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Glutaraldehyde-wheat protein-based adhesives for plywood

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Abstract: Wheat gluten protein hydrolysate was used as a biomass feedstock to prepare environmentally friendly protein-based adhesives, with hydrolyzed wheat protein as control. Glutaraldehyde was used to modify it to obtain a glutaraldehyde-wheat protein (GP) adhesive. Polyethylenimine (PEI) was also used as a crosslinking agent. Plywood has been prepared and tested, the performances of it used to measure the wheat gluten protein hydrolysate adhesive bonding performance. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were used to analyze the adhesive thermal properties and the microstructures of the cured adhesives by scanning electron microscopy (SEM). The results show that modification by glutaraldehyde can effectively improve the bonding performance of wheat protein adhesives, the plywood bonded strength having been improved by its addition. The effect of PEI as a crosslinking agent became evident. It can greatly improve the bonding properties of glutaraldehyde-modified wheat protein adhesives. TMA analysis indicates that the glutaraldehyde-modified GP adhesive has a higher storage modulus than the unmodified one. The modulus of the adhesive increased after adding the PEI cross-linking agent.

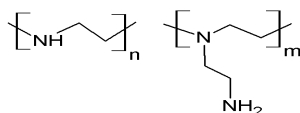
Key words: wheat protein; adhesive for wood; bonding performance; thermal performance

Introduction

Formaldehyde-based resins like urea-formaldehyde(UF) resin[1-4], melamine formaldehyde(MF) resin[5-6] and phenol-formaldehyde(PF) resin [7-9] are still the most widely used adhesives in wood industry. Due to the toxicity and carcinogenicity of formaldehyde, bio-sourced “natural” adhesives, such as tannin-based, lignin adhesive, carbohydrate adhesives, furanic resins, protein-based adhesive and unsaturated oil adhesives have attracted the ever-increasing interest of researchers [10], and have now become a hot topic in the field of wood adhesives.

Protein based adhesives, especially vegetable proteins, due to their low cost and ready availability, have been extensively studied. Among them, soy protein is the most studied of all. Its globular structure causes its reactive functional groups to be hidden within the structure, thus greatly limiting its application. It has been reported in the literature that by means of certain treatment

methods, more functional groups can be exposed and their reactivity improved [11-17]. However, due to the presence of a large number of hydrophilic groups in the protein such as amino groups, hydroxyl groups, carboxyl groups, etc., the water resistance of the protein adhesives is poor. To overcome this problem, considerable research work has been carried out. One approach has been to add a highly active substance that can react with these functional groups as a crosslinking agent [18-22].



Polyethylenimine(PEI) is a water-soluble polymer, which is very reactive. Moreover, it has been used to react with hydroxyl groups to crosslink cellulose for preparing paper with an improved wet strength. There are a large number of functional groups such as hydroxyl and carboxyl groups in the hydrolyzed protein adhesive, and they can combine with PEI with ease [23,24]. Thus, in the work presented here PEI was use as crosslinker for protein based adhesives to improve their bonding performances. To activate protein gelling and increase its reactivity, glutaraldehyde is used as a modifier to react with the hydrolyzed wheat protein. PEI is then used as crosslinker to obtain a good wheat protein adhesive.

2.1 Materials and methods

Glutaraldehyde(C₅H₈O₂, 50% water solution) used are of analytical grade (AR), obtained from Acros Organics, France; Soluble wheat protein obtained fromTereos-Syral(Mesnil-Saint-Nicaise, France; Hexamethylenetetramine obtained from Acros Organics(Geel, Belgium), Polyethylenimine(PEI) bought from Sigma Aldrich(St. Louis, USA).

2.2 Preparation of protein based adhesives

In order to expose more active groups of the protein, soluble wheat protein was degraded under alkaline conditions [21]. 60g water, 0.2g CaO and 0.4g NaOH were added to the flask, the agitator switched on and then 20g of wheat protein was added slowly. The mixture was heated to 90°C and kept at this temperature under stirring for 1h, then 7.5g of glutaraldehyde was added, and the reaction mixture kept for another 1h under stirring at the same temperature.

2.3 Preparation of three-layer plywood

3mm thick *Populus tremuloides* veneers were used to prepare three-plys laboratory plywood panels of 450mm×100mm×5mm dimensions with a gluemix spread of 300g/m²(dgl, double glue line). The panels were pressed for 6 minutes at 180°C and 1.5MPa pressure. The plywood so prepared was stored at ambient temperature for 2 days before it was tested.

Dry shear strength, 24h wet shear strength and 2h boiling water shear strength of the plywood panels were tested according to China National Standard GB/T 14074 (2006) [25], China National Standard GB/T17657 (1999) [26], and European Norm EN 636:2012 (2012) [27].

Thermomechanical Analysis (TMA)

The protein based adhesives were tested by thermomechanical analysis as per reference [28]. The samples were prepared by applying each adhesive between two beech wood plies, with dimensions of 21mm x 6mm x 1.1mm. The specimens were tested in non-isothermal mode between 25°C and 250°C at a heating rate of 10°C/minute with a Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship between force and deflection $E = [L^3/(4bh^3)][F/(\Delta f_{wood} - \Delta f_{adhesive})]$

allows the calculation of the Young's modulus E for each case tested.

FTIR

To confirm the presence of relevant structures, a Fourier Transform Infra-Red (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrophotometer. A blank sample tablet of potassium bromide, ACS reagent from ACROS Organics, was prepared for the reference spectrum. A similar tablet was prepared by mixing potassium bromide with 5% w/w of the sample powders to analyze. The spectrum was obtained in transmission measurement by combining 32 scans with a resolution of 2.0.

SEM

All the adhesives were cured at 103°C in the oven for a whole night, then cut to pieces of 5 mm×5 mm×3 mm dimension and covered with gold before scanning electron microscopy (SEM) analysis. The analysis was performed with a Hitachi Tabletop Microscope TM3000 (Hitachi HighTechnologies, Velizy, France) under vacuum, at a working distance of 6.4 mm and 15 kV acceleratingvoltage.

3 Results and discussion

3.1 Results of plywood performance

Plywood panels bonded with wheat protein based adhesives were prepared and 5% amount of hexamethylenetetramine based on solid protein adhesives was used as a hardener. Dry shear strength and wet shear strength after 24 hours cold water soaking and after 2 hours in boiling water of the plywood panels bonded both with the wheat protein (P) adhesive and with the glutaraldehyde-modified wheat protein (GP) adhesive are shown in the Fig 1. This shows that glutaraldehyde modification of the protein can greatly improve the bonding performance of the adhesive. The bond strength of plywood panels prepared with GP adhesive is significantly better than that of panels bonded with the unmodified wheat protein adhesive. Dry shear strength increases from 0.76MPa to 1.14MPa, an improvement of 50%. Equally, the wet shear strength shows a marked improvement also. A known drawback of vegetable protein adhesives is poor water resistance [10,17]. The wet shear strength after 24 hours cold water soaking of the plywood bonded with the GP adhesive is as high as 0.91MPa, this solving satisfactorily the pure wheat protein adhesive drawback (at 0.44MPa). Furthermore, compared to the unmodified wheat protein adhesive, the modified GP adhesive

presents good boiling water resistance, plywood shear strength after 2h in boiling water being 0.71MPa, which meet the China National Standard GB/T9846 requirements ($\geq 0.7\text{MPa}$). Many potentially reactive groups, such as amino groups, become accessible in wheat proteins degraded by complex alkali, groups which can react with glutaraldehyde to improve the bonding performance of the GP adhesive.

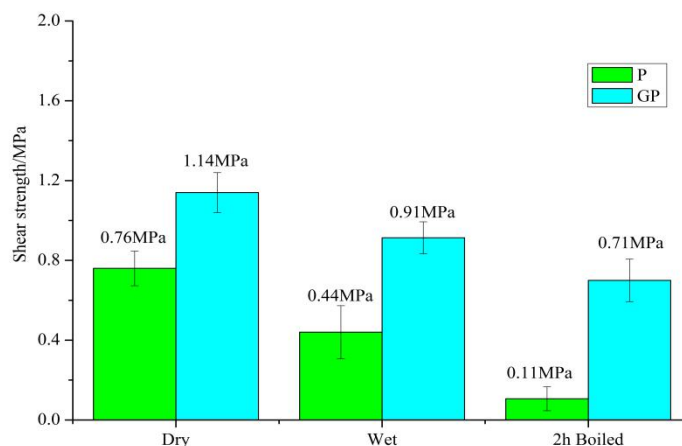


Fig.1 Performances of the plywood bonded with wheat protein adhesive and glutaraldehyde modified wheat protein adhesive

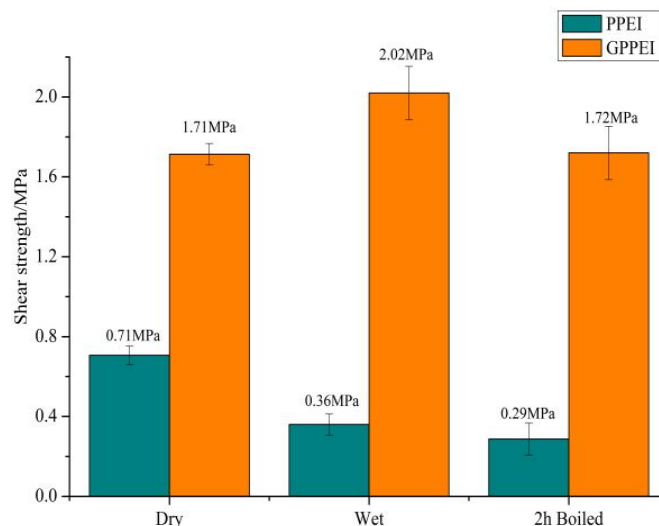


Fig.2 Performances of the plywood bonded with PPEI and GPPEI adhesives

To further improve the bonding properties of wheat protein adhesives, polyethyleneimine(PEI) has been added to the P and GP adhesives and used as a crosslinker. 3% by weight of PEI on liquid adhesive was thoroughly mixed with the P and GP adhesives before spreading on the plys. These mixed adhesives are called PPEI and GPPEI in this paper. Plywood panels were prepared and the dry shear strength, and both the wet strength after 24 hours cold water soaking and after 2 hours in boiling water were tested. The results are shown in Fig 2. Fig. 2 shows that the GPPEI adhesive by

PEI addition to the GP adhesive, presents a marked improvement in bonding performance compared to the GP adhesive alone. The wet shear strength after 24 hours cold water soaking and after 2 hours in boiling water are as high as 2.02MPa and 1.71MPa. Thus, they are higher than double that of the GP adhesive. There is no positive effect of the addition of PEI on the protein adhesive alone as the performance of the plywood bonded with the PPEI adhesive (Fig 2), the wet strength being lower. The reason may be that due to the higher reactivity of PEI, the viscosity of the adhesive increases sharply after its addition, hence that the ductility and permeability of the adhesive on the surface of the wood are lower.

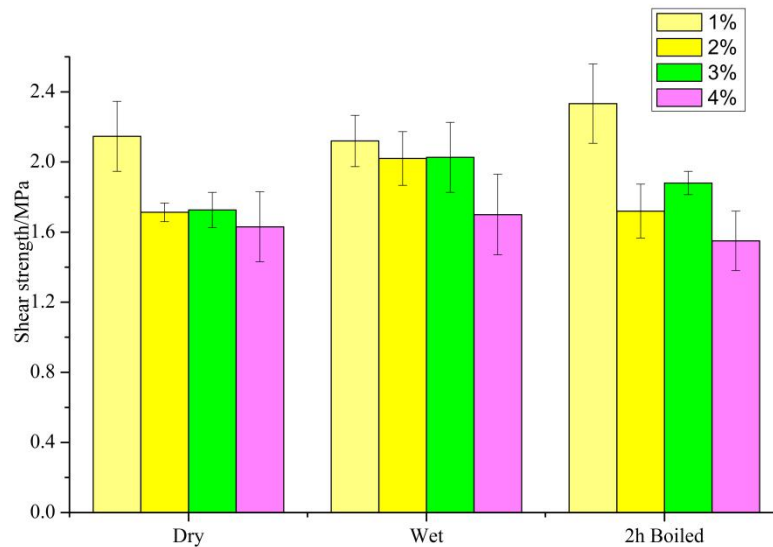


Fig.3 Performances of the plywood prepared by GPPEI adhesives with different addition amount of the PEI

The effect of the level of PEI addition on the performance of the GPPEI adhesives was investigated by adding 1%, 2%, 3%, and 4% of PEI on weight of the liquid GP adhesive. The results of the plywood bonded with them were tested and are showed in Fig 3. As can be seen from the results the bonding performance decreased with increasing additions of PEI, even if the decrease is not large. In reality, the viscosity of the adhesive progressively increases with increasing proportions of PEI being added. Such an excessively high viscosity is not conducive to an easy spreading of the adhesive, thus resulting in a reduced plywood performance.

Thermal performance analysis

The thermomechanical analysis (TMA) results of the unmodified wheat protein adhesive, the GP adhesive and of GP with 3% PEI are show in Fig. 4. The results shows that the storage modulus of the GP adhesive (3554MPa) is markedly higher than that of the unmodified wheat protein adhesive (2211MPa). This means that the GP adhesive gives a higher strength than the P adhesive [29,30]. This is also consistent with the plywood test results that shows that the GP adhesive has a better bonding performance than the wheat protein adhesive alone. After mixing with PEI the

maximum peak of the storage modulus for both the PPEI and GPPEI adhesives are improved, as shown by the curves in Fig 4. This proves that PEI can enhance the performance of protein adhesives [23,24]. In addition, all these adhesives reach the highest modulus at a similar temperatures (around 130°C), but the growth rate of the modulus curve of the GP adhesive is significantly higher than that of the unmodified protein adhesive. This indicates that GP is more reactive, and that protein adhesive can be activated by treatment with glutaraldehyde.

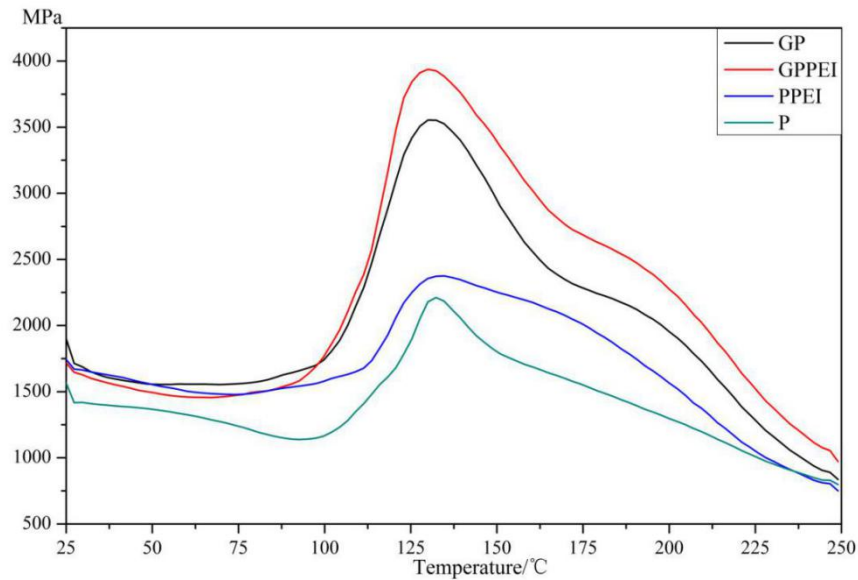


Fig.4 Thermomechanical analysis (TMA) spectra of wheat protein based adhesives

Differential Scanning calorimetry (DSC) was used to analysis the curing behavior of all protein adhesives, and shown in Fig 5. The results show that here is little difference in the curing peak temperature for all these adhesives. This means that the activation energy of curing is relatively close for them. It is also confirmed by the TMA analysis. The integrated area of the adhesive curing peak represents the extent of the exotherm during curing, thus denoting the degree of curing of the adhesive[31,32]. A larger peak area indicates a higher degree of cure. Therefore, as GPPEI is the adhesive with the largest peak (Fig.5), this means that it achieves the most complete cure during the hot press process as the curing temperature is 180 ° C. This is also one of the reasons for the excellent bonding performance of the GPPEI adhesive for plywood.

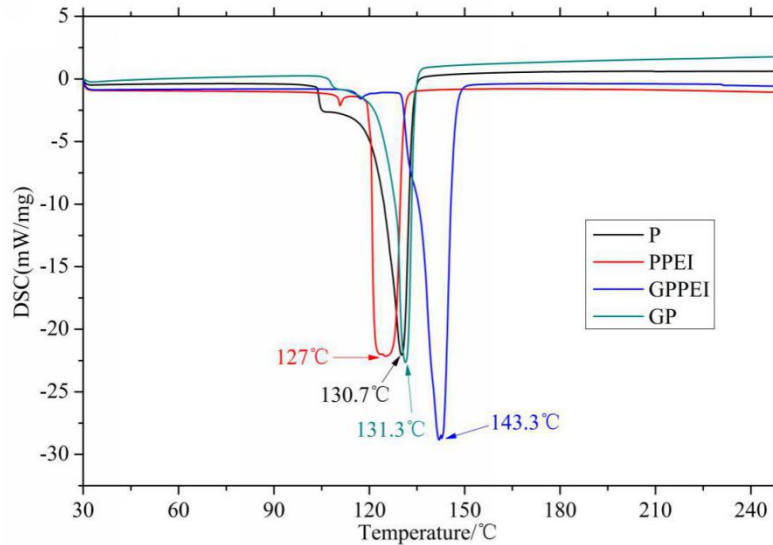


Fig.5 Differential Scanning calorimeter(DSC) spectra of wheat protein based adhesives

Analysis of FTIR

The FTIR spectra of the protein-based adhesives are shown in Fig.6. The wide peak nearby the 3300 cm^{-1} region in the curves of P and GP was characteristic of the O–H and N–H groups, which were then able to react with polyethyleneimine and formed C–O and C–N bonds. A peak at about 2930 cm^{-1} was attributed to the $-\text{CH}_2$ group. The main absorption peaks at 1655 , 1560 , and 1242 cm^{-1} are characteristic of the amide I (C=O stretching), amide II (N–H bending or C–N stretching), and amide III (C–N and N–H stretching)[33,34]. By comparing the curves of the adhesives P and GP after modification, their peaks shapes appear to be similar, which means that the glutaraldehyde modified wheat protein adhesive does not form new functional groups.

The absorption peak at 1112 cm^{-1} belongs to the C–O stretching vibration from $-\text{COO}-$ group, which weakens or even disappears in the PPEI and GPPEI spectra. This proves that reactions do occur between the PEI and protein adhesive or glutaraldehyde protein adhesive. Highly reactive amine groups can react with the C=O group to form a hydroxyl group. The absorption band of the disulfide bond or primary alcohol group were observed at 1055 cm^{-1} , which means that in the PPEI and GPPEI spectra more hydroxyl groups are produced compared to the P and GP adhesives. This confirms the reactions between the PEI crosslinker and the P or GP adhesive also, and that the hydroxyl group that forms is also the reactant for the subsequent curing reaction.

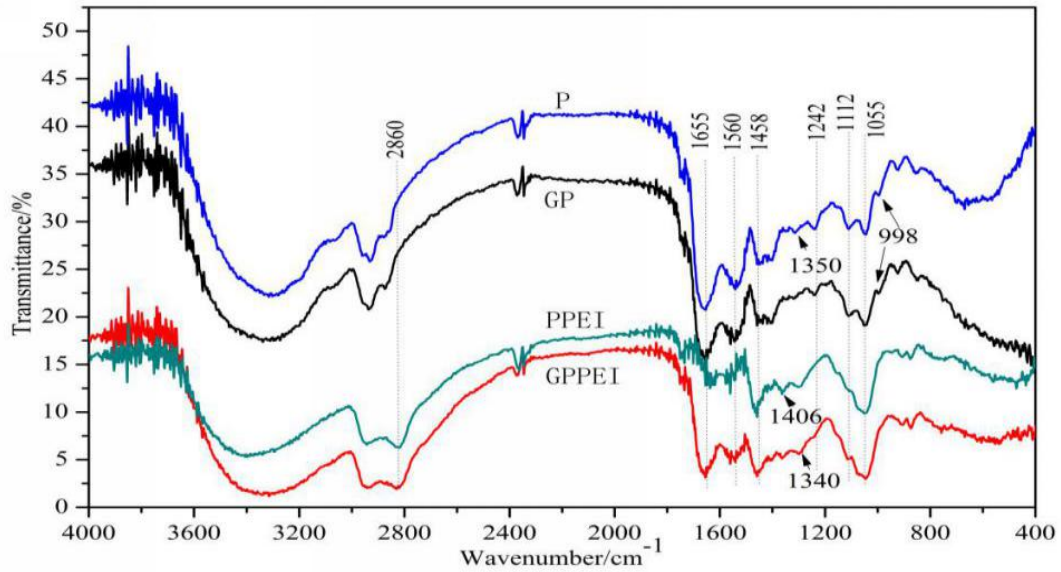


Fig.6 FTIR spectra of the wheat protein based adhesives

SEM

Scanning electron microscopy (SEM) of all the protein-based adhesives were tested by scanning electron microscopy (SEM) and the results as shown in Fig 7. Under the electron microscope, the surface morphology of the cured adhesive was observed at a magnification of 250X. Many large and deep cracks can be found in the cured wheat protein only adhesive (Fig.7, a). However, they become smaller, shallower and shorter in the glutaraldehyde modified GP adhesive(Fig.7,b).. This means that the GP adhesive has better toughness or is more elastic and better distributed the stresses than the wheat protein only adhesive. This is also one reason why the GP has a better bonding performance than the P adhesive. With the addition of PEI as a crosslinking agent, cracks(Fig.7,c) on the surface of the cured unmodified protein based PPEI adhesive significantly reduced compared with P adhesive(in the Fig.7,a), but there were still long cracks. However, it is shown in (Fig.7,d) that there are no cracks in the cured glutaraldehyde modified protein adhesive mixed with polyethylenimine(GPPEI), and it is perfect. This indicates that polyethylenimine can effectively improve the toughness or elastic of wheat protein-based adhesives, thereby improve bonding properties of its. This proves also the results of plywood performance in Figure 2.

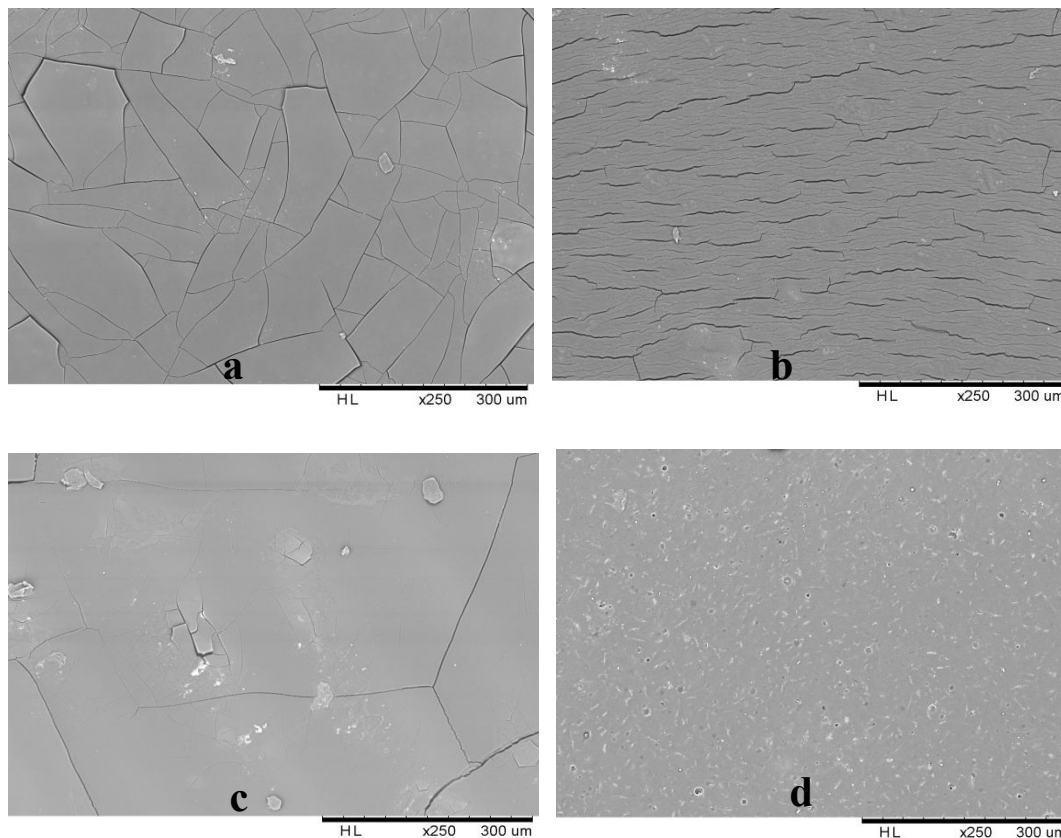


Fig.7 pictures of SEM results of the wheat protein based adhesives(a: wheat protein adhesive; b:Glutaraldehyde modified protein adhesive(GP); c: wheat protein mixed with PEI adhesive(PPEI); d: GP adhesive mixed with PEI(GPPEI))

4 Conclusion

Glutaraldehyde has a good modification effect on wheat protein adhesives. Compared with the unmodified protein adhesive (P), the dry shear strength of glutaraldehyde modified protein(GP) adhesives increased by 50%, in 24h cold water strength improving by more than 100% to arrive 0.91MPa. The effect of PEI as a cross-linking agent is obvious, which can greatly improve the bonding properties of GP adhesive. This is due to the modification of glutaraldehyde to make the reactive groups like -COOH and -OH increased, and these functional groups to react with the amine group in PEI, thus to improve bonding performance. TMA analysis showed that the glutaraldehyde-modified protein gel had a higher storage modulus than the unmodified one. The modulus of the adhesive increased after adding the PEI cross-linking agent, which confirmed the shear strength of the plywood test results. SEM can observe that the modified GP adhesive seems has better toughness than unmodified, however, this is not enough. When PEI is added, the toughness of the adhesive is better improved, and there is no crack on the surface of the cured adhesive GPPEI.

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