

预处理玉米秸秆提高糙皮侧耳菌丝基缓冲材料性能的研究

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摘要: 菌丝基缓冲材料因其可再生、环境友好等特点, 有替代石油基缓冲包装材料的潜力。但是, 菌丝基缓冲材料较差的缓冲性能制约了其商业化。为了提高菌丝基材料的性能, 本研究提出了一种新的菌丝基材料制备工艺, 首次对糙皮侧耳菌丝生长所需的主要培养基(玉米秸秆)进行了微波和碱预处理, 改善了玉米秸秆的物理结构和化学组成, 促进了菌丝的生长, 从而提高了菌丝基材料的性能。微波预处理在玉米秸秆表面产生的孔比碱预处理更多, 且孔径更接近于菌丝的直径, 使得菌丝与玉米秸秆之间的结合力更强。因此, 微波预处理制备的材料性能更好。经过微波预处理后制备的菌丝基材料(MTM)回弹率约为 50%, 是未预处理制备的菌丝基材料(UTM)的 1.3 倍, 是碱预处理后制备的菌丝基材料(ATM)的 1.1 倍。MTM 的压缩强度约为 600 kPa, 分别比 UTM 和 ATM 提高了约 40%和 20%。本研究有效提升了菌丝基材料的缓冲性能, 为其替代聚苯乙烯作为缓冲材料提供了可能。

关键词: 糙皮侧耳; 菌丝; 菌丝基材料; 培养基预处理; 缓冲

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Improving the performance of *Pleurotus ostreatus* mycelium-based cushioning materials by corn straw pretreatment

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Abstract: Mycelium-based cushioning materials are one of the most potential substitutes to petroleum-based cushioning packaging materials due to their renewable and eco-friendly characteristics. However, poor cushioning properties of these materials restrict their commercialization. To improve the performance of mycelium-based materials, a novel technology for the preparation of mycelium-based materials was proposed. The main substrate (maize straw) was pretreated by microwave and alkali, so that the physical structure and chemical composition of the *Pleurotus ostreatus* mycelium substrate were improved. This promotes the growth of mycelium and thereby improves the performance of the mycelium-based materials. Compared with alkali pretreatment, microwave pretreatment can produce more holes on the surface of the corn straw particles and the diameter of the holes is closer to that of the mycelia. Thus, the bond between the mycelia and the corn straw becomes stronger, therefore the performance of the material is better. The resilience of the microwave-pretreated mycelium-based material (MTM) was approximately 50%, 1.3 times that of the untreated material (UTM) and 1.1 times that of the alkali-pretreated material (ATM). Compressive strength of MTM is about 600 kPa, about 40% and 20% higher than that of UTM and ATM, respectively. This method has improved the cushioning properties of the mycelium-based material, offering the possibility of replacing polystyrene as a cushioning material.

Keywords: *Pleurotus ostreatus*; mycelium; mycelium-based materials; substrate pretreatment; cushion

近年来,随着生物可降解材料的需求日益增长,菌丝基材料因无污染、可再生等特点而具有代替石油基材料的潜力(Alemu *et al.* 2022)。在目前研发的低密度菌丝基材料中,平均压缩强度约为 300 kPa (Tacer-Caba *et al.* 2020)。力学性能差是制约菌丝基材料商业化应用的重要因素。而菌丝的生长状况是决定菌丝基材料力学性能的关键因素。

温度(Nashiruddin *et al.* 2021)、光照强度(Appels *et al.* 2018)、培养时间(Soh *et al.* 2020)、接种量(Rocha *et al.* 2020; Nashiruddin *et al.*

2021)、含水率(Nashiruddin *et al.* 2021),以及干燥温度(Rocha *et al.* 2020)等对菌丝的生长都有很大的影响(戴玉成 2023)。因此,这些因素对材料性能的影响也十分显著。适宜的温度、培养时间有利于提高材料性能。低接种量及高含水率会使菌丝基材料的抗压强度显著降低(Nashiruddin *et al.* 2021)。适宜的光照强度和二氧化碳浓度有利于提高菌丝体的密度,进而提高材料的力学性能(Appels *et al.* 2018)。此外,制备菌丝基材料所用的菌种和培养基质对材料性能的影响也很大。

目前,制备菌丝基材料最常用的菌种有糙皮侧耳、灵芝和云芝等(戴玉成等 2010; Attias *et al.* 2020)。以灵芝为菌种制备的菌丝基材料的性能通常优于其他真菌(Haneef *et al.* 2017; Silverman *et al.* 2020)。Bruscato *et al.* (2019)发现以灵芝为菌种制备的菌丝基材料抗压强度约为糙皮侧耳的 3 倍。培养基质对菌丝基材料性能的影响更为显著。以木屑为主要基质制备的菌丝基材料的性能通常比以秸秆或竹子制备的材料性能好(Joshi *et al.* 2020; Sun *et al.* 2020)。以菜籽油饼为基质制备的菌丝基材料压缩强度是以燕麦壳为基质制备的材料的 20 倍(Tacer-Caba *et al.* 2020)。综上所述,用更适宜菌丝生长的培养基制备的菌丝基材料性能更好。而真菌菌丝的生长除了与培养基有关,还与菌丝分泌的酶有关。真菌菌丝会分泌漆酶(司静等 2011a; 吴怡等 2019)、纤维素酶(马鸿飞等 2018)和木聚糖酶(曹永佳等 2021),将植物纤维或有机废料中的木质纤维素分解为营养物质并利用其生长。并且,真菌菌丝在生长时黏附在未被降解的木质纤维素材料上,将这些木质纤维素颗粒包裹起来,形成具有缓冲性能的多孔材料。因此,施加能够促进真菌菌丝分泌漆酶的物质能有效促进真菌菌丝的生长,从而提高菌丝基材料的性能。研究表明,适量添加阔叶树(曹永佳等 2021)、棉籽壳(韩美玲等 2017)、微量金属离子(司静等 2011b, 2011c)等有利于提高菌丝分泌漆酶活性的物质都能显著提升菌丝基材料的力学性能(Joshi *et al.* 2020; Zimele *et al.* 2020)。植物纤维的粒度也会影响菌丝基材料的性能(Soh *et al.* 2020)。一般纤维粒度 ≤ 0.5 mm 时,材料性能较好。在基质中添加支撑材料(Ziegler *et al.* 2016)和对材料进行热压后处理(Appels *et al.* 2019; Khoo *et al.* 2020)也会提高材料的力学性能。另外,研究表明玉米秸秆中纤维素含量较高可能提高材料的性能(Jonoobi *et al.* 2010; Lu *et al.* 2013)。

为了验证这一猜测,本研究用微波预处理和碱预处理 2 种方法对玉米秸秆进行预处理,以提高秸秆中的纤维素含量,并用预处理后的秸秆制备了糙皮侧耳-玉米秸秆菌丝基材料。另外,本研究对比了 2 种预处理方法对菌丝基材料性能的影响,并借助 FTIR、SEM 和 XRD 等表征手段揭示了预处理提高材料性能的机制。

1 材料与方法

1.1 供试材料

糙皮侧耳 *Pleurotus ostreatus*, 编号 1103, 购自吉林农业大学菌物研究所。玉米秸秆收集于吉林农业大学试验田。风干后碾磨,筛分得到 10–200 目的秸秆粉,室温保存。麦麸、玉米粉、土豆均为市售购得。本试验所用的试剂均购自国药集团。

1.2 方法

微波预处理玉米秸秆:取 40 g 秸秆粉,加入 400 mL 去离子水并搅拌均匀,用薄膜封口并扎微孔,静置 10 min 后,微波炉高温处理 3–5 min。

碱试剂预处理玉米秸秆:取 50 g 秸秆粉,加入 15% 的 CaO 后,加入 100 mL 蒸馏水,静置 1 h,使玉米秸秆初步热解。而后加入 2% 的 NaOH 和 3% H_2O_2 制得混合溶液,搅拌均匀,置于 50 °C 反应 2 h。

糙皮侧耳菌丝基-改性玉米秸秆多孔缓冲材料的制备参照 Zhang *et al.* (2019)的方法。将糙皮侧耳 1103 菌丝球过滤,从灭菌后的菌丝基材料培养基中称取 20 g,接种 15% (质量分数)的糙皮侧耳菌丝球后搅拌均匀,装入柱形中空玻璃模具(内径 50 mm)中,下层用可拆卸的玻璃圆片封口,上层用封口膜封口。将菌丝基材料置于培养箱中暗培养,每隔 7 d 取出压至 5 cm。菌丝基材料置于恒温培养箱中培养 20 d 后取出脱模,脱膜后的材料置于 60 °C 烘箱中干燥 24 h 后,得到干燥的菌丝基材料,保存备用。

1.3 性能测试

1.3.1 材料成分及结构检测

按照标准实验室方法分析玉米秸秆中的纤维素和木质素的含量(Sluis *et al.* 2008; Wu *et al.* 2023)。采用 FTIR 分析预处理前后玉米秸秆成分的变化(Lee *et al.* 2015)。用 X 射线衍射仪(XRD-7000, Shimadzu)测定玉米秸秆的结晶度(Sorn *et al.* 2019)。玉米秸秆的纤维素结晶度通过 MDI Jade 6 软件分析计算。采用扫描电镜(XL-30 ESEM FEG)分析观察玉米秸秆和菌丝基材料的微观结构(Su *et al.* 2018a)。玉米秸秆的比表面积通过 Brunauer-Emmet-Teller 法测定(Su *et al.* 2018b)。

1.3.2 几丁质含量

按照 Manzi *et al.* (2001)描述的方法分析菌丝基材料中几丁质含量变化。

1.3.3 菌丝基材料的性能

压缩强度和能量吸收率根据 GB/T 8168—2008《包装用缓冲材料静态压缩试验方法》中的方法 A 测试并计算；回弹率、吸水率和厚度膨胀率的测定参照 Zhang *et al.* (2016)的方法。

1.3.4 热稳定性

菌丝基材料的热稳定性通过热重分析仪(TGA/DSC3+, Mettler)进行表征。N₂ 氛围(99.99%)，流量为 100 mL/min，以 10 °C/min 的速率从 20 °C 加热至 800 °C。

2 结果与分析

2.1 预处理对菌丝基材料缓冲性能的影响

预处理显著提高了菌丝基材料的缓冲性能(图 1)。微波预处理后制备的菌丝基材料(MTM)和碱预处理后制备的菌丝基材料(ATM)的回弹率分别比未处理制备的菌丝基材料(UTM)提升了约 27%和 14%。MTM 的回弹率达 50.3%，略低于发泡聚苯乙烯(EPS)。MTM 和 ATM 中几丁质含量显著提高(图 2)，说明材料中菌丝的生物量更高(Haneef *et al.* 2017)。SEM 电镜图中也

可以明显地看到，MTM 和 ATM 中菌丝更致密(图 3)，生物量更高，这有利于菌丝基材料缓冲性能的提高。未处理的玉米秸秆(UT)表面存在结构致密的蜡质层，且其表面光滑，无孔洞(图 3A)。这使得菌丝难以在其表面附着生长，故 UTM 表面菌丝的生物量也较低(图 3D)。预处理破坏了玉米秸秆表面的蜡质层，使得玉米秸秆中的木质纤维素更容易被菌丝利用。预处理还使玉米秸秆表面产生大量微孔。这有利于更多的菌丝附着在其表面或穿过孔洞生长，从而形成更致密的菌丝网络(图 3E, 3F)。此外，预处理使玉米秸

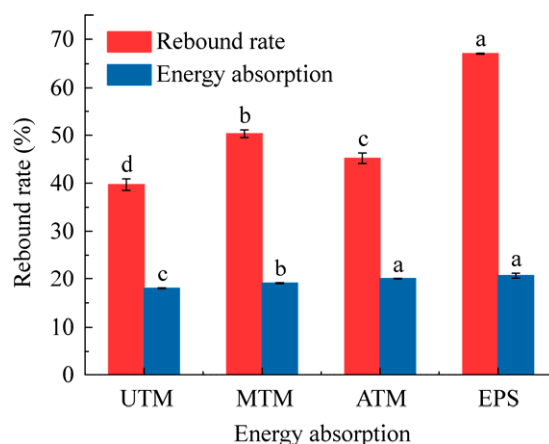


图 1 预处理对菌丝基材料回弹率和能量吸收率的影响(压缩至 50%时) UTM: 未经处理的玉米秸秆制备的菌丝基材料; MTM: 微波预处理玉米秸秆后的制备菌丝基材料; ATM: 碱预处理后的玉米秸秆制备的菌丝基材料; EPS: 发泡聚苯乙烯. 不同小写字母表示通过 ANOVA 方差检验的组件之间有显著差异($P < 0.05$). 下同

Fig. 1 Effects of pretreatment on the rebound rate and energy absorption rate of mycelium-based materials (when compressed to 50%). UTM refers to the mycelium-based materials prepared from untreated corn stalk; MTM refers to the mycelium-based materials prepared from microwave pretreatment of corn stalk; ATM refers to the mycelium-based materials prepared from alkali pretreatment of corn stalk; EPS refers to expanded polystyrene. Different lowercase letters indicate significant differences between components that pass the ANOVA variance test ($P < 0.05$). The same below.

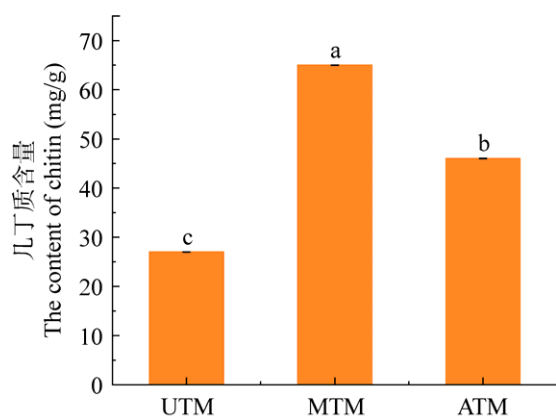


图2 预处理对菌丝基材料中几丁质含量的影响
Fig. 2 Effects of pretreatment on chitin content in mycelium-based materials.

秆的比表面积显著提高(表1),这有利于提高菌丝分泌的木质素降解酶的酶解效率,从而提高菌丝对玉米秸秆的利用率,进而提高菌丝基材料的性能。微波预处理后秸秆表面的孔洞比碱处理的小(图3B),且孔洞直径更接近于菌丝的直径,使得菌丝与秸秆颗粒的结合更紧密(图3E),而碱预处理后的玉米秸秆孔道过大(图3C),削弱了菌丝和秸秆之间的附着力(Yan *et al.* 2014; Xie

et al. 2018)。不仅如此,微波处理后玉米秸秆的比表面积约为碱处理后的3.5倍(表1),此时的玉米秸秆更适宜菌丝的生长。因此,MTM的缓冲性能也更好。

2.2 预处理对菌丝基材料机械性能的影响

微波和碱预处理都显著提升了秸秆中纤维素的含量(表1)。FTIR的结果显示预处理后的玉米秸秆在3 400–2 900 cm^{-1} 处的吸收峰增强(图4),这与纤维素的-OH伸缩振动有关,说明预处理提高了纤维素含量(Zhang *et al.* 2016; Dong *et al.* 2020; Xie *et al.* 2020)。此外,秸秆中纤维素结晶度的提高(图5),也说明预处理后纤维素含量提高(Dong *et al.* 2020)。因此,我们推测,预处理后制备的菌丝基材料机械强度应该会提高。事实的确如此,2种预处理都能使菌丝基材料的压缩性能显著提高(图6)。虽然微波预处理和碱预处理后纤维素的含量接近,但是MTM的压缩强度比ATM高10%,约是EPS缓冲材料的2.3倍。这是因为微波预处理后秸秆的比表面积比碱预处理的大,孔洞数量更多且孔径更

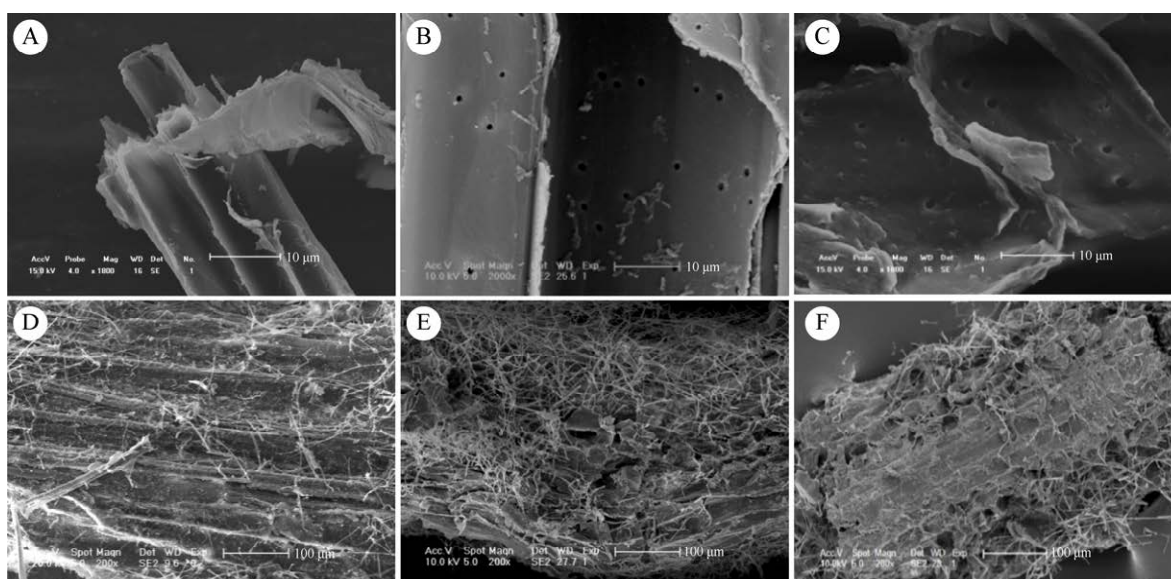


图3 SEM图 A, D: 未经处理的玉米秸秆及菌丝基材料. B, E: 微波处理的玉米秸秆及菌丝基材料. C, F: 碱处理玉米秸秆及菌丝基材料

Fig. 3 SEM images. A, D: Untreated corn straw and mycelium-based materials. B, E: Microwave-treated corn straw and mycelium-based materials. C, F: Alkali-treated corn straw and mycelium-based materials.

表 1 预处理后玉米秸秆的组分及结构特性

Table 1 Components and structural characteristics of pretreated corn straw

组分及结构特性	UT	MT	AT
Components and structural characteristics			
纤维素含量	34.17±0.3b	37.21±0.6a	37.95±0.4a
Cellulose content (%)			
木质素含量	14.45±0.17a	11.63±0.14b	10.58±0.08c
Lignin content (%)			
比表面积	0.035 6	1.394 5	0.404 5
Specific surface area (m ² /g)			
纤维素结晶度	33.72	49.20	53.61
Crystallinity of cellulose (CrI %)			

UT 为未经处理的玉米秸秆；MT 为微波预处理的玉米秸秆；AT 是玉米秸秆的碱试剂预处理. 同一行的不同小写字母表示通过 ANOVA 方差检验的组件之间有显著差异($P<0.05$)

UT refers to untreated corn straw; MT refers to microwave-pretreated corn straw; AT refers to the alkali reagent pretreatment of corn straw. Different lowercase letters on the same line indicate significant differences between components that pass the ANOVA variance test ($P<0.05$).

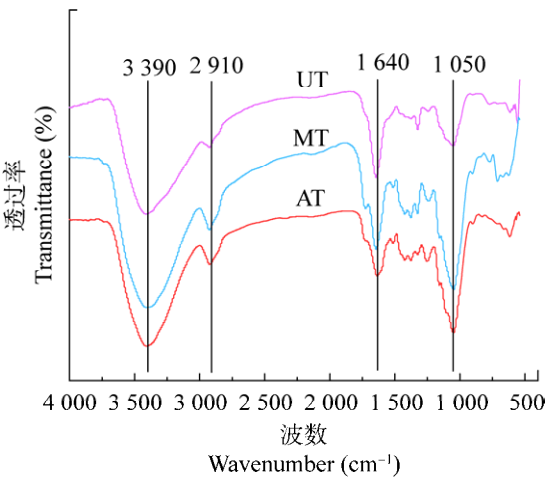


图 4 微波、碱预处理和未处理玉米秸秆的 FTIR 图
Fig. 4 FTIR spectra of microwave- and alkali-pretreated as well as untreated corn straws.

适宜, 使得 MTM 中菌丝的生物量远高于 ATM (图 2), 并且菌丝与秸秆间结合得更致密(图 3E)。菌丝生物量的提高有利于提升菌丝基材料的机械强度(Yang *et al.* 2017; Bruscato *et al.* 2019)。因此, MTM 的机械性能比 ATM 更好。

2.3 预处理对菌丝基材料耐水性能的影响

预处理会去除部分木质素并使一些亲水基团暴露, 可能会使得菌丝基材料的吸水性提高。然而, 预处理后菌丝的生物量也会提高, 菌丝具有较好的疏水性(Lopez-Ribot *et al.* 1991)。菌丝

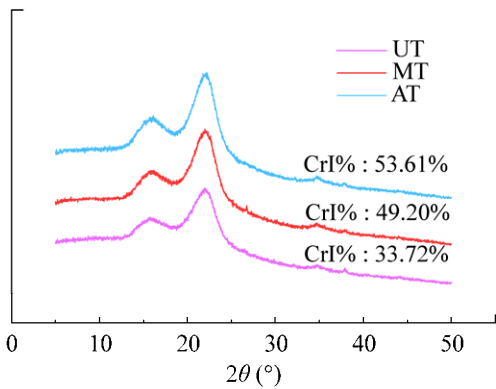


图 5 微波、碱预处理和未处理玉米秸秆的 X 射线衍射分析
Fig. 5 X-ray diffraction analysis of microwave, alkali pretreatment and untreated corn straw.

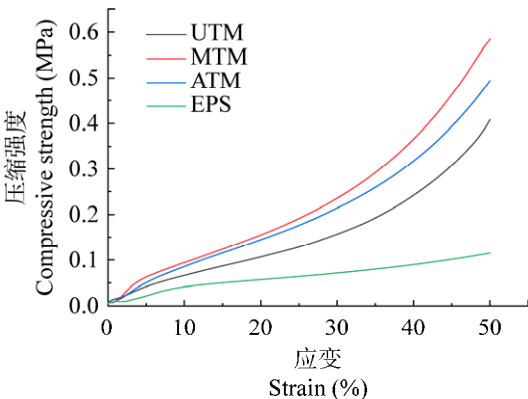


图 6 预处理对菌丝基材料压缩强度的影响
Fig. 6 Effects of pretreatment on compression strength of mycelium-based materials.

将秸秆颗粒紧紧地包裹,并形成更密集的菌丝网络(图 3E, 3F),这有利于提高菌丝基材料的耐水性能。预处理显著提高了菌丝基材料的耐水性能,MTM 和 ATM 的吸水率(图 7A)和 24 h 厚度膨胀率(图 7B)显著降低。MTM 的 24 h 吸水率约为 188%,较 UTM 降低了约 15%,较 ATM 低了约 8%。MTM 的耐水性能更好。一方面,这是由于 MTM 中菌丝生物量更高(图 2),使得材料的疏水性更好。另一方面,MTM 中菌丝把秸秆包裹住,形成了更致密的菌丝网络(图 3E),使得菌丝基材料的吸水速率及吸水量均显著降低(图 7A),厚度膨胀率也随之降低(图 7B)。因此,MTM 的耐水性能更好。

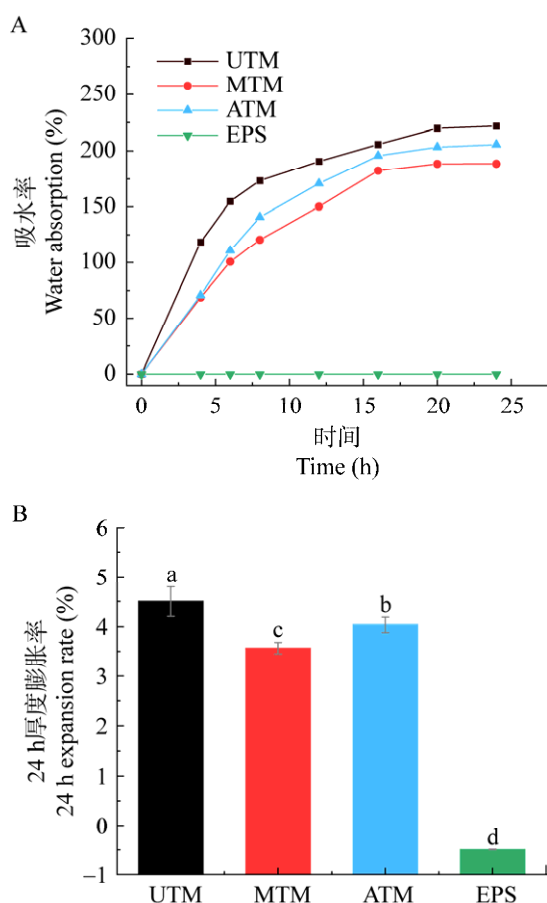


图 7 预处理对菌丝基材料吸水率(A)和厚度膨胀率(B)的影响

Fig. 7 Effects of pretreatment on water absorption rate (A) and thickness expansion rate (B) of mycelium-based materials.

2.4 预处理对菌丝基材料热稳定性的影响

预处理后制备的菌丝基材料热稳定性降低,但 MTM 和 ATM 的热稳定性没有显著性差异。TGA 曲线显示了菌丝基材料的 3 个降解阶段(图 8)。第一个阶段(100–200 °C)为菌丝基材料中水分蒸发而产生的初始失重阶段(Chougan *et al.* 2020)。第三阶段(350–800 °C)为材料中非纤维素成分的分解(Bruscato *et al.* 2019)。在这 2 个阶段菌丝基材料的失重速率和质量损失均无显著差异。第二个阶段(250–350 °C)为纤维素和半纤维素的热解,MTM 和 ATM 的质量损失率比 UTM 更大。预处理对菌丝基材料的热解速率无显著差异,但预处理能显著提高菌丝基材料的质量损失率。这是因为预处理后秸秆中的纤维素和半纤维素含量比未处理的秸秆更高(表 1)。可见,预处理后菌丝基材料的热稳定性降低。这也说明了预处理后菌丝基材料的可降解性提升。

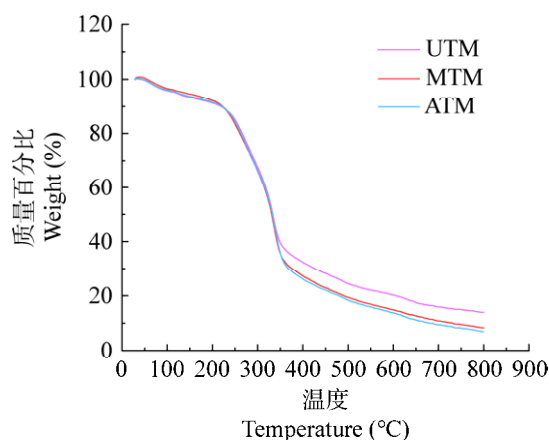


图 8 预处理对菌丝基材料热稳定性的影响

Fig. 8 Effects of pretreatment on thermal stability of mycelium-based materials.

3 讨论

菌丝基材料是一种有替代聚苯乙烯泡沫材料潜力的绿色可降解材料(Alemu *et al.* 2022)。然而,菌丝基材料的力学性能和耐水性能相较于 EPS 还有较大的差距(Jose *et al.* 2021),这制约了菌丝基材料的商业化。菌丝基材料的性能主要受

材料中菌丝的生物量(Attias *et al.* 2021)、形态(Appels *et al.* 2018)、机械强度(Cesar *et al.* 2021)等因素的影响。研究表明,提高培养基中纤维素的含量能够促进菌丝的生长(Haneef *et al.* 2017),而对培养基中的木质纤维素进行预处理能够有效提高培养基中的纤维素含量(Ponnusamy *et al.* 2019; Wu *et al.* 2023)。本研究以玉米秸秆作为菌丝基材料的主要培养基质。那么,对玉米秸秆进行预处理是否能提升菌丝基材料的性能?为了解决这一问题,本研究对玉米秸秆进行了微波和碱预处理,并研究了预处理对菌丝基材料性能的影响。

同预期结果一致,2种预处理方法都有效提高了玉米秸秆中的纤维素含量,进而提高了菌丝基材料的性能。与未处理的菌丝基材料(UMT)相比,预处理显著提高了菌丝基材料的缓冲性能。其中,微波预处理后制备的菌丝基材料(MTM)性能更好,回弹率达50.3%,虽略差于EPS缓冲材料,但MTM的回弹率与高弹性聚酯(HRPET)纤维和低熔点聚酯(LMPET)纤维组成的高弹力无纺布制备的高分子薄膜材料的回弹率接近(Jhang *et al.* 2021)。2种预处理方式制备的材料能量吸收效率与EPS差异性不大。可见,MTM更适宜作为缓冲材料。预处理可以提高菌丝基材料的缓冲性能是因为预处理提高了秸秆的比表面积,使得菌丝分泌的漆酶、半纤维素酶和纤维素酶等木质纤维素降解酶更容易与玉米秸秆接触,从而促进了菌丝的生长。预处理后制备的菌丝基材料中几丁质含量显著提高,说明材料中菌丝的生物量更高(Haneef *et al.* 2017)。SEM电镜图中也可以明显地看到,MTM和ATM中菌丝更致密,生物量更高。可见,预处理使得菌丝基材料中菌丝的生物量提高,进而提高了材料的性能。另外,MTM的缓冲性能比ATM更好。这是由2方面原因导致的。首先,微波处理后玉米秸秆的比表面积较碱处理后的大,这使得

菌丝能更好的生长,MTM中菌丝的生物量更高。其次,微波预处理后秸秆表面的孔洞比碱处理的小,且孔洞直径更接近于菌丝的直径,使得菌丝与秸秆颗粒的结合更紧密,而碱预处理后的玉米秸秆孔道过大,削弱了菌丝和秸秆之间的附着力(Yan *et al.* 2014; Xie *et al.* 2018)。因此,MTM的缓冲性能比ATM的好。

预处理还显著提高了菌丝基材料的压缩性能和耐水性能。这是由于MTM和ATM中菌丝生物量比UTM更大。微波预处理后秸秆的比表面积较碱预处理的大,孔洞也更适宜糙皮侧耳菌丝的生长。MTM中菌丝的生物量远高于ATM,并且菌丝与秸秆间结合得更致密。菌丝生物量的提高提升了菌丝基材料的机械强度(Yang *et al.* 2017; Bruscato *et al.* 2019)和疏水性(Lopez-Ribot *et al.* 1991)。因此,MTM的机械性能比ATM更好。MTM的压缩强度约为580 kPa,约是Santhosh *et al.* (2018)制备的菌丝基材料的1.7倍;MTM的24 h吸水率与木塑复合材料的吸水率相近(Pao & Yeng 2019),约为Zimele *et al.* (2020)制备的剑麻菌丝基复合材料的30%。另外,MTM的厚度膨胀率仅约为3.5%,与天然纤维等天然聚合物混合制备的可生物降解泡沫托盘(Kaisangsri *et al.* 2012)接近,较Zimele *et al.* (2020)制备的木屑菌丝基复合材料低了约13%。

综上所述,MTM虽然较EPS在耐水性能和缓冲性能方面仍存在一定的差距,但是,优于常见的生物基发泡材料。并且,MTM的可降解性更强,是一种具有商业潜力的绿色可降解材料。MTM未来可能被用于建材、隔音及隔热等更多领域。

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