

γ 射线对聚丙烯发泡材料亲油疏水性能的影响

蔡佩君 文 鑫 王小俊 严 坤 杨晨光

(湖北省纺织新材料与应用重点实验室 武汉纺织大学材料科学与工程学院 武汉 430200)

摘要 系统研究了 γ 射线辐照对两种聚丙烯 (PP) 泡沫材料亲油疏水性能的影响规律。等规聚丙烯 (iPP) 和高熔体强度聚丙烯 (HMSPP) 颗粒分别经热压制备成厚度为 1 mm 的片材, 然后通过超临界 CO_2 釜压发泡制备 PP 泡沫材料, 利用 γ 射线对发泡样品进行辐照处理。结果表明: 辐照后, 两种泡沫的熔点和结晶温度均下降, 泡孔孔壁出现裂纹, 泡沫断面粗糙度明显增加, 出现亲水性缺陷, 泡沫断面的抗液滴黏着性增加; iPP 泡沫水接触角增加 26.4%, HMSPP 泡沫接触角从 135.2° 增长至 141.8° , 几乎达到超疏水水平; 泡孔孔壁裂纹的出现, 增加了泡孔之间的连通性, 泡沫吸油渗透率变大, 吸油量明显增加。这为制备亲油疏水泡沫材料提供了方法。

关键词 γ 射线辐照, PP 泡沫, 超临界 CO_2 发泡, 疏水性, 吸油性能

中图分类号 TL13

DOI: 10.11889/j.1000-3436.2021.rj.39.030201

γ -ray effects on lipophilic and hydrophobic properties of polypropylene foaming materials

CAI Peijun WEN Xin WANG Xiaojun YAN Kun YANG Chenguang

(Hubei Key Laboratory of Advanced Textile Materials & Application, College of Materials Science and Engineering,
Wuhan Textile University, Wuhan 430200, China)

ABSTRACT The effects of γ -ray irradiation on the lipophilic and hydrophobic properties of two types of polypropylene (PP) foam materials were systematically studied. Isotactic polypropylene (iPP) and high-melt-strength polypropylene (HMSPP) sheets were prepared by hot pressing with a thickness of 1 mm, and then PP foams were prepared by supercritical CO_2 batch foaming. Finally, the foamed samples were irradiated with γ -rays. The results showed that the melting points and crystallization temperatures of the two foams decreased after irradiation. The scanning electron microscope images showed that the cell walls of both PP foams appeared cracks and the roughness of the foam's cross-section increased significantly. The water contact angle of iPP foam largely increased by 26.4%, and the contact angle of HMSPP foam increased from 135.2° to 141.8° , which almost reached the super-hydrophobic level. The enhanced roughness increased the hydrophilic defects and the droplet adhesion resistance. Moreover, the appearance of the cracks in the cell walls increased the connectivity between cells, which largely increased the foam oil absorption permeability and the oil absorption quantity. This study provides a method for preparing lipophilic and hydrophobic foam.

KEYWORDS γ -ray irradiation, PP foam, Supercritical CO_2 foaming, Hydrophobicity, Oil absorbency

基金资助: 武汉纺织大学科技创新项目(193143, 205009)资助

第一作者: 蔡佩君, 女, 2000 年 12 月出生, 现为武汉纺织大学材料科学与工程学院复合材料与工程专业在读本科生

通信作者: 杨晨光, 博士, 硕士生导师, E-mail: cgyang@wtu.edu.cn

收稿日期: 初稿 2020-10-30; 修回 2020-11-10

Supported by Science and Technology Innovation Project of Wuhan Textile University (193143, 205009)

First author: CAI Peijun (female) was born in December 2000, and now she is a junior undergraduate student majoring in composite materials and engineering at the School of Materials Science and Engineering, Wuhan Textile University

Corresponding author: YANG Chenguang, doctoral degree, master's supervisor, E-mail: cgyang@wtu.edu.cn

Received 30 October 2020; accepted 10 November 2020

CLC TL13

微孔聚合物泡沫材料质量轻、机械性能好、疲劳寿命长、冲击强度高、韧性高、刚度/质量比高、介电常数和热导系数低,用途广泛,被誉为“21世纪的新型材料”^[1-8]。微孔聚合物材料因具有以上优点以及特殊蜂窝结构,在建筑隔热、包装、能量吸收、汽车内饰、耐缓冲材料以及储能等领域得到广泛应用^[6, 9-15]。与聚乙烯(PE)、聚苯乙烯(PS)发泡材料相比,聚丙烯(PP)发泡材料具有高弯曲模量、高热稳定性、易回收性以及高回弹性等特点。因此,在交通运输,建筑,体育设施用品,包装以及家用电器等领域的应用均极具竞争力^[13, 16-20]。PP微孔材料作为最具应用潜力的聚合物发泡材料,其关键性能的研究,如隔热、抗压以及疏水亲油性能等,引起了国内外学者的关注和研究^[21-24]。Rizvi等^[21]通过引入聚四氟乙烯(PTFE)纳米短纤成功制备出具有良好亲油疏水性

的PP开孔发泡材料,其水接触角可达160°,表现出超疏水性能。

相比于填充、共混等方法,辐射法用于改变聚合物材料的物理和化学结构性能具有特殊的优点,如简化制备工艺流程、保持材料清洁度及提高回收性等。

本文研究了辐射对PP发泡材料的结晶、微孔结构以及疏水亲油性的影响(图1)。通过超临界CO₂釜压发泡的方法制备等规聚丙烯(iPP)和高熔体强度聚丙烯(HMSPP)两种泡沫材料,分别对两种PP泡沫材料进行辐照。辐照后两种PP泡沫微孔结构均出现破裂现象,孔壁上产生大量裂纹,泡沫断面粗糙度均明显变大,疏水性和亲油性增强。本文还研究了辐射对泡沫吸油渗透率的影响,并初步探讨了辐射对泡沫孔结构、亲油疏水性能及渗透率的影响。

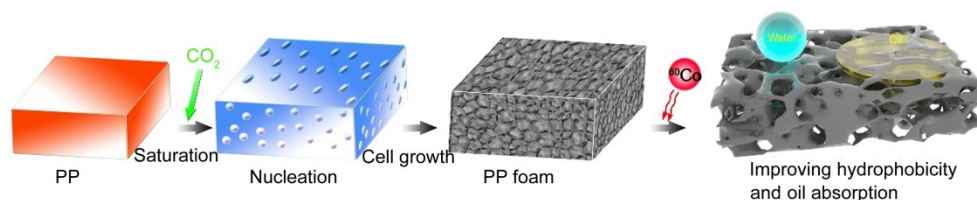


图1 辐照法制备亲油疏水PP发泡材料示意图

Fig.1 Schematic diagram of preparation of lipophilic and hydrophobic PP foaming materials by irradiation

1 材料与方法

1.1 原料

iPP (T30s, 颗粒), 上海石油化工股份有限公司, 密度 0.91 g/cm³, 熔融指数 3.0 g/min (负荷 2.16 kg, 230 °C); HMSPP (3005, 颗粒), 中国台湾塑料集团公司, 密度 0.90 g/cm³, 熔融指数 0.4 g/min (负荷 2.16 kg, 230 °C); 二氧化碳, 工业级, 99.95%, 祥埝气体站; ⁶⁰Co源: 圆柱体式γ射线源, 活度 1.85×10¹⁴ Bq, 中国科学院上海应用物理研究所。

1.2 样品制备

将iPP和HMSPP颗粒分别在开炼机上混合融化后于硫化成型机上热压20 min, 制成1 mm厚样品板材, 然后分别将PP板材(2~4 g)置于高压反应釜内; 用CO₂气体清洗反应釜以排出釜内空气,

通过高压液体泵充入CO₂至设定压力, 再将釜温升至发泡温度, 保持设定温度和压力30 min; 泄压释放CO₂气体, 平均减压速率约为10 MPa/s。具体实验装置见文献[25]。

1.3 测试表征

1.3.1 差示扫描量热(DSC)法测试

采用NETZSCH STA 449 F3 Jupiter型差式扫描量热仪测定了PP样品熔点和结晶度的变化。分别称取约10 mg PP样品置于氧化铝坩埚中, 温度扫描范围为30~200 °C, 升温速率10 °C/min, 氦气气氛, 流速20 mL/min。结晶度(X_c, %)由式(1)测定。

$$X_c = \frac{\Delta H_f}{\Delta H_0} \times 100\% \quad (1)$$

式中: ΔH_f 为加热过程熔融焓, J/g; ΔH_0 为100%聚丙烯结晶理论焓值(207.1 J/g)^[26]。

1.3.2 泡孔形貌分析

采用德国 Zeiss MERLIN Compact 14184 扫描电子显微镜对 PP 发泡材料进行断面观察, 使用 Image Pro Plus 软件分析电镜照片。平均孔径 (D_a) 由式 (2) 计算。孔密度 (N) 由式 (3) 计算。

$$D_a = \frac{\sum d_i n_i}{\sum n_i} \quad (2)$$

式中: D_a 为平均孔直径, μm ; n_i 为泡孔数量; d_i 为孔直径, μm 。

$$N = \left(\frac{n}{A} \right)^{3/2} \times R_v \quad (3)$$

式中: N 为孔密度, cm^{-3} ; n 泡孔数量; A 为电镜照片面积, cm^2 ; R_v 为发泡倍率。

1.3.3 泡沫表观密度和发泡倍率

采用密度瓶法测量发泡材料表观密度 (ρ_f), 计算见式 (4)。

$$\rho_f = \left(\frac{a}{a + b - c} \right) \rho_w \quad (4)$$

式中: a 、 b 和 c 分别为泡沫样品质量、密度瓶装水总质量和泡沫样品浸没密度瓶中的总质量, g ; ρ_w 为水的密度, g/cm^3 。

采用密度瓶法测量 PP 泡沫样品的密度, 发泡倍率 (R_v) 计算见式 (5)。

$$R_v = \frac{\rho_s}{\rho_f} \quad (5)$$

式中: ρ_s 为未发泡 PP 密度, g/cm^3 。

iPP 和 HMSPP 两种泡沫微孔结构参数如表 1 所示。

表 1 iPP 和 HMSPP 两种泡沫微孔结构参数
Table 1 Microcellular structure parameters of iPP and HMSPP foams

样品 Samples	孔径 / μm Cell size	孔密度 / cm^{-3} Cell density	膨胀率 Expansion ratio
iPP 泡沫 iPP foam	132.6	3.7×10^6	3.6
HMSPP 泡沫 HMSPP foam	58.7	6.1×10^7	7.8

1.3.4 接触角测试

将泡沫干燥后, 经液氮冷却后脆断, 裁切断面, 用双面胶固定于载玻片后, 置于工作台上。利用微量进样器调整液滴的量, 使其在针头形成液滴, 待液滴在材料表面稳定后, 通过摄像系统采集图像。接触角为液滴接触表面左右接触角的平均值。

1.3.5 吸油性能测试

将泡沫样品切成质量为 0.04 g 的方体若干个,

置于盛放油品的烧杯中, 每隔 30 s 取出样品, 去除样品表面油膜, 称取质量, 直至样品质量不再变化。

2 结果与讨论

2.1 泡沫 DSC 分析

图 2 显示了 iPP 和 HMSPP 泡沫材料辐照前后的 DSC 熔融和结晶变化曲线。

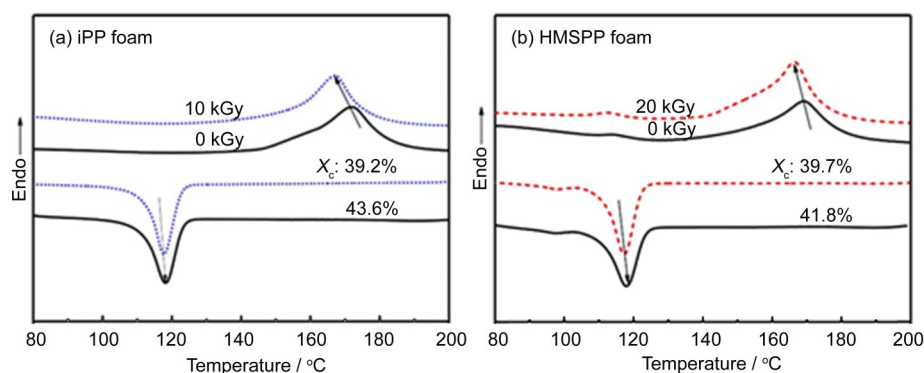


图 2 iPP (a) 和 HMSPP (b) 泡沫样品辐照前后的 DSC 熔融和结晶曲线
Fig.2 DSC melting and crystallization curves of iPP (a) and HMSPP (b) foams before and after irradiation

从图2可知,辐照后,iPP泡沫的熔点明显降低,结晶温度和结晶度均有轻微下降。HMSPP泡沫材料辐照后的DSC曲线变化表现出与iPP相似的下降趋势。辐照后,泡沫材料的熔点降低主要是由于PP结晶区域受到破坏,使结晶区产生缺陷,破坏了结晶区的完整性,使得泡沫在较低的温度开始融化,导致熔点降低。另外,辐照能够增强分子链运动,造成PP结晶过程表现出滞后现象。这之前研究工作的结果相同^[14, 24-25]。另外,相比于HMSPP,iPP熔点下降更加明显,这与iPP分子链含侧甲基支链有关,辐照易裂解,熔点下降较大。

2.2 辐照对PP泡沫微孔结构的影响

图3对比了两种PP泡沫辐照前后的断面微孔结构形貌的变化。从图3(a)可以看出,吸收剂量为10 kGy时,iPP泡沫微孔孔壁出现较多的裂纹(虚线圆内),微孔结构受到较大程度的破坏;HMSPP泡沫微孔结构表现出相似的现象,在微孔孔壁上也出现了裂纹。这主要是由于辐射裂解造成的。对于纯PP,辐照过程中裂解和交联同时发生,裂解占主导作用^[27]。另外,由于PP泡沫材料具有微孔结构,高能射线的照射不仅会造成PP分子链断裂,同时会对泡孔薄壁造成破坏,可能会增加泡孔之间的连通性。

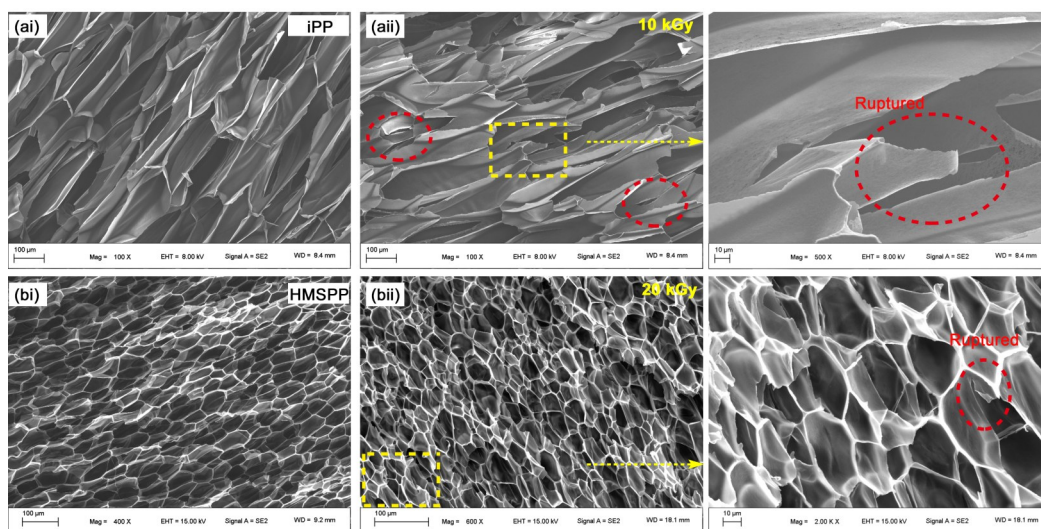


图3 iPP (a)和HMSPP (b)泡沫样品辐照前后微孔结构的变化
Fig.3 Cellular structure changes of iPP (a) and HMSPP (b) foams before and after irradiation

2.3 辐照对PP泡沫亲油疏水性的影响

良好的吸油材料必须同时具备疏水性和亲油性,即能够主动吸油而不吸水。iPP和HMSPP泡沫材料分别被裁切成长方体,用于亲油疏水性测试,如图4(a)所示。接触角测试结果(图4(b)、(c))表明,未辐照的泡沫材料表现出一定的疏水性,而辐照后,iPP和HMSPP泡沫材料的疏水性均明显提升。吸收剂量为10 kGy时,iPP泡沫水接触角从103.1°增加到130.3°,增幅超过26.4%。吸收剂量为20 kGy时,HMSPP泡沫水接触角增长至141.8°,几乎达到超疏水水平^[21]。综上,PP泡沫辐照后疏水性明显增加,这主要归因于泡沫断面粗糙度的变化。泡沫辐照后,内部微孔结构受到破坏,孔壁上出现大量的裂纹,增加了断面的粗糙度,使得断面上产生亲水性缺陷,

增加了泡沫断面的抗液滴黏着性,可解释为界面接触从高黏着的Wenzel态(Up)到低黏着Cassie态(Down)的转变^[28-29],如图4(d)模型所示。根据Cassie-Baxter非润湿性理论^[28],疏水性是因为在材料表面与水滴之间形成了连续的空气气隙,如图4(d)虚线所示,说明PP泡沫材料辐照后,断面粗糙度增加,疏水性变好。

发泡材料作为吸油材料,除了亲油疏水性能,在实际应用中,其吸油速率和吸油量也是一个关注点。图4(e)显示了泡沫的主动吸油性,可以看出,泡沫可以选择性吸收水表面的油品。为了研究材料的吸油速率和吸油量,将相同质量的泡沫样品在辐照前后分别浸入油品中,测定其吸油率与时间的关系。如图5所示,在12 min内,材料吸油逐渐接近饱和状态,并且之后吸油量趋于平

衡。从饱和吸油量可知,辐照后,泡沫吸油量明显增加,增长超过60%。另外,辐照前后泡沫吸油达到饱和所需时间基本相同,说明辐照后泡沫吸油速率提高。而iPP和HMSPP两种泡沫在前90 s内的吸油曲线重合,辐照后的泡沫平均吸油速率高于未辐照泡沫。这主要因为泡沫辐照后,

高能射线对泡孔壁造成破坏,出现裂纹,增加了泡孔之间的连通性,提高了吸油过程中的渗透率,因此吸油量明显增加。另外,根据毛细管吸附理论,孔壁细裂纹增加了吸附驱动力,出现“泵吸”现象,因此,辐照后的泡沫在90 s后的吸油速率高于未辐照泡沫。

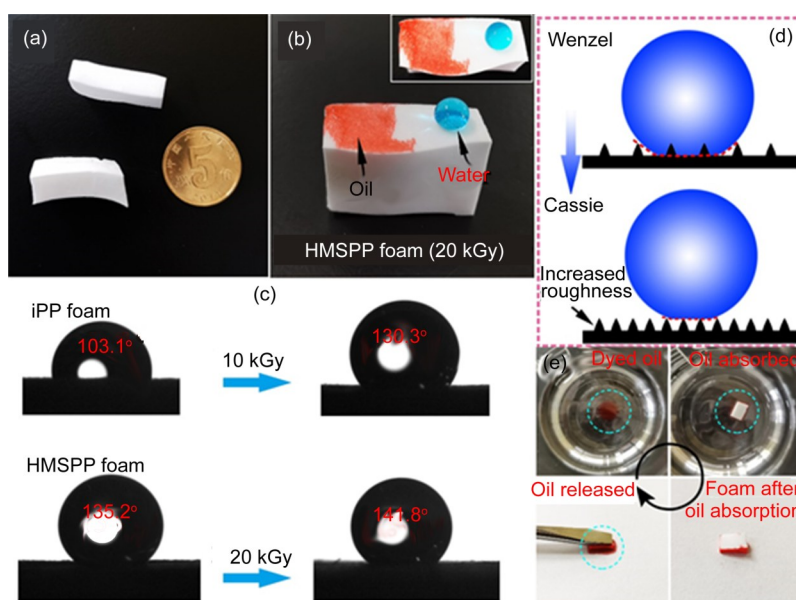


图4 泡沫照片(a);HMSPP泡沫亲油疏水照片(20 kGy)(b);泡沫样品辐照前后接触角照片(c);水滴接触表面模型示意图(d);泡沫对苏丹红IV染色的油的循环吸油(e);彩色见网络版

Fig.4 Photograph of the foams (a); test for hydrophobic and lipophilic properties of foams (b); photographs of contact angle of foam samples before and after irradiation (c); schematic diagram of droplet contact surface model (d); cycle sorption process of oil dyed with Sudan IV by HMSPP foam (e); color online

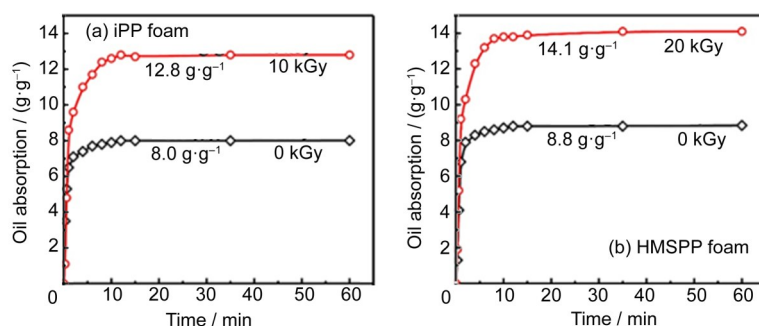


图5 iPP (a)和HMSPP (b)泡沫吸油量与时间的关系曲线

Fig.5 Curves of oil absorption against time of iPP (a) and HMSPP (b) foam

3 结论

系统研究了 γ 射线辐照对两种PP泡沫材料亲油疏水性能的影响。结果表明:辐照后,PP泡沫的熔点和结晶温度下降,泡孔孔壁出现裂纹,泡沫断面粗糙度明显增加,出现亲水性缺陷,疏水性明显提高;iPP泡沫水接触角增加26.4%,

HMSPP泡沫接触角从135.2°增长至141.8°,几乎达到超疏水水平;由于泡孔孔壁裂纹的出现,泡孔之间的连通性增加,泡沫吸油渗透率提高,吸油量和吸油速率明显增加,吸油量增长超过60%。本工作通过辐射改性法提高了PP发泡材料的亲油疏水性能,对于开拓发泡材料的商业前景,扩大应用范围等意义重大。

参考文献

- Collias D I, Baird D G, Borggreve R J M. Impact toughening of polycarbonate by microcellular foaming[J]. *Polymer*, 1994, **35**(18): 3978-3983. DOI: 10.1016/0032-3861(94)90283-6.
- Park C B, Cheung L K. A study of cell nucleation in the extrusion of polypropylene foams[J]. *Polymer Engineering & Science*, 1997, **37**(1): 1-10.
- Park C B, Behraves H, Venter R D. Low density microcellular foam processing in extrusion using CO₂[J]. *Polymer Engineering and Science*, 1998, **38**(11): 1812-1823. DOI: 10.1002/pen.10351.
- Bao J B, Nyantakyi A Jr, Weng G S, *et al.* Tensile and impact properties of microcellular isotactic polypropylene (PP) foams obtained by supercritical carbon dioxide[J]. *The Journal of Supercritical Fluids*, 2016, **111**: 63-73. DOI: 10.1016/j.supflu.2016.01.016.
- Kong W L, Bao J B, Wang J, *et al.* Preparation of open-cell polymer foams by CO₂ assisted foaming of polymer blends[J]. *Polymer*, 2016, **90**: 331-341. DOI: 10.1016/j.polymer.2016.03.035.
- Yang C G, Wang M H, Zhang M X, *et al.* Supercritical CO₂ foaming of radiation cross-linked isotactic polypropylene in the presence of TAIC[J]. *Molecules*, 2016, **21**(12): E1660. DOI: 10.3390/molecules21121660.
- Al Tawil E, Monnier A, Nguyen Q T, *et al.* Microarchitecture of poly(lactic acid) membranes with an interconnected network of macropores and micropores influences cell behavior[J]. *European Polymer Journal*, 2018, **105**: 370-388. DOI: 10.1016/j.eurpolymj.2018.06.012.
- Zhao J C, Zhao Q L, Wang L, *et al.* Development of high thermal insulation and compressive strength BPP foams using mold-opening foam injection molding with *in situ* fibrillated PTFE fibers[J]. *European Polymer Journal*, 2017, **98**: 1-10. DOI: 10.1016/j.eurpolymj.2017.11.001.
- Suh K W, Park C P, Maurer M J, *et al.* Lightweight cellular plastics[J]. *Advanced Materials*, 2000, **12**(23): 1779-1789.
- 邢哲, 吴国忠, 黄师荣, 等. 用超临界二氧化碳发泡制备辐射交联聚乙烯微孔材料[J]. *辐射研究与辐射工艺学报*, 2008, **26**(4): 193-198.
XING Zhe, WU Guozhong, HUANG Shirong, *et al.* Preparation of microcellular cross-linking polyethylene foams using supercritical CO₂[J]. *Journal of Radiation Research and Radiation Processing*, 2008, **26**(4): 193-198.
- 王谋华, 邢哲, 刘伟华, 等. 辐射改性聚丙烯的超临界二氧化碳发泡性能研究[J]. *辐射研究与辐射工艺学报*, 2014, **32**(2): 020303.
WANG Mouhua, XING Zhe, LIU Weihua, *et al.* Study on supercritical carbon dioxide foaming properties of radiation modified polypropylene[J]. *Journal of Radiation Research and Radiation Processing*, 2014, **32**(2): 020303.
- Tiuc A E, Vermesan H, Gabor T, *et al.* Improved sound absorption properties of polyurethane foam mixed with textile waste[J]. *Energy Procedia*, 2016, **85**: 559-565. DOI: 10.1016/j.egypro.2015.12.245.
- Yang C G, Xing Z, Zhang M X, *et al.* Supercritical CO₂ foaming of radiation crosslinked polypropylene/high-density polyethylene blend: Cell structure and tensile property[J]. *Radiation Physics and Chemistry*, 2017, **141**: 276-283. DOI: 10.1016/j.radphyschem.2017.07.028.
- Yang C G, Xing Z, Zhang M X, *et al.* Radiation effects on the foaming of atactic polypropylene with supercritical carbon dioxide[J]. *Radiation Physics and Chemistry*, 2017, **131**: 35-40. DOI: 10.1016/j.radphyschem.2016.10.018.
- Yang C G, Xing Z, Zhao Q, *et al.* A strategy for the preparation of closed-cell and crosslinked polypropylene foam by supercritical CO₂ foaming[J]. *Journal of Applied Polymer Science*, 2018, **135**(6): 45809. DOI: 10.1002/app.45809.
- Suh K W, Park C P, Maurer M J, *et al.* Lightweight cellular plastics[J]. *Advanced Materials*, 2000, **12**(23): 1779-1789.
- Xu Z M, Jiang X L, Liu T, *et al.* Foaming of polypropylene with supercritical carbon dioxide[J]. *The Journal of Supercritical Fluids*, 2007, **41**(2): 299-310. DOI: 10.1016/j.supflu.2006.09.007.
- 杨晨光, 赵全, 王谋华, 等. 伽马射线辐照对聚丙烯超临界二氧化碳发泡的影响[J]. *辐射研究与辐射工艺学报*, 2018, **36**(1): 010301. DOI: 10.11889/j.1000-3436.2018.rj.36.010301.
YANG Chenguang, ZHAO Quan, WANG Mouhua, *et al.* Gamma-ray irradiation effects on scCO₂ foaming behavior of polypropylene[J]. *Journal of Radiation Research and Radiation Processing*, 2018, **36**(1): 010301. DOI: 10.11889/j.1000-3436.2018.rj.36.010301.
- 杨晨光, 邢哲, 谭海容, 等. 超临界二氧化碳制备辐射交联微孔聚丙烯材料的研究进展[J]. *辐射研究与辐射工艺学报*, 2019, **37**(1): 010101. DOI: 10.11889/j.1000-

- 3436.2019.rj.37.010101.
- YANG Chenguang, XING Zhe, TAN Hairong, *et al.* Research progress in preparation of cross-linked polypropylene foam using supercritical CO₂[J]. Journal of Radiation Research and Radiation Processing, 2019, **37** (1): 010101. DOI: 10.11889/j. 1000-3436.2019. rrj.37.010101.
- 20 杨晨光, 赵全, 张茂江, 等. 聚四氟乙烯微粉对超临界 CO₂发泡聚丙烯泡孔结构及性能的改善[J]. 材料导报, 2019, **33**(21): 3547-3551. DOI: 10.11896/cldb.18050235.
- YANG Chenguang, ZHAO Quan, ZHANG Maojiang, *et al.* Improving cellular structure and property of supercritical CO₂ foamed of polypropylene via the addition of PTFE micropowder[J]. Materials Reports, 2019, **33**(21): 3547-3551. DOI: 10.11896/cldb.18050235.
- 21 Rizvi A, Chu R K M, Lee J H, *et al.* Superhydrophobic and oleophilic open-cell foams from fibrillar blends of polypropylene and polytetrafluoroethylene[J]. ACS Applied Materials & Interfaces, 2014, **6**(23): 21131-21140. DOI: 10.1021/am506006v.
- 22 Yang C G, Xing Z, Wang M H, *et al.* Merits of the addition of PTFE micropowder in supercritical carbon dioxide foaming of polypropylene: ultrahigh cell density, high tensile strength, and good sound insulation[J]. Industrial & Engineering Chemistry Research, 2018, **57** (5): 1498-1505. DOI: 10.1007/BF02699185.
- 23 Zhao J C, Wang G L, Wang C D, *et al.* Ultra-lightweight, super thermal-insulation and strong PP/CNT microcellular foams[J]. Composites Science and Technology, 2020, **191**: 108084. DOI: 10.1016/j. compscitech.2020.108084.
- 24 Cherukupally P, Sun W, Wong A P Y, *et al.* Surface-engineered sponges for recovery of crude oil microdroplets from wastewater[J]. Nature Sustainability, 2020, **3**: 136-143. DOI: 10.1038/s41893-020-0472-2.
- 25 Yang C G, Xing Z, Zhao Q, *et al.* A strategy for the preparation of closed-cell and crosslinked polypropylene foam by supercritical CO₂ foaming[J]. Journal of Applied Polymer Science, 2017, **135**(6): 45809. DOI: 10.1002/app.45809.
- 26 Velasco J I, Morhain C, Martinez A B, *et al.* The effect of filler type, morphology and coating on the anisotropy and microstructure heterogeneity of injection-moulded discs of polypropylene filled with aluminium and magnesium hydroxides. Part 2. Thermal and dynamic mechanical properties[J]. Polymer, 2002, **43**(25): 6813-6819. DOI: 10.1016/s0032-3861(02)00669-9.
- 27 Auhl D, Stange J, Münstedt H, *et al.* Long-chain branched polypropylenes by electron beam irradiation and their rheological properties[J]. Macromolecules, 2004, **37**(25): 9465-9472. DOI: 10.1021/ma030579w.
- 28 Cassie A B D, Baxter S. Wettability of porous surfaces[J]. Transactions of the Faraday Society, 1944, **40**: 546-551. DOI: 10.1039/tf9444000546.
- 29 Wang L M, Wei J J, Su Z H. Fabrication of surfaces with extremely high contact angle hysteresis from polyelectrolyte multilayer[J]. Langmuir: the ACS Journal of Surfaces and Colloids, 2011, **27**(24): 15299-15304. DOI: 10.1021/la2039448.