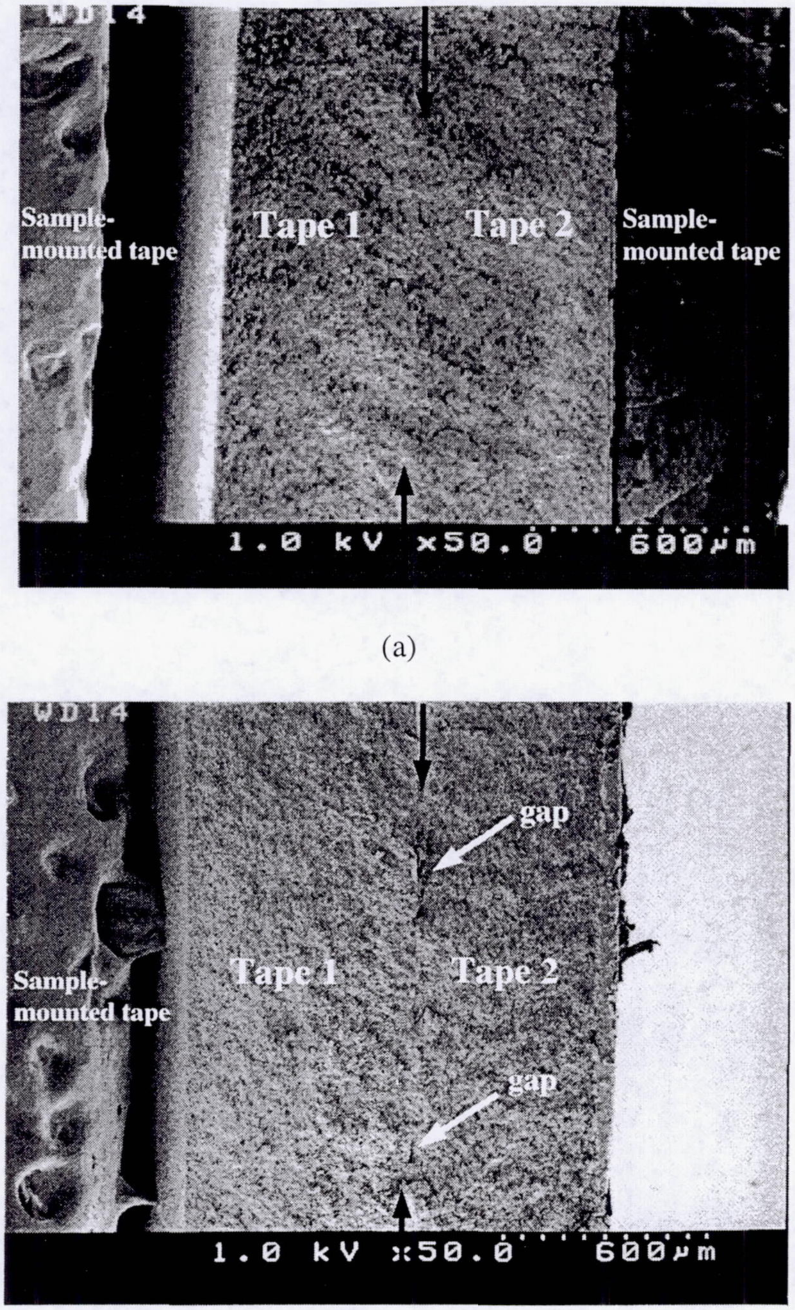


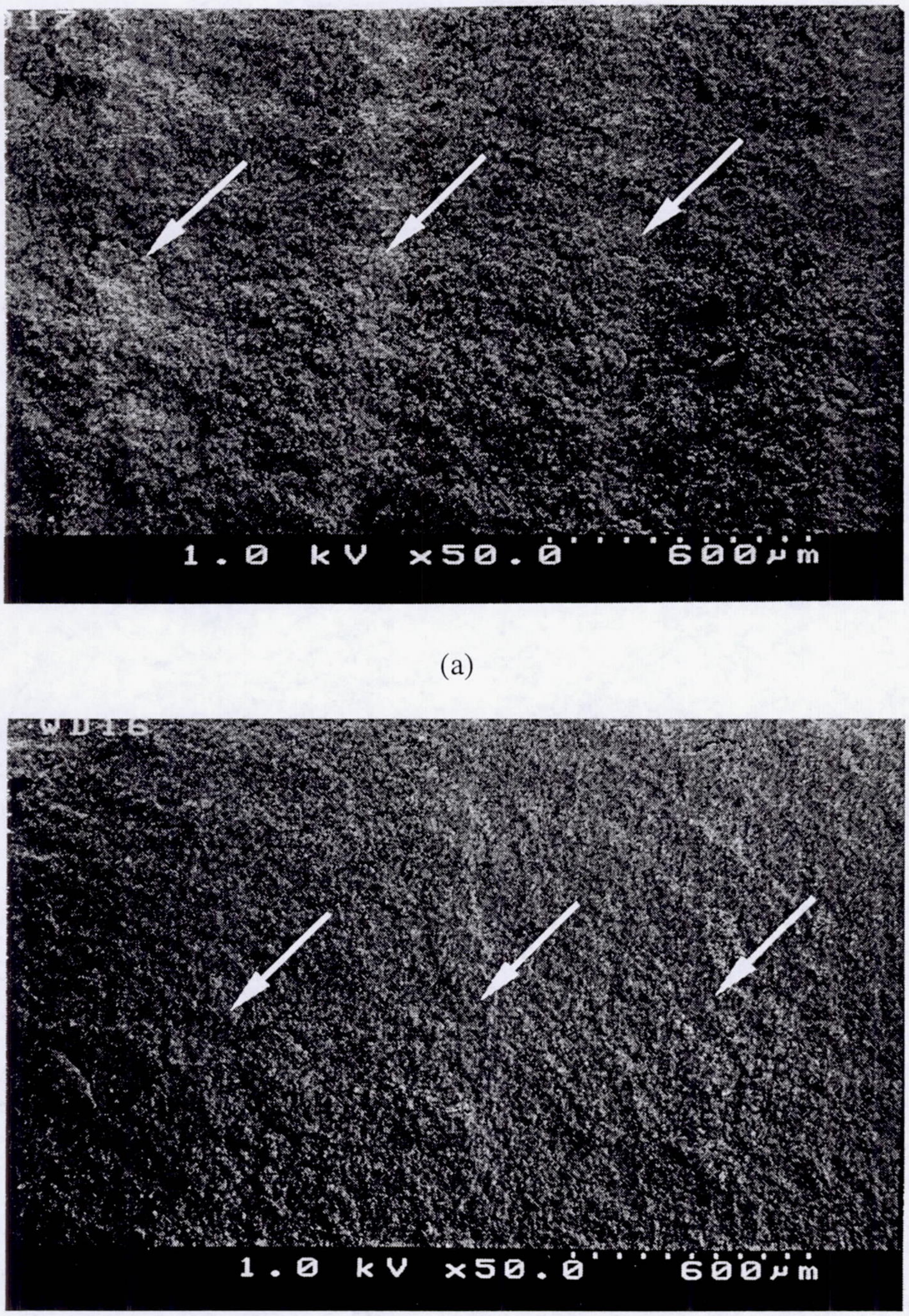
**Fig.3.** Normalized weight loss of solvents from 10-layer adhesive laminated tapes. The adhesives are the mixture of ethanol-toluene (2:3 by weight) combined with different amount of PPG. The normalized weight of solvent is the weight after excluding the weight of green tape and PPG



(a)

(b)

**Fig. 4.** Fracture surface of 2-layer laminated green specimens; (a) ethanol-toluene mixture (2:1 by weight), 24 h. at room temperature,(b) ethanol:toluene:PPG (2:1:2 by weight), 24 h. at room temperature (PPG = 0.002g/cm$^2$) Black arrows indicate the interface between two green tapes.



(a)

(b)

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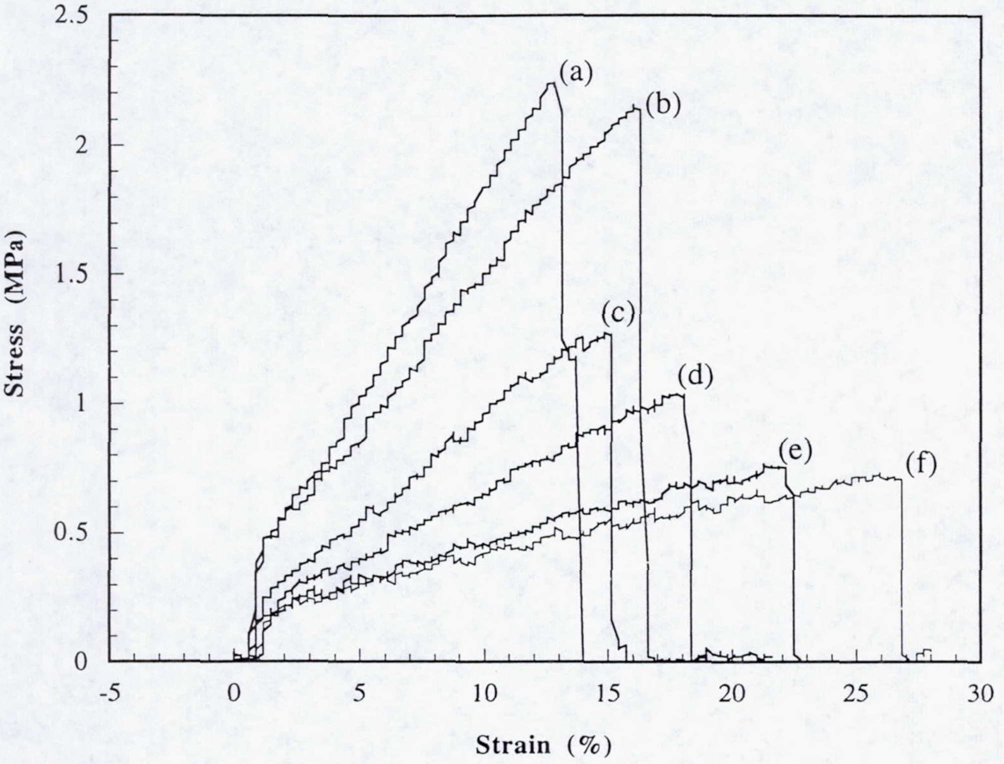
(c)

**Fig. 5.** Fracture surface of ten-layer laminated green tape specimens (600 μm/layer) 0.002g/cm$^2$ of PPG (cont'd). The interfacial patterns disappear after; (c) 36 h. at 80°C

Assume that Figure 5
will be reorganized
for publication



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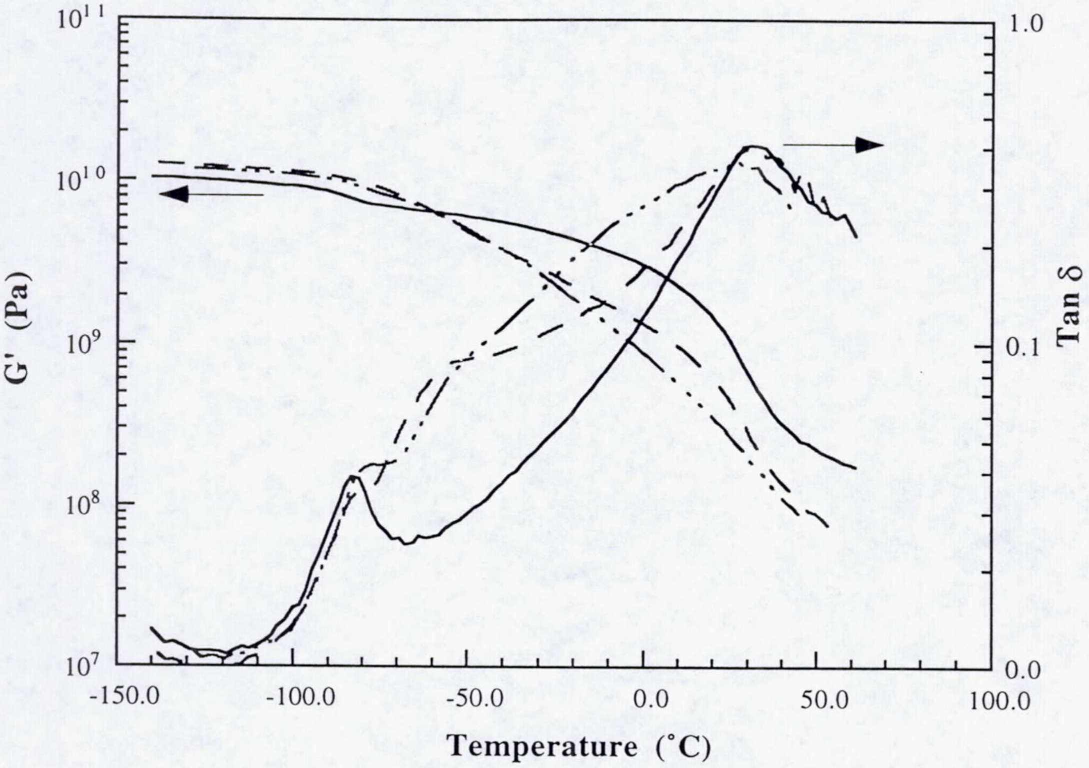

**Fig.7.** Dynamic mechanical spectra of as-receive green tape (——) vs adhesive-coated tape aged 6 hours at room temperature (----) and 2 days at room temperature (— · ·), respectively.

The peak at -60°C disappears and the PVB transition moves to lower temperature. Should be part of text.

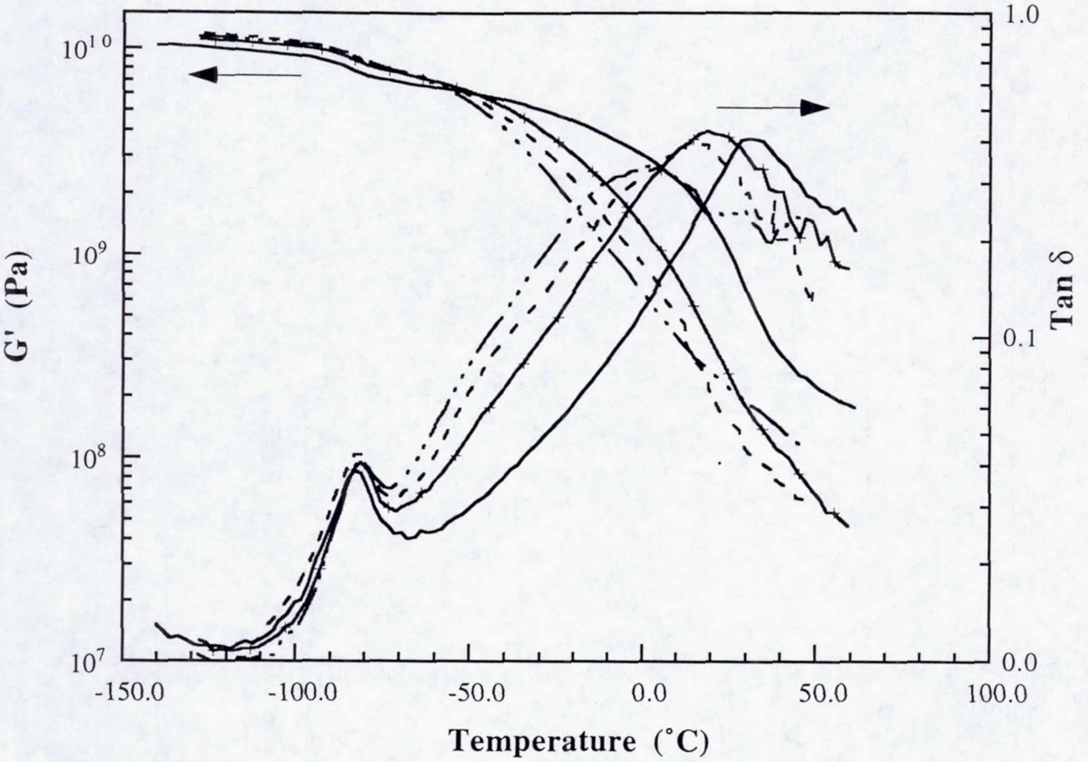

**Fig.8.** Dynamic mechanical spectra of as-received green tape (——),
PPG-coated tape at room temperature for 17 days (—+—), May want to change to more clearly different symbol.
PPG-coated tape heated at 80˚C for 5 hours (- - -), and
PPG-coated tape heat at 80˚C for 6 days (—····)
~~The PVB transitions move to lower temperature after~~ Should be in text.
~~long contact-time at room temperature or heating to 80˚C~~