防油纸在食品包装中的研究进展

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摘要：目的 概述防油包装纸在食品包装领域的研究现状，为进一步拓宽防油纸的研究方法和适用领域提供参考。**方法** 对国内外研究成果及现状进行总结，重点介绍机内加工防油纸和后加工防油纸，分析实现纸张防油的方法和机理。**结果** 防油包装纸常应用于各种含脂物品的包装，因此会涉及食品、工业、医疗等领域，其研究方式、实现方法和实验成果尤为重要。虽然防油包装纸种类较多，生物质防油纸的研究也层出不穷，但食品安全、回收降解和成本问题一直无法同时兼顾。**结论** 防油包装纸和纸板在食品包装领域受到广泛关注，尤其生物质防油剂在该领域的研究潜力较大。

关键词：防油纸；阻隔性；生物质防油剂；粗糙结构
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Research Progress of Oil-proof Packaging Paper Based on Plant Fiber

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ABSTRACT: The work aims to summarize the research status of oil-proof packaging paper in food packaging, and to provide a reference for further expanding the research methods and applicable fields of oil-proof packaging paper. By summarizing the domestic and foreign research results and current situation, the paper focused on the in-machine oil-proof paper and post-process oil-proof paper, and analyzed the method and mechanism of achieving paper oil-proofing. Oil-proof packaging paper was often used in the packaging of various fat-containing articles, so it was often involved in the fields such as food, industry, and medical treatment. Its research methods, implementation methods, and experimental results were particularly important. Although there were many types of oil-proof packaging paper, and the research on biomass oil-proof paper was endless. Food safety, recycling, degradation and cost issues have not been able to be considered at the same time. Oil-proof packaging paper and paperboard have received extensive attention in food packaging. Particularly, biomass oil-proofing agent has great the research potential in this field.

KEY WORDS: oil-proof paper; barrier property; biomass oil-proof agent; rough structure

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在生活多元化的今天，含油物质在食品、工业产品以及医药行业中的应用也越来越广泛，因此在选择包装材料时除必须具有较好机械强度外，还需具有良好的油脂阻隔性能。石油基化合物由于分子间隙小，阻隔性能好，大多不易与油脂互溶，所以常用作防油材料。这些合成高分子聚合物应用性较广，尽管具备优异的防油性能，但在自然条件下降解能力较弱[1]。随着大众对“白色污染”关注度的持续升高，人们更倾向于使用降解性能良好的纸包装材料。纸本身具有多毛细孔结构，透气度较大，在未加工处理过的纸很容易被油脂润湿。纸张防油性能的方法与工艺直接关系到环保和人类健康，因此针对防油纸的防油机理和加工工艺的研究得到了相关学者的广泛关注。

在查阅相关文献的基础上，笔者拟从机内加工纸和后加工纸 2 个方面对防油纸的方法和原理及研究现状进行综述，以期能为相关学者提供参考。

1　机内加工防油纸

常采用以下方式制作机内加工防油纸，通过提升原浆的打浆度来缩小纤维之间的间隙，从而减少油脂的透过率；在纸张成型之前向浆内添加防油剂来增加纸的阻隔性，或者降低纸的表面能从而达到防油效果。

由相关文献可知，该领域的学者会单独使用上述 2 种方式来制作机内防油纸，但是更多会同时采用这 2 种研究方式，为了表述方便，文中仍对这 2 种方式分别进行叙述。

1.1　提高打浆度

研究表明，油脂之所以能渗透纸张，是借助于纤维的毛细现象。纤维错综复杂交织在一起，其间存在大量间隙，形成油脂可以穿透的“通道”[2]。国内在较早时期采用提高纸浆打浆度的方法以缩小纤维之间的空隙，从而增强纸的防油性[3]。随着纤维变短，溶液中的羟基和氢键含量也会增加，羟基会捕捉纤维上的氢键，从而将纤维聚集到一起。刘丽[4]选用本色蔗渣浆进行打浆处理，分析了打浆度对防油性能的影响，结果表明当打浆度较高时，纤维较短小，纤维之间排列较紧凑，纸的透气度大幅度下降，油脂对纸张的润湿性能下降。在一定范围内提高打浆度有利于降低油在纸上的润湿性能[5]。

1.2　浆内添加防油剂

当浆内添加防油剂后，首先与纤维表面的羟基结合，封闭纤维之间的空隙，减少油脂透过率。浆内添加的方式现在应用较少，原因是防油剂用量大，且在抄纸过程中防油剂会大量流失。助留剂的添加可提高防油剂的留着率，常见的助留剂有阳离子淀粉、聚丙烯酰胺、PVA 等，助留剂与防油剂结合后可增强分子链长度，再与纤维结合，纤维间接具有“憎油”性[6−7]。

Glory Team Industry 生产的防油剂防油机理却与此不同，防油剂的加入没有与羟基进行结合，而是与纸浆中的细小纤维结合成类胶物质，然后类胶物质与纤维结合，并填充到间隙内，干燥后可增强纸的阻隔性[8]。

2　后加工防油纸

2.1　降低油在纸张表面的润湿性能

为了降低油脂在纸表面的润湿性，目前国内外主要通过涂布含氟防油剂溶液来降低纸张表面来实现。根据 Young 方程[9]可知，当液体的表面张力大于固体的表面能时（或者说接触角大于 90°），纸张不能被浸润。传统 C_8 型含氟防油剂由于良好的防油效果，在防油纸领域应用广泛，涂覆到纸张上后，纸的表面张力会大幅降低。纤维的羟基比较容易与防油剂中亲水基团结合，从而形成稳定结构，防油剂分子一端可以牢牢附着在纤维表面，剩余柔顺性较好的含氟长链可以整齐地排列在纤维表层，形成一层极薄的膜，由于氟原子和碳原子之间形成的键比较短，2 个氟原子之间形成的范德华力基本将碳链包围，这种具有良好空间屏蔽作用的分子链形成膜使得油脂分子无法被轻易穿透，因此可以减弱纸张被油脂浸润的能力[10−12]。纸的防油等级随着纸张表面防油层的厚度和密实性的增加而增加，纸张达到 5 级防油等级仅需涂覆极少量含氟防油剂[13]。

传统 C_8 型含氟防油剂在国外食品及其包装中受到强烈抵制，原因是含氟防油剂的分子链在高温环境下会断裂，形成新的化合物，如全氟辛烷磺酸（PFOS）[14]和全氟辛烷酰胺（FOSE）等物质，这些物质无法在人体和自然环境下降解，会随着食物链进入人体内，经过长时间累积后可引发各种慢性疾病[15−17]。为了减弱这些物质对人体的危害，常与生物质防油剂复配[18]。这种方式虽然减少了 C_8 型含氟防油剂的用量，但是该防油剂毒性本质并未改变。为了减弱其毒性，又要利用氟元素在阻油方面的优势，国内外研究发现含氟防油剂的碳链越长，在加热条件下越不稳定，如果缩短碳链长度，防油剂不但稳定性得到增加，而且在高温下产生的分解物毒性也减弱。如 C_6 或 C_4 型短链含氟防油剂，即使加热也不会产生 PFOS 这类毒性较大的物质[19]；氟硅防油剂兼具氟硅二者的优点，此类防油剂既可以迅速与纤维牢固结合到一起，又可以将硅材料良好的稳定性、耐溶剂性叠加到防油剂上，而且在加热情况下不易分解，从根本上解决了 PFOS 等物质对人体的危害[20−21]；引入氧原子等杂原子的含氟防油剂，杂原子的引入改变了主链的结构，这种

改变对防油剂的防油性影响不大，但是其受热分解物被人体吸收过程被中断，人体无法直接吸收，直接解决了有毒产物在体内积累的难题[22]。

2.2 提高纸对油的阻隔性

2.2.1 淋膜法

常见的汉堡包装盒、炸鸡餐盒以及纸杯等纸塑产品都是在纸基表面采用喷淋工艺形成 1 层致密聚合物薄膜，从而防止水和油脂等分子的渗透。常见的聚合物有聚丙烯（PP）、聚乙烯（PE）和聚氯乙烯（PVC）[23]等。从本质上讲，纸基淋膜后可以达到阻油效果，但是纸本身不具备防油性能。虽然聚合物选择面比较广，但大部分淋膜纸都存在有害物质迁移、废气污染降解以及耐穿刺性差等缺点[24]，且淋膜后防油纸聚合物与纤维紧密结合，难以分离，造成回收成本增大等难题，限制了淋膜纸的推广[25]。

2.2.2 涂覆生物质防油剂

食品安全和环保问题一直受到国内外的广泛关注，可降解的生物质防油剂现成为研究热点，此种防油剂解决了传统防油剂有毒和难自然降解的问题。作为食品包装中的一项新技术，防油剂通过涂布后制备的防油纸可直接应用于食品包装。常见的生物质防油剂包括多糖、蛋白质和聚乳酸等，这些物质不但容易获取而且对人体无毒。

2.2.2.1 多糖

多糖应用于生物质防油剂的研究是近年来广大学者比较关注的方向，常见的多糖有淀粉[26−28]、壳聚糖[29−31]、海藻酸钠[32−33]、羧甲基壳聚糖[34]以及纳米纤维素[33,35]等。多糖溶液具有一定粘度，可作为胶黏剂，而溶液和纤维的极性相近，因此二者可以结合，多糖溶液分子间的粘合以及凝聚粘合等粘合作用将纤维与涂层结合在一起，干燥后会降低纸张的透气度[36−39]。多糖溶液的成膜性较好，涂覆于纸张表面后会迅速填充纸张表面的凹陷，并形成 1 层均匀的膜，增强了纸的表面光滑度和密度[40]。有的多糖中带有羟基基团，这样多糖溶液不但可以形成良好的阻隔层，而且还具有一定排斥油脂的性能，可以进一步提高涂布纸防油性能[41]，因此多糖用量的增加可以增强涂布纸的防油等级[42]。

多糖防油剂大多具有较好的防油性，但也具有一定粘性，若想达到理想效果，通常要增大溶液浓度，但此时溶液流动阻力太大，不利于涂布。多糖防油剂和油脂具有较高的表面能，虽然多糖可以形成致密的阻隔层，但是油脂会在纸张表面迅速铺开，防油纸抗润湿性较差。

表面能主要由极性组分和色散力两部分组成[43]。根据杨氏方程可知，如果降低多糖防油剂的表面能，则纸张抗润湿性得到增强。与表面能较低的生物质材料复配，虽然阻隔性可能会减弱，但是同样可以达到防油效果[44]；经电晕处理后隔离涂层的耐油脂性明显低于未经处理的样品，因为电晕放电穿透处理后涂层表面发生了化学变化。电晕处理增加了涂层的表面能，特别是在正处理电压之后，而负放电导致表面能的极性部分发生了更大变化，涂层的防油性显著提高，因此多糖防油剂极性组分所占比率对发挥防油作用至关重要[45]。

2.2.2.2 蛋白质

蛋白质溶液比较容易成膜，同等浓度的溶液，蛋白质溶液的粘度比多糖溶液小，因此更利于涂布。国外研究者多采用玉米醇溶蛋白[46]、大豆分离蛋白[47−49]、乳清蛋白[50−51]以及小麦蛋白[52]等为涂层原料来制备防油纸。有学者已经研究了基于蛋白质的生物聚合物薄膜作为食品包装材料和涂层材料，并已广泛用作食品包装的阻隔层，以延长加工食品的保质期。蛋白质结构较复杂，含有氢键、二硫键、羧基以及氨基等结构，这些结构使蛋白质具有稳定骨架，当蛋白质溶于水中时，二硫键等会被破坏，可重新形成新的二硫键，继而形成稳定的网状结构，因此形成的膜具有良好的稳定性。有研究表明[47]，蛋白质在 pH 值为 10 左右的加热环境下会变性，会改变蛋白质的形状，蛋白质网络被破坏，从球形结构变成链状结构，分子链的束缚减弱，融化速率加快，涂覆后纸的阻隔性和机械强度较高。添加增塑剂（比如甘油、蔗糖）会增强涂层的柔韧性，涂层不易开裂。蛋白质溶液大多带负电荷，与纤维的相容性不强，常与带相反电荷的生物聚合物复合（比如壳聚糖），二者之间形成的强离子交联键具有较好的生物相容性，从而增强涂层与纸纤维之间的连接。

2.2.2.3 聚乳酸

聚乳酸（PLA）可由农业资源发酵而来，经自然催化可降解为无污染的小分子物质，PLA 在生物酶作用下可转变成能被直接吸收的有益物质，在自然状态下具有良好的稳定性[53]。目前在医疗领域已经得到推广，被国内学者视作具有极大潜力的新型可降解材料[54]，是石油基材料的理想替代品，大大减少了碳的足迹，不会对全球环境造成危害。PLA 在食品包装材料、餐具和陶器以及现代农业中应用较广泛，具有优良的保鲜、抑菌、防水等作用，在食品、工业、生物医疗等包装领域得到广泛关注，美国 FDA 认为聚乳酸是适用于所有食品的包装材料[55−56]。各种聚乳酸都含有小部分结晶，分子排列比较紧密，分子含有酯基，因此具有良好的疏水型。但是聚乳酸有较大侧基，分子间隙比较大，在阻气方面有一定缺陷，常常采用物理改性[57]、化学改性[58]、复合改性[59]等方法来缩小间隙，减少空间位阻，破坏分子网络结构等改善其性能。交联改性[60]、共聚改性[61]以及表面改性[62]等化学改性方法，直接作用于聚乳酸骨架，使其变成网

络结构或者引入疏油基团来改善防油性[63]。复合材料改性可以发挥叠加效果，弥补各组分不足又不会减弱其优点，因此添加纳米材料一直是近年研究的热点，复合后包装材料的相容性、降解性和阻隔性都大幅提高，因此常将碳纳米管、纳米氧化钛和纳米氧化锌等材料作为填充剂来提高 PLA 的阻隔性[64−66]。

2.2.3　涂蜡或复合金属箔

在纸张表面涂蜡或复合金属箔在防油纸中使用比较少，主要是这种防油纸在食品安全和回收方面存在问题。复合金属箔常采用类似于真空镀铝的方法在纸张表面形成一层极薄的阻隔层来阻油，此种防油纸具有极佳的阻隔性，尤其针对小分子气体，但是纸张耐折性差，易形成针孔，不透明[67]。为改善镀金属膜纸的不足，现在采用物理淀积法将氧化硅和氧化钛等材料复合到纸张上，得到性能更佳的防油纸[68]。

2.3　构建粗糙结构

荷叶独特的纹理和粗糙表层激发了人们对超疏水表层的研究，人们尝试采用提高表面粗糙度的方法来减少液体与表面的接触面积，从而实现阻隔的效果。近年来激光刻蚀[69]、软复制[70−71]、水滴模板法[72−73]等技术逐渐从超疏水领域延伸到超疏油的研究上。Yao 等[74]采用微流乳液模板法，利用咪唑酸锌骨架 8 制得的多孔膜具有相互连接的固体结构和均匀的蜂窝状微腔，相互连接的多孔结构润湿过程不同于独孔结构，当液体沉积物覆盖顶部开口时，气穴被密封在相应的微腔中，因为微腔被封闭并彼此分开；将水和大豆油滴到表层时，所有液体的接触角均大于 90°，形成的封闭微腔可以防止水滴和油脂横向渗透。纸板通过这种方法不但可以获得憎液性，而且摩擦性能也大幅降低，在食品包装领域应用性较强[33,75]。为了确保纸张表面涂层粗糙结构的均匀性，选用静态工艺，制得的蜂窝结构大小和排列比较均匀，防水防油效果更佳[76]。水滴模板法近年来在增强材料表面光滑度降低摩擦因数[77−78]、提高湿度传感器灵敏度[79]以及增强拉伸强度[80]等领域的研究也成为热点。

3　结语

防油包装纸在我国需求量极大，其巨大的消费市场与功能和成本密切相关。随着包装朝绿色化和需求多元化方向发展，国内外研究者正致力于研究环保及易降解的防油包装纸。生物质防油包装纸在食品和医疗领域的应用越来越广泛，壳聚糖、海藻酸钠和聚乳酸等材料已成为研究防油包装纸的热点，但溶液粘度、成本和加工工艺等因素也限制了其使用。生物质材料在防油包装纸领域的应用拥有巨大潜力，相关研究人员需要深度挖掘，以推动环保防油包装纸的发展，这对我国快餐行业的意义重大。

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