Facile transformation of poly(phenyl ether) by C-H borylation: A viable method to new aromatic materials

*Daijun Feng,[1] Satish Mishra,[2] Nuwayo E. Munyaneza,[1] Santanu Kundu,[2] and Colleen N. Scott.[1]**

Dr. D. Feng, Dr. S. Mishra, N. E. Munyaneza, Prof S. Kundu, and Prof C. N. Scott
Mississippi State University, Mississippi State, MS 39762, USA.
1. Department of Chemistry, 310 President Circle
2. Dave C Swalm School of Chemical Engineering, 323 Presidents Circle

E-mail: cscott@chemistry.msstate.edu

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Abstract: C-H functionalization is a mild method for the direct transformation of inert C-H bonds to the desired product. Herein, the C-H borylation reaction is employed to convert poly(phenyl ether) (PPE) to the borylated analog (PPE-Bpin) for further functional group transformation into other products. We explored the conversion of PPE to an adhesive (PPE-ADH) by the combination of a PPE epoxy resin (PPE-ER) and a triamine. The GPC trace shows no noticeable degradation in the polymer's backbone following the C-H borylation and subsequent reactions. The PPE derivatives are all thermally stable with onset of degradation temperatures (T_d onset) over 350 ºC and degradation temperature (T_d) over 400 ºC; in comparison, PPE has a T_d onset at 344 ºC and T_d of 388 ºC. The white colored adhesive has a glass transition temperature (T_g) of 79 ºC, with an adhesion energy of 12 kJ/m^2 at room temperature due to cohesive fracture.

1. Introduction

High performance or engineering polymers have superb thermal stability, chemical resistance, and mechanical durability. As such, they find applications as adhesives, coatings, industrial fabrics, and structural components for the biomedical and aerospace industries.[1] Examples of high-performance materials include aromatic polymers containing esters, amides, ethers, and sulfones functionalities, which also makes them non-degradable under typical environmental conditions. Unfortunately, due to their tedious processing methods, high-performance polymers are usually expensive. Consequently, it is vital to upcycle these materials through the introduction of new properties to broaden their applications, add value, and extend their usage, while maintaining their original properties. For this process, modifying their structures through post-functionalization is a viable approach to introduce new properties to these polymers.[2]

Post-functionalization of aromatic polymers can damage the polymer and lead to diminished material's performance, when very harsh reaction conditions are used. The most common method to post-functionalize aromatic polymers is the electrophilic aromatic substitution (EAS) - (e.g., sulfonation,[3] bromination,[4] chloromethylation,[5] amidoalkylation,[6] alkylation[7] and acylation[8]). However, the highly reactive carbocation intermediate can lead to the destruction of the polymer's backbone through chain scission or other undesirable side reactions.[9] While there have been efforts to mitigate polymer degradation such as the use of alternative Lewis acids, or changing the order in which the reagents are added,[10] these approaches only reduce, but not prevent the side reactions. Apart from EAS, other reactions used to modify aromatic polymers include the radical functionalization with elemental halogens (Br_2 and Cl_2),[11] radical-mediated perfluoroalkylation,[12] and hypervalent iodine as a radical group-transfer.[13] Unfortunately, these reactions also produce highly reactive intermediates that cause chain scission resulting in the loss of the original polymer properties and increase the polydispersity (PDI or Đ). To achieve the desired outcome of upcycling of aromatic polymers without destroying the original polymer, a non-destructive method is needed to post-functionalize the polymers.

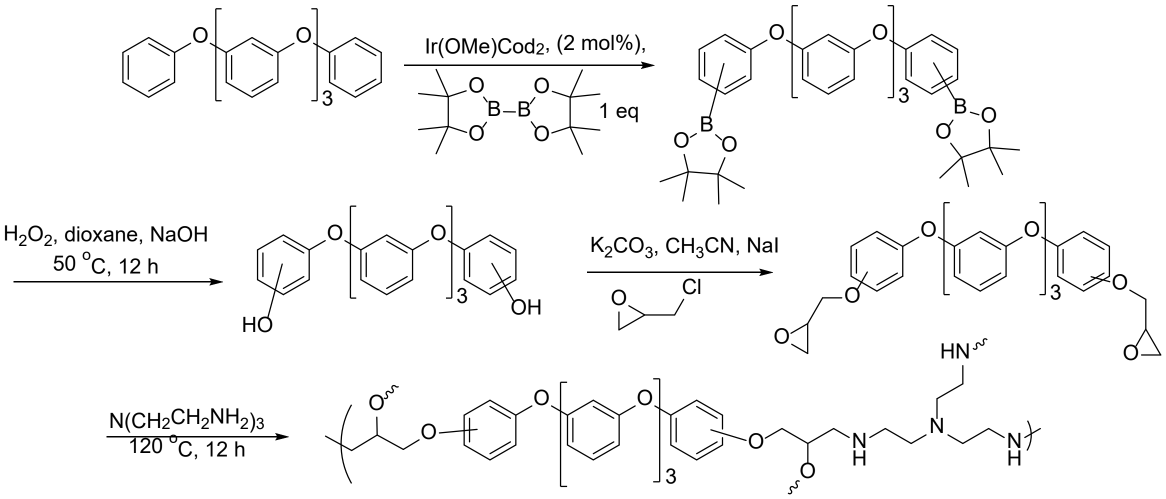
The transition-metal catalyzed direct functionalization of Csp^3–H and Csp^2–H bonds is being widely developed.[14] The direct C–H functionalization of aromatic groups to make both

C-C and C-heteroatom bonds is a powerful approach for post-functionalization of polymers, especially reactions that do not require directing groups. For example, the iridium-catalyzed aromatic C-H borylation reaction is a viable method to functionalize aromatic groups because it does not produce undesirable side reactions from highly reactive intermediates.[15] The regioselectivity is controlled by steric rather than electronics factors and the reaction tolerates a variety of functional groups including carbonyl, nitrile, and halide groups.[15b] An example of the mild condition of the C-H borylation was demonstrated with polystyrene (PS) by Bae and coworkers.[16] They showed that the tacticities (atactic, isotactic, and syndiotactic) and PDI of the polystyrene was retained during the reaction, verifying that the reactivity was on the benzene ring and not at the benzylic position.[16a] Bae's group also reported the post-functionalization of poly(arylene ether sulfone) (PSU) and determined that there was no noticeably change in the polydispersity following the reaction.[17] Leibfarth and co-workers developed a mild condition to incorporate a trifluoromethyl group unto polystyrene through a photocatalytically generated electrophilic fluoroalkyl radical.[18] Although a radical intermediate was generated during the reaction, there was no evidence of bond scission in the polymer's backbone.

Our group is investigating the C-H borylation of aromatic polymers such as poly(phenyl ether) (PPE) as a way to access new materials with outstanding physical and chemical properties. In spite of its extremely low molecular weight (M_n) (DP ~ 5-6 units) compared to conventional polymers, PPE is an optically clear oil with excellent thermal (T_d ~ 440 ºC – 465 ºC),[19] chemical oxidative,[19b] and ionizing radiation stability.[20] Its compatibility with most metals and elastomers makes it suitable for high-temperature applications in extreme conditions such as formulation for jet engine lubricants, diffusion pump fluids, high vacuum fluids, high-temperature hydraulic lubricants and greases, and heat transfer fluids.[20b,21] To investigate the transformation of PPE to a new material through the C-H borylation and further functional group transformations, we explored its conversion to an epoxy adhesive and determined its chemical and thermal properties. Herein we report our results.

2. **Result and Discussion**

PPE was subjected to the iridium-catalyzed aromatic C-H borylation reaction with bis(pinacolato)diboron ($B_2(pin)_2$) to give the boronate ester functionalized PPE (PPE-Bpin) (**Scheme 1**). The reaction was performed under neat conditions because no reaction occurred in solvents. The PPE-Bpin compound was oxidized to the phenolic group (PPE-OH) using a basic hydrogen peroxide solution, which was then converted to the epoxy resin (PPE-ER) with epichlorohydrin. The epoxy resin was used in the adhesive studies by reacting with a triamine hardener.



Scheme 1. Preparation of the PPE-ADH

After each functional group transformation, the products were confirmed by ^{1}H NMR spectroscopy (**Figure 1**). The PPE-Bpin compound was confirmed by the presence of the pinacol ester methyl groups that resonate around 1.5 ppm. The amount of Bpin incorporated into the polymer was determined by ^{1}H NMR to be 2 Bpin per PPE chain by the ratio of the pinacol esters' dimethyl groups to the aromatic proton peaks of the PPE (**Figure S1**). The PPE-OH compound was confirmed by the presence of the phenolic OH peaks that resonated at 9.64 and 9.83 ppm, suggesting that the phenolic OH groups are in different environments.

Additionally, the absence of the dimethyl groups of the pinacol ester also confirms the transformation to the PPE-OH. The PPE-ER was confirmed by the absence of the phenolic groups and the appearance of the methylene protons (3.8 – 4.0 and 2.7 – 2.8 ppm) and methine protons (~4.3 ppm). After the epoxy resin was cured with tris(2-aminoethyl)amine in a 3:2 molar ratio, the resulting white colored adhesive (PPE-ADH) was insoluble in DMSO and other common NMR solvents and therefore no ^{1}H NMR spectrum was obtained.

Once the structures of each PPE derivatives were confirmed, the PPE, PPE-Bpin, and PPE-ER were subjected to size exclusion chromatography (SEC) to determine the stability of the polymer's backbone during each reaction transformation. SEC analysis revealed a slight increase in the M_n after the C-H borylation as seen by the shorter retention time in the GPC trace (**Figure 2**). The M_n increased as expected from 410 to 630 Da with the addition of the

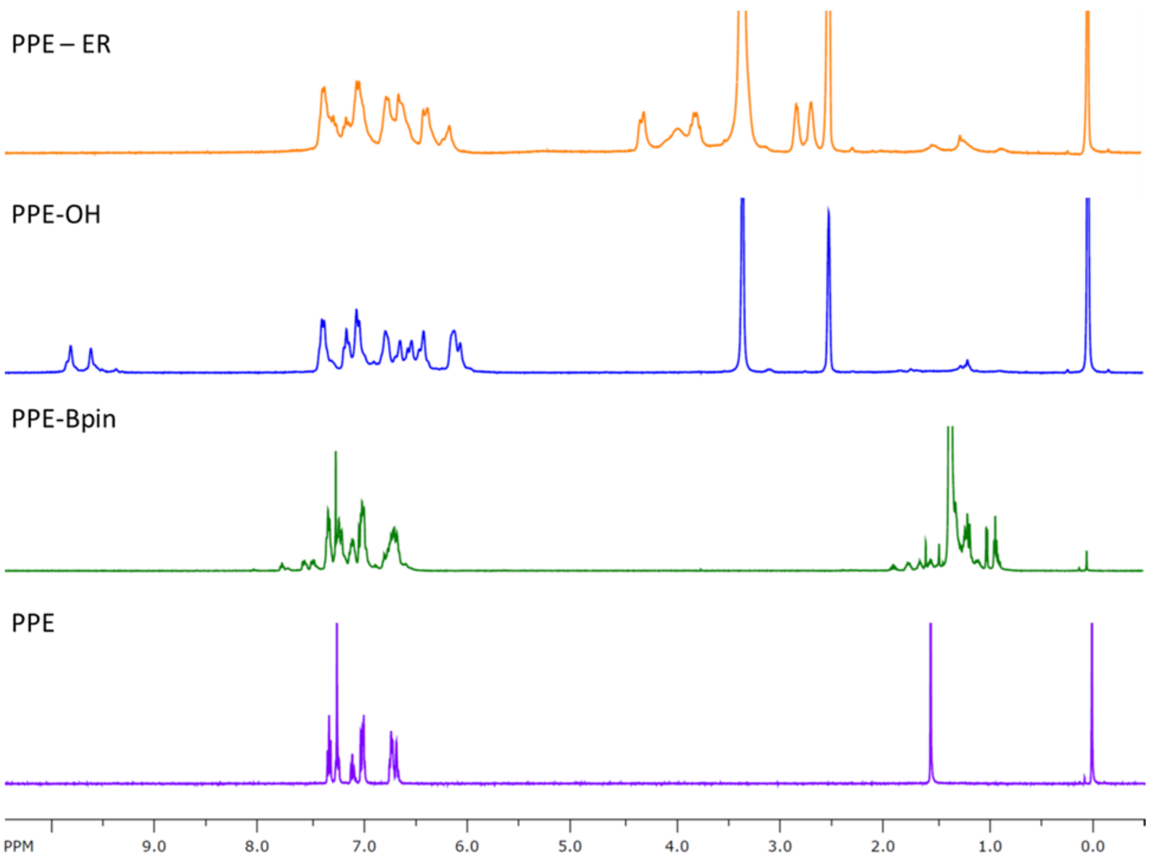


Figure 1. ^{1}H NMR of the different products of PPE

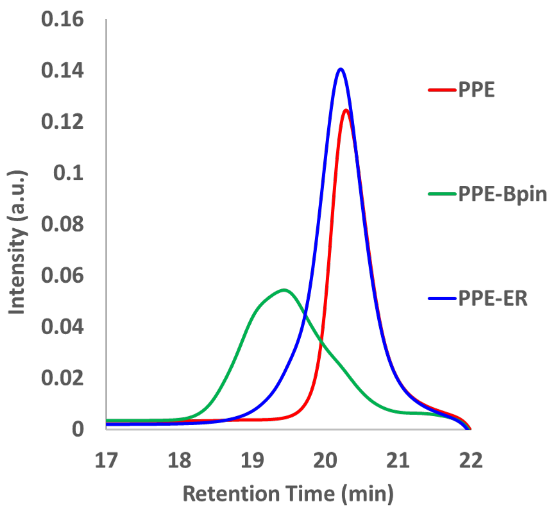


Figure 2. GPC data for PPE, PPE-Bpin, and PPE-ER

boronate ester (**Table 1**). Additionally, the PDI did not change very much with only a slight increase from 1.04 to 1.10, which is a result of the low functionalization of the polymer. Furthermore, additional transformation of the polymer did not cause an increase in the PDI, suggesting that the polymer maintained its backbone structure and full functional group transformation occurred during each reaction. For example, PPE-ER only gave a slight increase in the M_n over PPE (450 vs 410 Da, respectively) and a PDI of 1.07 (**Table 1**), which is expected with the low functionalization of epoxy groups. Unfortunately, we were unable to obtain SEC data for PPE-OH and the adhesive under the same conditions due to their insolubility in the THF solvent.

Table 1. TGA, DSC and GPC data for PPE and its derivatives.

Polymer	T_d onset (°C)	T_d (°C)	T_g (°C)	M_n (g/mol)	M_w (g/mol)	PDI
PPE	344	388	-	410	430	1.04
PPE-B	452	479	21	635	700	1.10
PPE-OH	331	395	24	-	-	-
PPE- ER	398	436	39	450	480	1.07
PPE-Adhesive	380	432	79	-	-	-

The polymeric products were also analyzed for their thermal stability. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) were obtained from each derivative and the results are reported in **Figure 3** and summarized in **Table 1**. The polymer maintained its thermal stability throughout the synthetic transformations and the polymeric

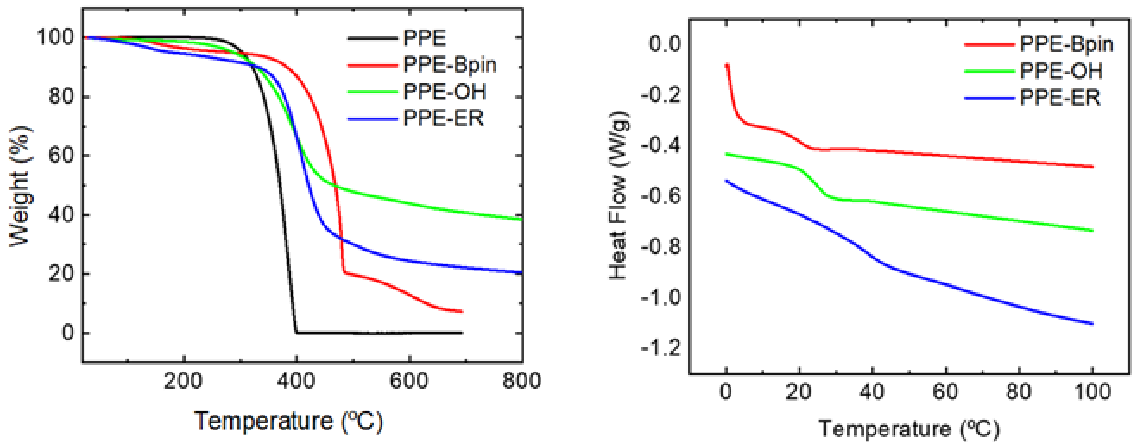


Figure 3. Overlay of TGA curves of PPE, PPE-Bpin, PPE-OH, PPE-ER (A) and DSC curves for PPE-Bpin, PPE-OH, PPE-ER (B).

derivatives were slightly more stable to thermal degradation compared to the starting PPE. For example, the degradation temperatures were higher than PPE for all the polymeric derivatives (**Figure 3A)**. While the T_d (onset) was determined to be over 300 °C for the polymers, 5 -10% of the polymers' mass was lost before reaching 300 °C. This small loss in mass is not observed in the original PPE, and could be a result of trapped reagents, or small decomposition of the functionalized PPE. The polymers' glass transition temperatures (T_g) increased moderately for PPE-Bpin, PPE-OH, and PPE-ER (21, 24, and 39 °C, respectively) (**Figure 3B**). The results of the thermal properties of PPE demonstrate that the thermal stability of PPE was maintained throughout the synthetic transformation.

Once it was determined that the polymer is thermally stable and did not degrade during the C-H functionalization and subsequent formation of the epoxy resin, it was converted to an epoxy adhesive. Consequently, PPE-ER was combined with tris(2-aminoethyl)amine in various ratios (**Table 2**) to produce a white colored adhesive (**Figure S4**). As the ratio of triamine to epoxy resin approaches 2:3, meaning a 1:1 molar ratio of the two components, the decomposition temperature of the adhesive increases to a maximum of 430 °C with an onset of degradation at 377 °C (**Figure 4A**). The T_g for cross-linked product of sample 5 was measured at 79 °C, which demonstrates that this adhesive is functional at temperatures slightly above room temperature (**Figure 4B**).

Table 2. Thermal analysis and adhesion strength data for the adhesive made from different ratios of amine: epoxy resin.

Samples	Composition (triamine:PPE-ER)	Molar ratio (triamine:PPE-ER)	T_d onset (°C)	T_d (°C)	Adhesion energy (kJ/m^2)
1	30%	3:10	325	388	2.3
2	50%	1:2	343	392	4.8
3	60%	3:5	377	413	6.1
4	75%	3:4	374	407	7.5
5	**100%**	**1:1**	**377**	**432**	**12.3**
6	120%	6:5	366	402	8.4
7	150%	3:2	368	403	6.0

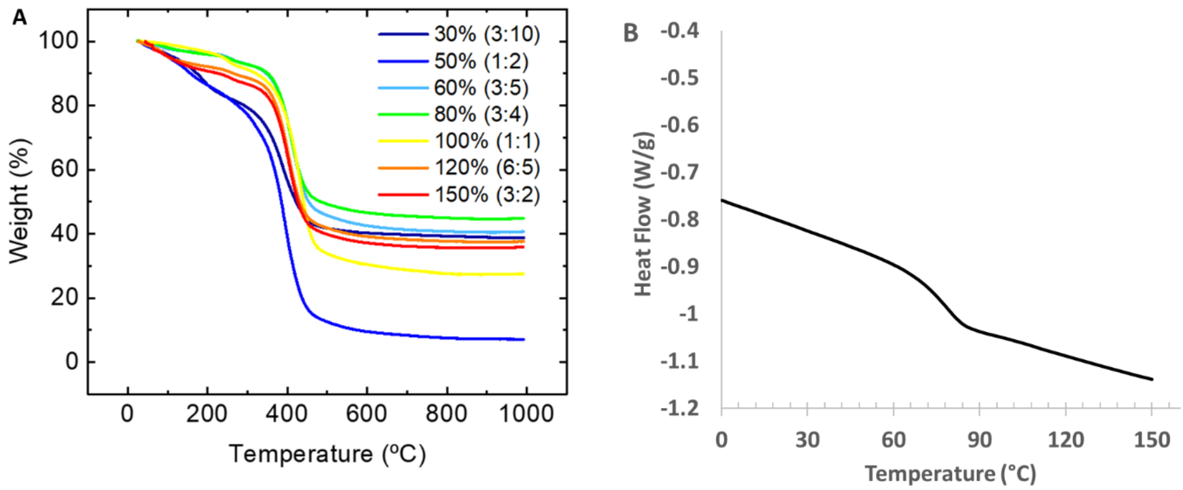


Figure 4. TGA curves of different ratios of PPE-ER;triamine (A); DSC curve of 1:1 molar ratio of PPE-ER:triamine (B).

The different ratios of PPE-ER: triamine were also analyzed to study the adhesion properties. Adhesion properties are generally denoted by two important parameters: the yield stress value or adhesive strength, i.e. the peak value of the stress before failure and the adhesive energy, which is determined by the area under the stress-displacement curve. The yield stress represents the maximum load that the adhesive can sustain before failure, while the fracture energy is the total energy absorbed before the adhesive fails; therefore, both yield stress and strain are represented. A nonlinear strain-stiffening trend was observed between the force and the displacement for all the samples (**Figure 5**). The adhesion energy increases gradually with an increase in triamine content, reaching a maximum of 12.3 kJ/m^2 when the molar ratio of the epoxy resin and triamine became 1:1 (sampe 5 **Table 2**) due to cohesive fracture. A decrease in the adhesion energy upon further addition of triamine can be attributed to the saturation of epoxy crosslinking site with triamine. A similar plot of the Force-Displacement is shown in Figure S5. These results demonstrate that the amine: epoxy molar ratio of 1:1 is optimum for good adhesion behavior. The adhesive energy for sample 5 is an order of magnitude higher than thermosetting anhydride cured epoxy resin incorporated with silica nanoparticles and MWCNTs (≈0.2 kJ/m^2),[22] epoxy resin modified with polystyrene-b-polybutadiene-b-poly (methyl methacrylate) block copolymer (≈0.3 kJ/m^2/),[23] and cellulose nanocrystal doped epoxy adhesives (0.38 kJ/m^2).[24] It is interesting to note that this moderate adhesive energy was obtained even with the low number of the epoxy unit and a small polymer chain. Figure 5 displays the maximum yield stress of ≈5 Mpa for sample 5, which is comparable to some

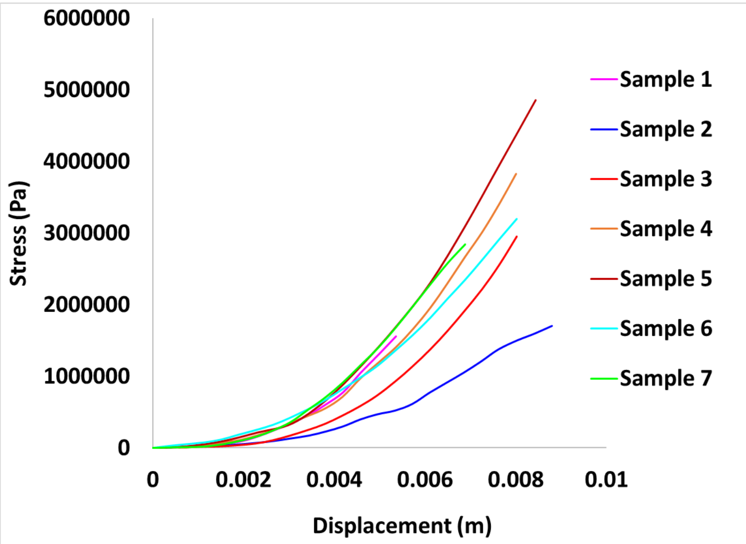


Figure 5. Stress/Displacement curves for adhesives made from different ratio of amine : epoxy resin. Percent amine are Sample 1 (30%); Sample 2 (50%); Sample 3 (60%); Sample 4 (75%); Sample 5 (100%); sample 6 (120%); Sample 7 (150%).

polyamide adhesives,[25] but lower than hyperbranched aromatic epoxy (≈15 MPa)[26] and aromatic copolyester thermosets (≈12-16 MPa)[27] signifying a modest load-bearing capability of our adhesive.

3. Conclusion

We have successfully demonstrated the use of C-H borylation reaction to functionalize PPE without destruction of the polymer's backbone. It was determined that the amount of Bpin incorporated into the polymer was 2 Bpin per PPE chain. Further functionalization of the PPE-Bpin to the epoxy resin also did not result in destruction of the polymer. Moreover, the thermal properties (T_d and T_g) of the PPE derivatives and the final adhesive were higher than the original PPE. Although we started from an oil, to our delight, we were able to obtain a white adhesive with an adhesion energy of 12 kJ/m^2, which correlates to an adhesive strength of 5 MPa at room temperature, even with a low original functionalization of PPE. We were pleased to achieve our goal of demonstrating the effective transformation of PPE into another useful material and were delighted to see that the adhesive energy was in the moderate range for polymers, even at the low functionalization of the polymer. This work demonstrates the feasibility of making new materials from existing ones, which is beneficial to the field of polymer upcycling.

4. Experimental Section/Methods

Reagents were purchased from Aldrich, Fisher Scientific, and Oakwood Chemicals and were used without further purification unless stated. Poly(phenyl ether) (Santavac-5P was purchased from Scientific Instrument Service. All solvents were reagent grade and used as such unless otherwise mentioned. Dry and degassed CH_2Cl_2, THF, and toluene were obtained from a VAC solvent purification system.

^{1}H NMR spectra were recorded on a Brüker AVANCE III 500 MHz spectrometer in deuterated solvents (Cambridge Isotope Laboratories, Inc.). Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvents as an internal standard and J values are expressed in Hz. The Peak multiplicities are abbreviated as follows:

s (singlet), d (doublet), t (triplet), m (multiplets). Differential scanning calorimetry (DSC) measurements were performed on TA Q20 under nitrogen flow cooling with heating/cooling rates of 10 °C/minute. The data was collected for the second heating cycle. Thermogravimetric analyses (TGA) was performed using a TA Q50 and decomposition trace was collected under a N_2 flow rate of 25 mL/min and ramping rate of 10 °C/min. Gel permeation chromatography was performed Tosoh GPC system with tetrahydrofuran as the mobile phase (flow rate 1 mL/min), calibrated with polystyrene standards. The adhesive measurements were performed on a Mark-10 machine with 10 kN load cell. The adhesive strength of polyphenylether epoxy resins were assessed by lap shear testing according to ASTM 1002 on rectangular aluminum 5-up substrates (Dimension: 5.125" L x 5.75" W x 0.063" T). Aluminum substrates were obtained from Alkemix Corporation (Lap Shear T2024T3B 5-up). The thickness of the films was determined by a Filmetrics profilm3d profilometer.

Synthesis of Compound PPE-Bpin

A pressure vessel tube (25 mL) was placed in a nitrogen-filled glovebox and charged with polyphenyl ether (1.10 g, 2.0 mmol), bis(pinacolato)diboron (500 mg, 2 mmol), (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (66 mg, 0.020 mmol) and 4,4-di-tert-butyl-2,2-bipyridine (52 mg, 0.020 mmol). The solution was heated at 80 °C in a sealed reaction vessel for 4 h. The crude product was purified by flash chromatography on silica gel using a 1:1 ratio of dichloromethane and hexane as the eluent to give the product (1.60 g) as a glassy solid in 99% yield. ^{1}H NMR (126) MHz, $CDCl_3$, δ): 7.19-7.23 (m, 3H), 7.08-7.12 (m, 2H), 6.98-7.03 (m, 5 H), 6.64-6.49 (m, 6H), 1.30-1.33 (m, 24H).

Synthesis of Compound PPE-OH

A 1:1 mixture of a 2.0 M aqueous solution of NaOH and 30% H_2O_2 (2 mL) at 0 °C was added to a 50 mL single-neck flask, which was charged with a solution of PPE-Bpin (800 mg, 1 mmol) in THF (5 mL). The mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was diluted with 15 ml water and extracted with 3 x 15 mL diethylether. The aqueous solution was acidified with 1 M HCl (5 mL) and extract with diethylether (3 x 15 mL). The combine organic layers was dried with anhydrous Na_2SO_4, concentrated under reduced pressure to give a yellow sticky product, which was purified by flash chromatography on silica gel with dichloromethane as eluent to give 520 mg of PPE-OH in 96% yield. ^{1}H NMR (126 MHz, DMSO-d_6, δ: 9.64-9.83 (m, 2 H), 7.41-6.07 (m, 18H).

Synthesis of Compound PPE-ER

Potassium carbonate (425 mg, 3.0 mmol) and epichlorohydrin (270 mg, 3 mmol) were added to a solution of PPE-OH (280 mg, 0.5 mmol) in CH_3CN. The flask was sealed and refluxed for 24 h. The reaction was cooled to room temperature, filtered, and extracted with ethyl acetate(20 mL). The combine organic layers was concentrated under reduced pressure and purified by column chromatography on silica get with (30% ethyl acetate: hexane) as the eluent to give 227 mg of PPE-ER as an oil in 74% yield. ^{1}H NMR (126 MHz, DMSO-d_6, δ: 7.40 -6.17 (m, 20H), 4.33-4.30 (m, 2H), 3.90-3.97 (m, 4H), 2.68-2.62 (m, 4H).

Adhesive Measurement:

Al 5-up panels were cleaned with a fresh Kim wipe soaked in acetone, followed by wiping with a second Kim wipe soaked with ethyl acetate. The panels were dried in air before used. A 10 mL solution of PPE-ER (**S1**) (200 mg/mL) and 5 mL solution of N1,N1-bis(2-aminoethyl) ethane-1,2-diamine (**S2**) (100 mg/mL) were prepared in THF. Seven vials were each charged with 250 μL of **S1**, followed by the addition of **S2** in the following volume: 30 μL, 50 μL, 60 μL, 80 μL, 100 μL, 120 μL, 150 μL as samples 1-7 respectively. Each vial was then diluted with 250 μL of THF. After stirring for 30 mins, the solutions were drop-cast onto the 1 cm x 1 cm region at the end of a clean Al 5-up substrate and then the solvent was evaporated at room temperature in a fume hood (10 minutes), followed by drying in a high vacuum desiccator for at least 2 hours. The average thickness of the films was 32 μm, which was measured with a profilometer. Pairs of substrates were overlapped in an antiparallel arrangement, clamped with two clams, and transferred to a pre-heated air oven at 60 °C overnight. To avoid the slippage of the sample, both sides of the Aluminum panel's free end were smeared with epoxy resin and allowed to cure for a day. The bars were then clamped in the crocodile grip of the Mark-10 machine. To apply the load, the top bar was stretched with ~ 0.25 mm/s while keeping the bottom bar fixed. Force vs. travel time was collected with 20 data points per second while stretching the bars. A sudden decline in the force was marked as the point of joint failure and the data up to peak force was used for calculating the adhesive energy. The adhesive energy of each test was calculated by estimating the area under the curve of force vs. distance. The energy was then normalized by the area upon which the adhesive was applied to obtain the adhesive energy.

Supporting Information

Supporting Information for TGA, DSC, and ^{1}H NMR in the form of pdf files is available from https://www.sciencedirect.com.

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Declaration of Competing Interest

The authors declare no known competing financial interests.

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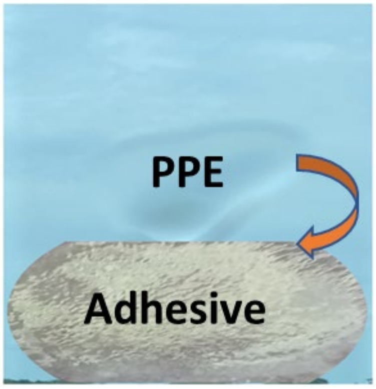

Data of availability

The raw/processed data required to reproduce these findings are available from the corresponding author on reasonable request.

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