Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2024, **26**, 4493

Received 15th January 2024,
Accepted 8th April 2024

DOI: 10.1039/d4gc00221k

rsc.li/greenchem

Scalable superhydrophobic coatings with recycled polypropylene†

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Polypropylene (PP), a preferred choice of material for superhydrophobic coatings, often encounters solubility challenges due to its chemical inertness. This work addresses the persistent solubility challenges in polypropylene (PP) coatings by partially oxidizing PP to enhance its solubility at lower temperatures. The elevated solubility makes coatings with PP solution at room or near room temperatures feasible for widespread substrate application, rendering the process scalable, environmentally friendly and safer. Additionally, this approach enhances coating characteristics and eliminates the need to initially synthesize sample with specific morphology and surface roughness. Utilizing recycled PP for coating also aids to address the issue of plastic pollution.

The superhydrophobic surface ranks among the top 20 research frontiers in materials science due to its diverse applications in self-cleaning, anti-corrosion, antifouling, anti-icing, anti-fogging, oil–water separation, and more.[1] Over the past years, there has been a substantial surge in demand and advancement within this sector. According to analytical reports, the global market for superhydrophobic coatings is expanding at a compound annual growth rate of 25.6%, with the market size estimated to reach USD 3–4 billion by 2026.[1a] A superhydrophobic surface is defined by a water contact angle that exceeds 150°. This phenomenon is a result of both surface chemistry and surface architecture, such as surface energy and micro-nano scale surface roughness.[1c,2] The fabrication of superhydrophobic surfaces presents practical challenges, primarily linked to the selection of precursors, substrates, and techniques to achieve the desired surface morphologies. Reported methods include perfluoro silane grafting,[3] nanoparticles coating,[4] polymer solution coating,[5] moulding from textured template,[6] and deposition of precursors using pulsed laser techniques.[7] Developing practical and scalable methods for fabricating superhydrophobic surfaces is significant and remains a focal point of current research. Enhancing the durability of superhydrophobic coatings is another critical focus in this domain due to the susceptibility of these coatings to lose their superhydrophobic properties when their surface hierarchical structures are compromised. Recent advancements have introduced innovative methods for creating robust superhydrophobic coatings, including biomimetic and self-healing techniques, yielding promising results.[8]

Polymers have been extensively investigated as primary materials for the development of superhydrophobic coatings.[3–7] Some polymer surfaces are designed to replicate the hierarchical micro/nanostructures found in natural superhydrophobic surfaces, such as lotus leaves and cicada wings.[1c,d,2,9] One notable example involves the synthesis of microspheres with nano-scaled rough surfaces using a block copolymer of polypropylene and poly(methyl methacrylate) (PP-PMMA).[10] These microspheres exhibit remarkable superhydrophobicity, with water contact angles reaching up to 160°. Within the realm of polyolefins, polypropylene (PP) stands out as a low surface energy polymer, making it a prominent choice for superhydrophobic coatings.[11] The hydrophobic properties of a polypropylene coating vary based on the precursor and the chosen coating methods. Notably, a coating derived from an isotactic polypropylene solution often demonstrates greater hydrophobicity compared to one prepared from an atactic polypropylene solution.[11a] Additionally, the hydrophobicity could be improved by employing a mixed solvent, such as mixture of xylene and methyl ethyl ketone, instead of a single solvent to dissolve polypropylene.[5,11c]

One major restriction in polypropylene coatings is its low solubility in common solvents. Polypropylene (PP) is a nonpolar polyolefin and remains insoluble in common solvents at or near room temperatures, making it an ideal material for chemical containers and food packaging. However, this chemical inertness presents a significant challenge for its practical

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† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d4gc00221k**

application in coatings. In existing literature, aromatic solvents like toluene and xylene have been utilized, and temperatures typically ranging between 120 °C–135 °C (near boiling point of solvents) are necessary to dissolve polypropylene.[11d,12] A temperature of 100 °C is still necessary to dissolve isotactic PP at 20 mg L^{-1} in mixed solvent of xylene and methyl ethyl ketone.[11c] Undoubtedly, such high-temperature requirements pose hindrances, particularly when coating substrates of substantial dimensions or surface area. In the reported literature papers, the applications are usually demonstrated for dip coating onto small items using high temperature PP solutions,[5,12d,13] while spray coating onto large area substrates are barely encountered. Moreover, aromatic solvents pose toxicity risk, and their increased atmospheric content resulting from elevated temperatures should be avoided.

In our present study, we are actively addressing the challenges associated with solubility in polypropylene coatings. Our strategy involves partially oxidizing polypropylene to modify its polarity, facilitating better solubility at lower temperatures. The oxidation process is carried out using our previously developed molten plastic method without the need for a solvent.[14] Recycled centrifuge tubes were used as a polypropylene source. It turned out that the resultant partially oxidized polypropylene (OPP) exhibits enhanced solubility in toluene, achieving concentrations of up to 10 mg mL^{-1} at room temperature, or even higher concentrations at near room temperatures (*e.g.*, 50 °C–60 °C). The OPP concentration in the toluene solution is sufficiently elevated to enable direct application for coatings. We therefore demonstrated spray and dip coatings at or near room temperatures using OPP in toluene solutions for various substrates, including fabric, wood, cardboard, and ceramic. It is interesting that the features of the coatings derived from this functionalized OPP also vary with the alterations in solubility and crystallization behaviour. All coatings demonstrate remarkable superhydrophobicity, owing to the unique morphology of PP particles, thereby eliminating the need to synthesize superhydrophobic OPP microspheres through phase separation.[14] The outcomes of this work showcase an effective method for improving superhydrophobic coatings from polypropylene and contribute to the resolution of plastic pollution issue.

Because polypropylene is a non-polar polymer, it is almost insoluble in most organic solvents at room temperature. Envisaging that the solubility of polypropylene would change with altered polarity, we tried to oxidize PP by using a "molten plastic method".[14] The reaction was carried out under aerobic condition in an open vial without any solvent. At reaction temperatures, typically 220 °C, PP melted and became stirrable. Potassium persulphate ($K_2S_2O_8$) was used as a catalyst which generated free radicals $SO_4^{-\bullet}$ from the cleavage of –O–O– bond under the high temperature conditions[15] and this initiated the oxidation of PP. The successful oxidation was verified by FT-IR analysis as shown in Fig. 1A. The structures of oxidized polypropylene (OPP) samples remained intact in comparison to pristine PP plastic; however, new absorbance attributable to carbonyl groups of oxygenated products (ketone, aldehyde and carboxylic acid) appeared at around 1720 cm^{-1}.[16] The XRD patterns of PP and OPP are basically the same (Fig. 1B), showing that the crystalline structure of OPP does not change after partial oxidation. However, the peak intensities for the XRD pattern of OPP are weaker compared with those of the original PP. This change suggests a lower crystallinity of OPP, possibly due to changed crystalline behaviour which in turn resulted in different morphology of OPP particles. The functionalized OPP demonstrated improved solubility compared to the original PP (Table S1†). At room temperature, OPP can be dissolved in xylene or toluene at concentrations up to 10 mg mL^{-1} (inset of Fig. 1B); in contrast, pristine PP cannot be dissolved even at concentration as low as 1 mg mL^{-1}. Temperature of 50 °C is necessitated to fully dissolve PP in toluene at 1 mg mL^{-1}, and boiling point temperature (110 °C) is required to fully dissolve PP in toluene at 10 mg mL^{-1}. It is also found that aromatic solvents such as toluene and xylene are more effective in dissolving OPP than other solvents such as methyl isobutyl ketone (MIBK). Evidently, the solubility of PP is notably improved through partial oxidation.

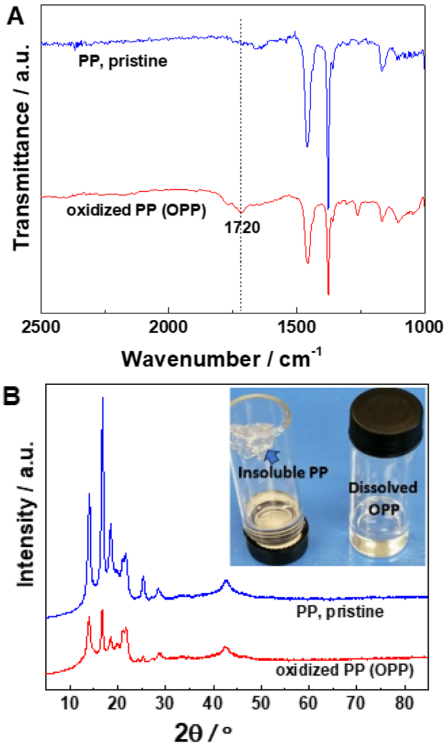

Fig. 1 (A) FT-IR profiles of PP and OPP. (B) XRD patterns of PP and OPP. The inset of (B) shows different solubilities of PP and OPP in toluene at room temperature.

Spray coating is a more viable option for covering large area substrates. Nevertheless, there has been few reports on spray coating with PP, primarily due to its limited solubility. The favourable solubility of the partially oxidized polypropylene (OPP) employed in the current work allows its application at lower temperatures, particularly, in spray coatings on expansive substrates such as fabric, wood, cardboard, and ceramic, as illustrated in Fig. 2. Interestingly, the shape of OPP particles (about 1.5 μm) on all the different substrates resembles that of rice grains, a characteristic not observed in other coatings with pristine PP. The unique characteristics of samples obtained from spray coatings with OPP in toluene solution set them apart from those produced *via* coatings with hot PP solutions.[5,12d,13] For example, microspheres of PP was obtained when the hot PP/xylene solution (120 °C) was dropped onto glass substrate,[11a] and network structure was achieved when PP in xylene-methyl ethyl ketone solution (100 °C) was dropped onto glass.[11c] It is envisaged that the functionalized OPP exhibits distinct crystallization behaviour compared to PP, owing to its partially oxidized structure with altered polarity and solubility. The fabric (Fig. 2A) used in this spray coating is originally superhydrophilic and absorbs water completely (with a water contact angle of zero). After spray coating with OPP, the fibres of the fabric were well coated with OPP grains, undergoing a distinct transformation into a superhydrophobic state with a water contact of more than 150°. The changes in wettability after OPP coating for other substrates are also remarkable (Fig. 2B–D), signifying the current method is effective and applicable for the coating of a wide range of materials. For all the coatings, only the water contact angle for cardboard (144°) is lower than 150°. This might be due to the protecting layer on cardboard and the hydrophobicity could be improved by multiple coatings. The sliding angle, tested for a smooth coating on glass, is about 3.2°.

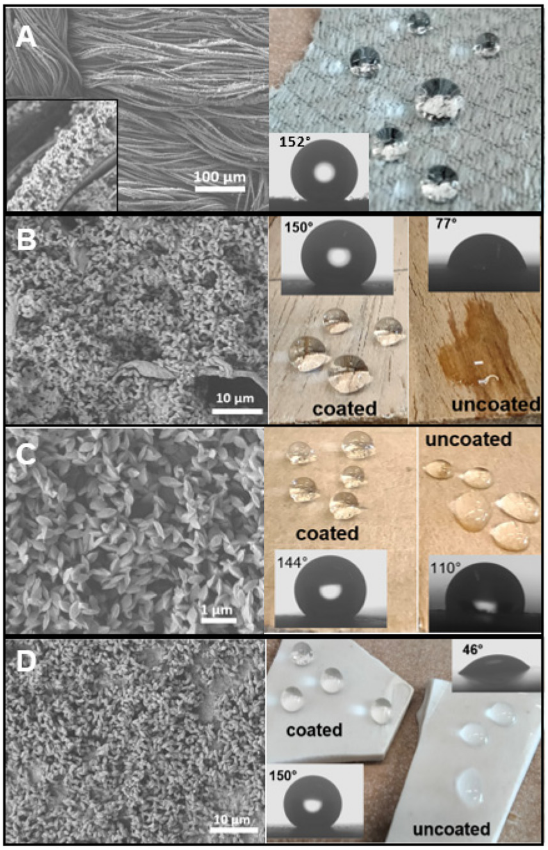

Fig. 2 Spray coatings with OPP in toluene solution (10 mg mL^{-1}) at room temperature. (A) Fabric; (B) wood; (C) cardboard; (D) ceramic.

Dip coating was specifically showcased for fabric due to its flexible nature, allowing it to be easily folded and submerged into the OPP solution. The fabric is originally superhydrophilic and was the same as the one used in Fig. 2A. For dip coating, higher OPP concentrations (20–40 mg mL^{-1}) were employed, and the solution temperature was elevated to 60 °C to ensure OPP achieved a full solubility. The fabric was submerged into the OPP solution for one minute, subsequently taken out and dried at 80 °C. This dip coating treatment also transformed the fabric's nature from superhydrophilic (water contact angle zero) to superhydrophobic state (water contact angle 154°). Scanning electron microscopy (SEM) analysis revealed that OPP particles attached on the fabric's fibres are microspheres with hierarchical micro/nano structures (Fig. 3). Such OPP microspheres resemble the papillae found on lotus leaf in terms of both size and morphology.[1d,9] The hierarchical micro/nano structures of papillae could increase surface roughness and induce the superhydrophobicity on lotus leaf. The different morphologies of OPP particles from spray coating and dip coating should be ascribed to the different concentrations of OPP in toluene solutions as well as the different OPP crystallization conditions. The current coating approaches that could be operated at room temperature or near room temperature offer practical advantages in terms of their implementation. Methyl isobutyl ketone (MIBK) was also tried as a greener solvent for the dip coating of the same fabric. It turned out that OPP can also be evenly dispersed onto the fibres and the fabric changed from superhydrophilic to superhydrophobic (Fig. S1†). The difference is that when MIBK is

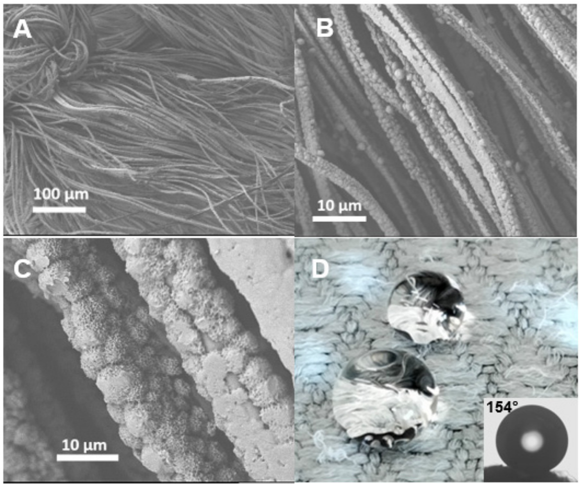

Fig. 3 (A)–(C) SEM images of superhydrophobic fabric from dip coating. Dip the fabric into OPP/TL (30 mg mL^{-1}, 60 °C) for one minute, taken out and dried in oven at 80 °C overnight. (D) Water droplets on the superhydrophobic fabric which was initially hydrophilic before coating with OPP.

used as a solvent for coating, a higher temperature (*e.g.*, 80–100 °C) was applied because of its lower solubility for polypropylene.

To better understand the advantages associated with the use of partially oxidized polypropylene (OPP) for coatings, comparison studies using pristine PP/toluene solutions for dip coatings were also performed, with the SEM results shown in Fig. 4. It turned out that when PP concentration was very low, such as at 1 mg mL^{-1}, the fibres were not effectively wrapped with PP (Fig. 4A). However, at higher PP concentrations, *e.g.*, 5–10 mg mL^{-1}, PP did not disperse well, leading to agglomerations and resulting in fibres adhere to each other (Fig. 4B & C). This significantly altered the appearance of the fabric and its tactile feel (Fig. 4D). The less favourable outcomes of coatings from pristine PP are easily comprehensive. As aforementioned, PP is almost insoluble in toluene at room temperature. After removing the submerged fabric from the hot PP/toluene solution, PP quickly crystallized from the absorbed solution, resulting in the formation of big and irregular agglomerations.

Ensuring robust durability is a pivotal aspect for coatings in practical applications. To enhance the bonding between OPP and the substrate, epoxy was utilized as an adhesive. In the dip coating process, the adhesive was directly introduced into the OPP/toluene solution. For spray coating, the adhesive in a toluene solution was initially sprayed onto the fabric before coating with the OPP/toluene solution. Fig. 5 shows the transition of superhydrophobicity for the coatings. For both samples (originally superhydrophilic) prepared by spray coating or dip coating, the water contact angles decreased to lower than 150° after 100 rubs, however, remained at higher than 145° after 200 rubs. On the fabric that underwent spray coating, the water contact angle reduced from 158° to 134° after 500 rubs (Fig. 5A). Meanwhile, the dip-coated fabric only showed a slight decrease in the water contact angle from 156° to 142° after 500 rubs (Fig. 5B). This disparity arises because dip coating ensured that all fibres were uniformly coated with OPP, whereas spray coating covered only the surface fibres with OPP. Scanning Electron Microscope (SEM) images (Fig. S2†) demonstrate that PP particles adhered to the fibres after the abrasion test, corroborating the coatings' durability.

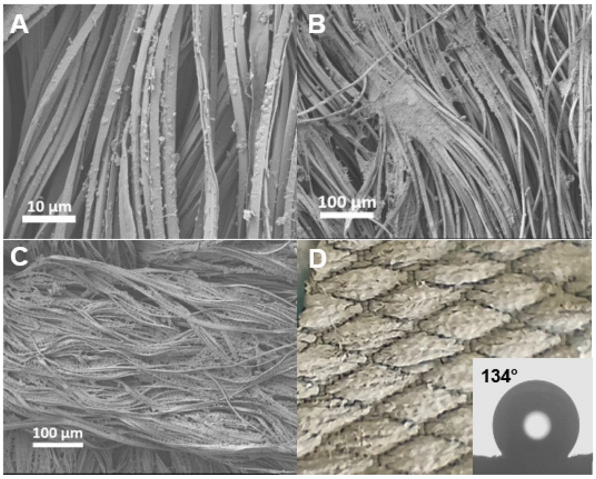

Fig. 4 Dip coating of fabric using pristine PP/toluene solutions at concentrations of (A) 1 mg mL^{-1}; (B) 5 mg mL^{-1}; (C) and (D) 10 mg mL^{-1}. The fabric was submerged into the PP/toluene solutions (80–110 °C) for one minute, taken out and dried in oven at 80 °C overnight.

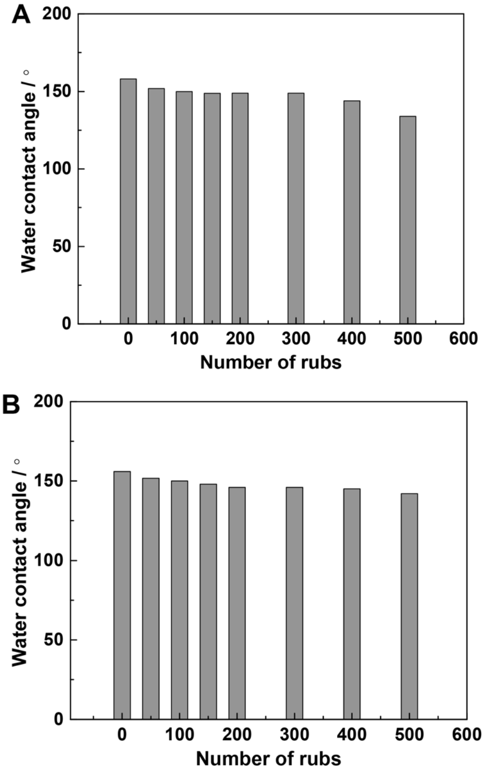

Fig. 5 Durability testing for OPP coated fabric. (A) Spray coated, pre-coated with epoxy/toluene of 10 mg mL^{-1}, then OPP/toluene of 10 mg mL^{-1}. (B) Dip coated with a toluene solution containing epoxy 5 mg mL^{-1} and OPP 20 mg mL^{-1}. Rub the fabric with tissue paper, one rub consisted of one back-and-forth abrasion.

In summary, our study demonstrates the enhancement of superhydrophobic coatings through the use of partially oxidized polypropylene (OPP). By using a straightforward molten-plastic method for oxidation, polypropylene (PP) underwent successful functionalization, resulting in improved solubility and distinctive coating features compared to pristine PP. Additionally, this method eliminates the requirement for high temperatures to dissolve polypropylene, making the current coating procedures more practical and safer for application on expansive substrates, effectively addressing a persistent challenge in PP coatings. The oxidation process is solvent-free, and the source of PP can be either fresh or recycled material, rendering this method environmentally friendly and sustainable.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), Institute of Bioengineering and Bioimaging (Biomedical Research Council), Agency for Science, Technology and Research.

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