Comprehensive Investigation of the Behavior of Polyurethane Foams Based on Conventional Polyol and Oligo-Ester-Ether-Diol from Waste Poly(ethylene terephthalate): Fireproof Performances, Thermal Stabilities, and Physicomechanical Properties

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1. INTRODUCTION

Polyurethane foams (PUFs) are reported as being one of the most versatile engineering polymeric foams, which are widely used in a broad variety of high-performance applications, ranging from acoustic insulation materials used in transportation to thermal and electrical insulation materials used in refrigeration technology, construction and building industries, furniture, and appliances, because of the lack of difficulty in handling and combination of exclusive properties, such as their light weight, low density, low thermal conductivity, low moisture absorption, high energy-absorbing ability, and great physicomechanical properties.1−3

In view of the increasing demand for PUFs, polymer scientists are exploring the replacement of petrochemical polyols with green, sustainable, and biorenewable polyols, such as vegetable oils and lignocellulosic biomass, which is currently under consideration. This ongoing movement could solve growing concerns caused by the utilization of petroleum feedstocks in polyol production, such as high energy consumption, environmental concerns, global warming resulting from uncontrolled human activities, depletion of fossil fuel reserves, and fluctuation in oil prices. Among the bioresource options, vegetable oils are one of the most promising contestants and are readily available for the production of biobased polyols. Traditional biobased PUF formulations have been prepared by the reaction between diisocyanates and vegetable oil-based polyols from soybean oil and castor oil,4,5 rapeseed oil,6 and sunflower oil.7 Recently, liquid polyols obtained from biomass feedstocks such as cork8 and bamboo,9 along with polyols from vegetable oils, have attracted great attention as suitable renewable materials for the production of biobased PUFs.

In addition, instead of using polyols from bioresources, the chemical recycling of polymers is also an effective way to replace fossil fuels for the chemical production of polyols with...
polyls recycled from plastic waste. Therefore, the proportion of 
virgin petrochemical-based resins that accumulate in the 
environment and/or end up being incinerated can be reduced 
with chemical recycling. Poly(ethylene terephthalate) (PET) is 
a semicrystalline polymer with high toughness, high strength, 
light weight, and transparency that is widely used to 
manufacture textiles, photographic and X-ray films, disposable 
beverage and soft-drink bottles, as well as materials for food 
packaging. PET does not directly affect the environment, but 
due to its massive volume of thermoplastics produced by the 
irresponsible utilization by society and its nonbiodegradability 
and chemical resistance, PET could be considered the most 
recyclable polymer among all thermoplastics.10 Therefore, 
there is an increasing demand for the development of recycling 
techniques and technologies, such as mechanical and chemical 
recycling, to successfully get PET waste back to its original 
state and/or generate valuable raw materials from which a new 
product can be made. Among these recycling methods, 
chemical recycling is the most effective and acceptable 
approach to totally/partially decompose PET wastes into 
monomers/oligomers for the formation of value-added 
polymers.1,13 The glycolytic depolymerization of PET is the 
most important chemical technique, in which glycols, such as 
ethylene glycol (EG), diethylene glycol (DEG), propylene 
glycol (PG), glycerol, or their mixtures, are commonly used as 
glycolysis reagents. Interestingly, in view of the glycolysis 
reaction, the transesterification reaction degraded PET into 
monomers for the production of virgin PET as well as 
promoted the formation of α,ω-dihydroxy terminal materials 
(polyls), which can be further reacted with other chemicals to 
generate unsaturated polyester resin,13–16 alkyd resin,17 and 
PUFs.18 Recently, there have been a few studies utilizing 
acrylic polyester polyls from glycolysis of PET to fabricate 
PUF. Aiga Ivdre et al.19 used a mixture of polyls from 
depolymerization of PET bottles using PG and from rapeseed 
oil to produce PUF. It was pointed out that the compression 
strength and compression modulus of the prepared PUF were 
higher than those of PUF obtained from commercially 
available polyls. Dong et al.20 have published a comprehensive 
work about recycling of postconsumer PET bottles into PUF. The 
authors used DEG as a glycolysis reactant and crude 
glycerol as a trifunctional additive. The results showed that the 
highest values of the compressive strength, density, and 
thermal conductivity were obtained at 15 wt % loading of 
crude glycerol.

PUFs are highly flammable materials because of their large 
surface area, open-cell foam structure, and elemental 
composition (carbon, hydrogen, oxygen, and nitrogen). During 
the burning process, combustible PUFs release a large amount 
of heat and toxic smoke/gases, such as carbon monoxide, 
hydrogen cyanides, and isocyanates, which have numerous 
adverse effects on human health and lead to many environ-
mental concerns when exposed to a flaming resource.21 Therefore, incorporation of flame-retardant (FR) additives into 
PUFs is the driving force toward the enhancements of fire-
resistant behaviors as well as thermal stability to meet special 
requirements and opens a wide range of applications that are 
currently obstructed because of the lack of anti-fire safety in 
the case of neat PUFs. Traditionally, FRs are mainly composed 
of halogenated additives, which make PUFs good FRs. However, these FRs are very harmful to people’s health and 
the environment because these halogen-based compounds will 
release corrosive and toxic smoke during burning. As a 
consequence, the development of nonhalogen and eco-friendly 
FRs is a recent research direction in the world. Thus, 
numerous research studies toward good fire-resistance PUFs 
by using halogen-free FRs in single use or a combination have 
been carried out.22–24

As halogen-free FRs, organo-phosphorus and phosphorus– 
nitrogen compounds exhibit a mode of FR action in the gas 
phase and/or condensed phase, indicating their outstanding 
fire protection. For example, we have already used triphenylphosphate (TPP) as a phosphorus-containing FR and 
aluimum trihydroxide (ATH), a commonly used metal 
hydroxide FR, to enhance the fire retardancy of rigid PUF 
fabricated from an oligo-ester-ether-diol, a new product of the 
glycolysis of PET wastes.25 However, TPP and ATH were 
added with a rather high loading (25–125 phr) into r-PUF to 
efficiently obtain a fireproof performance, corresponding to 
the achievement of the UL-94 V-0 ranking. Mengjuan Li et al.18 
studied the FR rigid PUF prepared from a bis(2-hydroxyethyl) 
terephthalate as a diol, a product of chemical recycling of PET 
waist from textile sources using EG and dimethyl methyl-
phosphonate (DMMP) as a phosphorus FR. The result 
showed that the limited oxygen index (LOI) value of PUF 
was increased to 27.69% with the loading of 18 phr DMMP. 
Recently, phosphorus–nitrogen-containing compounds have 
been identified as newly effective candidates for FRs that 
satisfy the specific requirements for anti-fire safety at low 
loading and govern the critical factors in environmental issues. 
Phosphorus–nitrogen FRs produced less toxic smoke when 
they were burning and presented higher thermal stability than 
phosphorus compounds alone.

The FR mechanism of phosphorus–nitrogen compounds 
generally acts in the gas phase through the formation of active 
free radicals (PO, PO, and HPO) that play an important 
role in trapping hydrogen and hydroxyl radicals (H and OH). 
These FRs also promote the generation of protective residual 
char on the material surface during pyrolysis, which prevents 
heat, oxygen, and flammable gases from attacking the interior 
polymer.

As a member of the phosphorus–nitrogen FR family, DAP 
has been used as an effective halogen-free FR for many 
inhertently flammable polymers as well as their compo-
sites.26–28 Like many phosphorus–nitrogen FRs, DAP 
avoides its fire-resistance through the synergistic effect of a 
physical mode and a chemical mode (Figure 1). Fuel dilution 
and cooling effects contributed to slowing down heat and fuel-
transfer processes during polymer combustion, while phos-
phorus active free radicals that transferred from phosphorus

![Figure 1. Strategy for obtaining fire-safe foams by incorporating DAP additive.](https://dx.doi.org/10.1021/acsomega.0c04555)
derivatives could deactivate H* and OH* radicals to cause combustion. In addition, the acceleration of char formation achieved via pyrophosphoric acid and other phosphorus-containing residual chars also contributes to enhancing the flame retardancy of the polymer materials. Taking advantage of its good compatibility, low toxicity, and good fire-resistance performance, DAP is highly expected to be a proper choice for fire-proof polymers.

Building on the abovementioned knowledge, in this study, the fire-resistance abilities and thermal stabilities of r-PUF prepared from an oligo-ester-ether-diol, a product of chemical recycling of PET* wastes using DEG as a glycolysis reagent and DAP as a phosphorus–nitrogen FR, were comprehensively investigated. Furthermore, the corresponding comparisons and characterization of the fire resistance and thermal stability performances of r-PUF and c-PUF (PUF derived from commercial polyol) in the presence of phosphorus–nitrogen compounds were first introduced in this investigation. Their physicomechanical properties were also studied. Based on the outcomes of our previous studies, a relatively high loading of TPP or ATH in the r-PUF formulation can be reduced via the utilization of DAP as a phosphorous–nitrogen-containing FR. The results of this study also proved that r-PUF/FRs obtained from PET-DEG glycolytic products not only meet all fire-resistance demands for polymer applications but also deal with reducing the accumulation of waste PET bottles in the environment and improving waste disposal.

2. RESULTS AND DISCUSSION

2.1. Structural Morphology of the Prepared Foams.
The foam density determined as the ratio of foam weight to its geometrical volume and cell morphology are important parameters that greatly affect foam fire retardancy and physical-mechanical properties. Figure 2 shows the microscopy images of the prepared PUFs. As given in Table 1, r-PUF exhibited a density of 71.0 kg/m³ and a mean cell size of 360 μm, whereas c-PUF formed with a lower density of 45.6 kg/m³ and a larger cell size of 436 μm, indicating that the r-PUF foam formed with fine cells under similar preparation conditions was denser than c-PUF. The different polyol types used in our study could be a reason for the density difference between the final r-PUF and c-PUF foams. The density of the PUF foams tends to increase by the addition of DAP into PUF and its increased content. It is quite common to find that adding a denser additive to the foam material could increase the foam density. Indeed, the foam density increased considerably from 71 kg/m³ for neat r-PUF to 83 kg/m³ and 106 kg/m³ for the r-PUF/DAP foams at 5 and 15 php DAP, respectively. Additionally, a density increase as the DAP content increased was observed for the c-PUF and c-PUF/DAP foams.

The presence of DAP at different contents in the reactant mixtures affected not only the density but also the cell structure of the final foams. For all neat PUF and PUF/DAP foams, the mean cell sizes tended to decrease by DAP incorporation, and the DAP content increased. A similar observation in terms of the density and cell size change for foams by the addition of additives was also reported in the literature.29,30 During the formation and growth of cells, DAP and most additives could play the role of heterogeneous nucleation sites, resulting in a reduction in the foam cell size. For instance, the mean cell diameters were remarkably changed from 360 μm for neat r-PUF to 288 μm for r-PUF/DAP15.

Notably, r-PUF/DAP at 15 php DAP formed an even cell structure with a high foam density of 106.2 kg/m³ and a mean cell size of 288 μm, whereas c-PUF/DAP at the same FR loading showed respective values of 55.4 kg/m³ and 427 μm (Table 1). Consequently, these considerable differences in density, mean cell size, and morphology between r-PUFs and c-PUFs were likely to affect the thermal behavior, combustibility, and mechanical properties of the PU foams.

2.2. Fire Performance. The two combustion tests of the vertical and horizontal burn methods were applied to determine the flammability of the PUF samples in this study. An extra surface combustion test for the bulk foam materials and the LOI measurement was also used to illustrate the efficiency of DAP in improving the flame resistance of PUF. The test results and detailed descriptions and evaluations of all prepared PUF samples are given in Table 1, and sample photos taken during the combustion tests are shown in Figures 3 and 4.

The PU foams are combustible materials that are severely burned during the tests. The c-PUF and r-PUF exhibited a similar outcome of completed combustion, which was followed by an evaluated failure and combustion at different rates. Indeed, r-PUF burnt at a burning rate of 120 mm/min, which was much slower than the speed at which c-PUF burned, 225 mm/min, indicating the better fire-resistance property of r-PUF. Similar to the horizontal burning test, Figure 3 shows rapid and widespread flame growth for c-PUF, whereas the combustion of r-PUF took place more slowly (Table 1). However, no dripping of any PUF specimens was observed during the tests. The LOI measurement evaluating the minimum oxygen percentage needed to maintain combustion for at least 3 min was used to illustrate the combustion test results. Principally, materials with LOI values below 21% are estimated to be highly combustible, whereas higher LOI values mean more oxygen is required to support combustion.31 The measured LOIs of r-PUF and c-PUF are comparable, with values of 20 and 19%, respectively, demonstrating their high flammability.

The incorporation of DAP into PUFs led to remarkable improvements in reducing the combustibility of the PUF and even achieved a fire self-extinguishing foam at proper FR loadings. Despite no rating being achieved at a small DAP amount of 5 php, r-PUF/DAP, burnt at a decreased rate of 80
mm/min, and the flame spread more slowly for r-PUF/DAP than for neat r-PUF, which had a burning rate of 120 mm/min (Table 1 and Figures 3 and 4). As expected, when more DAP was added into the foam, better fire resistance was observed. A significantly decreased rate of 29 mm/min was achieved for r-PUF with 10 php of DAP. Raising the DAP loading to 15 php, r-PUF/DAP15 expectedly exhibited the best fire-resistant performance among all PUF/DAP foams prepared in this study. Figures 3 and 4 clearly show that r-PUF/DAP15 specimens were successfully fire-resistant, with combustion stopping 5 s after the removal of the 2nd flame application.

The combustion test with the specimen dimensions of 50 × 50 × 25 mm³ applied to the foam material also presented a similar observation, with no sign of subsequent combustion and no severe damage to the tested specimen (Figure S1). Notably, the neat r-PUF sample was charred completely by its ignition under burning, whereas the specimens of r-PUF/DAP endured flame ignition and kept their original shapes, demonstrating the high efficiency of DAP in improving the flammability of r-PUF, as expected. Additionally, with an LOI value of 24%, r-PUF/DAP15 was classified as a self-extinguishing material, which agreed well with its combustion results.

The fire resistance and decomposition mechanism of DAP shares some similarities to other phosphorus–nitrogen intumescent FRs.32–34 Reportedly, initial DAP decomposition generally produces volatile gases of NH₃, H₂O, and phosphorus acid. While the generated volatiles can physically serve as dilute combustion fuels and cool down the combustion temperature, the produced phosphoric acid can transform into active phosphorous radicals in a gas phase to deactivate H⁺ and OH⁻ radicals during combustion. In addition, the contribution of the condensed phase via pyrophosphoric acid and other phosphorus-containing residual chars to the flame retardedness of the polymer material was also involved.

The FR performance of c-PUF/DAP improved. The c-PUF samples with DAP loadings of 15 and 30 php all passed the horizontal burning test, which was defined as no burning being sustained after 30 s of flame application. Although the use of the optimized DAP loading of 15 php resulted in the fire-extinguishing r-PUF sample, it was insufficient for c-PUF to meet any rating specification. The vertical specimens of c-PUF/DAP combusted up to the sample-holding clamp and

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Photographs of the c-PUF (a) and r-PUF (b) with and without DAP after 30 s of burning during the horizontal burning test.

![Figure 4](https://example.com/figure4.png)

**Table 1.** DAP Loading, Density, Cell Diameter, Combustion Test Results, and LOI Value of the Prepared r-PUFs and c-PUFs

| samples² | DAP loading (php)³ | density (kg/m³) | average cell diameter (μm) | horizontal burning (mm/min) | vertical burning | LOI (%) |
|----------|--------------------|-----------------|-----------------------------|-----------------------------|------------------|---------|
| r-PUF 0  | 71.0 ± 2.3         | 360 ± 44        | 120                         | No rating                  | 20               |
| r-PUF/DAP5 5 | 83.0 ± 1.3         | 401 ± 69        | 80                          | No rating                  | 10               |
| r-PUF/DAP10 10 | 86.1 ± 0.64       | 387 ± 78        | 29                          | No rating                  | 10               |
| r-PUF/DAP15 15 | 106.2 ± 3.8       | 288 ± 29        | 20                          | self-extinguishing (2 s/5 s) | 24               |
| c-PUF 0  | 45.6 ± 0.2         | 436 ± 43        | 225                         | No rating                  | 19               |
| c-PUF/DAP15 15 | 55.4 ± 1.4        | 427 ± 63        | 38                          | No rating                  | 22               |
| c-PUF/DAP30 30 | 58.1 ± 0.8        | 364 ± 58        | 31                          | No rating                  | 31               |

²r-PUF and c-PUF are represented for PU foams fabricated from the oligo-diol product of PET glycolysis and the commercial polyol, respectively. Subscripted numbers of 5, 10, 15, and 30 denote DAP loadings incorporated into the foams. ³Parts per hundred polyols by weight. *Evaluated according to ASTM D1622. ⁴Evaluated from microscopy images. ⁵The flames combusted up to the specimen-holding clamps. ⁶Not measured.
The cone calorimeter is a performance-based fire testing apparatus that correlates well with large-scale fire tests and is commonly used to determine the FR performance of materials.35 Heat release rate (HRR), peak heat release rate (PHRR), and total heat released (THR) of c-PUF/r-PUF with 15 php DAP loading were recorded and are shown in Figure 5. Both PHRR and THR of r-PUF/DAP15 were lower in comparison to those of c-PUF/DAP15. The HRR of c-PUF/DAP15 increased rapidly at the beginning of the test and reached the maximum value, PHRR, faster than that of r-PUF/DAP15. Moreover, the PHRR of c-PUF/DAP15 was also higher than that of r-PUF/DAP15 which resulted in a higher and sharper peak than r-PUF/DAP15. The lower PHRR and THR indicated that a higher residual char layer was formed during combustion and increased the FR properties of r-PUF/DAP15. Last, the duration for the combustion to complete for r-PUF/DAP15 increased rapidly at the beginning of the test and finally remained as a completely charred residual, even with a DAP loading reaching 30 php.

According to the previous performance discussion in the previous section, PUFs without and with 15 php of DAP are selected for Thermogravimetric analysis (TGA) measurements to investigate their thermal durability. The results, including the onset temperature, the temperature values of which are likely to slow down the combustion and flame spread of the PU foams. Additionally, a similar finding of the apparent density effect on the fire-resistance property of PUF modified by expandable graphite or ammonium polyphosphate was reported by Yang et al.39 Thus, high density leads to a lower flame spread rate.

2.3. Thermal Behavior and Fire-resistance Modes.

According to the fire performance discussed in the previous section, PUFs without and with 15 php of DAP are selected for Thermogravimetric analysis (TGA) measurements to investigate their thermal durability. The results, including the onset temperature, the temperature values of which are likely to slow down the combustion and flame spread of the PU foams. Additionally, a similar finding of the apparent density effect on the fire-resistance property of PUF modified by expandable graphite or ammonium polyphosphate was reported by Yang et al.39 Thus, high density leads to a lower flame spread rate.

Figure 5. HRRs and THRs of c-PUF/DAP15 and r-PUF/DAP15.

Figure 6. Correlation between the density and fire performance of PUF and PUF/DAP.
pyrolysis products and char residues. The TG and DTG curves in Figure 7 indicate that r-PUF derived from oligo-diol-containing aromatic compounds was much more thermally stable than c-PUF, as its two DTG peaks were significantly less intense and were observed in higher temperature ranges. c-PUF started to decompose at 240 °C and lost a mass of ca. 70% by the first degradation stage, whereas r-PUF foam was more stable, with a higher T_onset of 280 °C and a mass loss of ca. 50%. Furthermore, T_10, T_40, and the residue content at 800 °C of r-PUF were considerably higher than those of c-PUF, confirming that r-PUF has better thermal stability.

By comparing the TG and DTG curves of PUFs, the PUF/DAP foams also showed two decomposition stages in the temperature range from 200 to 600 °C overall but with a gradual weight loss at the second step instead. Moreover, it is obvious that T_onset, T_10, and T_40 of the two PUF/DAP samples were lower than those of neat PUFs because of the decomposition of DAP in the mixtures at the early stage. Indeed, r-PUF/DAP15 exhibited T_onset, T_10, and T_40 values of 262, 284, and 346 °C, respectively, which were all lower by approximately 18–42 °C than the corresponding temperatures of 280, 304, and 388 °C of r-PUF. On the other hand, the second degradation stage of PUF/DAP shifted to a higher temperature range and had a gradual weight decrease compared to the weight of PUF, which was believed to be a consequence of the early degradation of DAP. The r-PUF/DAP15 foam lost 60% of its weight at 587 °C and retained a charred content of ca. 33.6% at 800 °C, while these values for r-PUF were 514 °C and 24.9%, illustrating the charring acceleration of DAP. The thermal stability of c-PUF also changed by DAP incorporation, confirming the effect of DAP on the thermal behavior of the PU foams. The thermal stability and combustion behavior results obtained for PUFs agree with each other, as discussed in the above section.

Additional experiments in which the PUF and PUF/DAP15 foams were incinerated in a furnace at various temperatures of 300, 500, and 700 °C were carried out to further understand how the foams alter during combustion and degradation. Figures 8 and S2 and Table 3 present the appearance, weight loss trend, and remaining content of the as-prepared and incinerated foams recorded after each temperature, respectively.

Table 2. Thermal Properties of c-PUF and r-PUF with and without DAP

| Samples        | T_onset (°C) | T_10 (°C) | T_40 (°C) | T_60 (°C) | Char residues at 800 °C (%) |
|----------------|--------------|-----------|-----------|-----------|----------------------------|
| r-PUF          | 280          | 304       | 388       | 514       | 24.9                       |
| r-PUF/DAP15    | 262          | 284       | 346       | 687       | 33.6                       |
| c-PUF          | 240          | 279       | 330       | 354       | 13.7                       |
| c-PUF/DAP15    | 234          | 273       | 324       | 360       | 19.7                       |

Figure 7. Experimental TG and DTG curves of neat PUF and PUF/DAP.

Figure 8. Photographs of the as-prepared and incinerated foams at different temperatures.

A small residue content of 1.9% (Figure 8, Table 3) remained at 700 °C for r-PUF, whereas almost no char of c-PUF would be expected.
and TG analysis, outcomes are consistent with the above combustion discussion better shapes during incineration. The additional incineration as expected. Notably, the foams with 15 php of FR were more considerably higher than those for their corresponding PUFs, DAP15 foams clearly showed char contents of 12.5% for r-PUF remained as incineration was completed. The PUF/DAP after Incineration at Various Temperatures Table 3. Residues of r-PUFs and c-PUFs with and without DAP shown in Figure 10.

**Figure 9.** Compression stress–strain curves of PUF and PUF/DAP.

important factors that affects the physical and mechanical properties of PUFs. No DAP agglomeration was found in the microscopy images, which indicated good compatibility between DAP and PUF. Compared with the cells of the c-PUF system (Figure 2), those of r-PUF and r-PUF/DAP were smaller and more uniform in size and exhibited thicker cell struts, which may be responsible for the improvements in the compressive strength.

Filler particles act as nucleation sites for cell formation, and more cells start to nucleate at the same time. There is less gas available for their growth, which leads to a decrease in the size of the cell. Furthermore, the incorporation of unreacted DAP into the PUF causes an increase in the viscosity of the mixture, which inhibits cell growth and results in smaller cell sizes compared to neat PUF.43,44 PUFs are reported as being one of the most versatile engineering polymeric foams and are widely used in the construction and building industries. To avoid moisture-related problems in building components and enclosures, understanding moisture storage and transport phenomena is of crucial importance. Hygroscopic materials, such as foam materials, have the ability to adsorb and desorb moisture with variations in surrounding conditions.35 Figure 10 shows the sorption measurement sequences of the samples under 33, 55, and 75% humidity levels.

![Image](https://dx.doi.org/10.1021/acsomega.0c04555) 33059

**Figure 10.** Sorption measurement sequences of the samples under 33, 55, and 75% humidity levels. The adsorption and desorption isotherm results obtained for PUF/DAP showed almost no significant difference from neat PUF, and both are low moisture-capacity materials. The sorption isotherms of r-PUF and r-PUF/DAP exhibited normal hysteresis curves; however, the desorption curves of c-PUF and c-PUF/DAP showed higher losses in comparison with the adsorption curves. These losses could be due to the biodegradation of the materials in a high moisture environment. c-PUF was prepared from a commercial polyol that is hydrolyzable and results in smaller cell sizes compared to neat PUF.43,44 Meanwhile, rPUF was derived from PET containing an aromatic ring that is more thermally stable and has less hydroscopic stability. However, these conclusions need further study and discussion.

3. CONCLUSIONS

In general, the outcomes of this study showed that r-PUF with and without DAP showed significantly higher flame retardance, better thermal stabilities, and better mechanical properties than c-PUF with and without DAP. The c-PUF samples with DAP loadings of 15 and 30 php all passed the horizontal burning test, which was defined as no burning being sustained after 30 s.
of flame application, but the flames combusted up to the specimen-holding clamps in the vertical burning test. Meanwhile, the use of the optimized DAP loading of 15 php resulted in the fire-extinguishing r-PUF. r-PUF/DAP_{15} and c-PUF/DAP_{15} had LOI values of 24 and 22\%, respectively. The thermal properties of PUF/DAP_{15} foams were considerably better than those of PUFs, as expected. Notably, the foams with 15 php of DAP were more thermally stable in the high-temperature range and retained better shapes during incineration.

The fire-resistance performance of the r-PUF and c-PUF systems improved with increasing the apparent density. Low density gives rise to quick melting and to high flame propagation. Higher density means that the fire-retardant behavior is better because of a more compact burned layer and a lower flame spread. The compressive strength values of r-PUF and r-PUF/DAP were significantly higher than those of c-PUF and c-PUF/DAP. Compared with the cells of the c-PUF system, those of r-PUF and r-PUF/DAP were smaller and more uniform in size and exhibited thicker cell struts, which may be responsible for the improvements in the compressive strength. The sorption isotherms of r-PUF and r-PUF/DAP exhibited normal hysteresis curves, and the PUF systems were low moisture capacity materials.

4. EXPERIMENTAL SECTION

4.1. Materials. The diol and polyol reactants used in this study were prepared from two sources of a glycolysis product of wasted PET bottles and a commercial polyol, respectively. Methylene diphenyl diisocyanate (MDI) (Voracor CE101) with 31.0\% NCO, viscosity of 210 mPas at 25 °C, and density of 1.23 g/cm³ at 25 °C and commercial polyol (VOR-ACORCR765) were provided by Dow Chemical, Guangzhou, China. The FR DAP was purchased from Guangdong, China. Poly-methyl-alkyl-siloxane, used as a surfactant in PUF preparation, was purchased from BYK, Germany. Catalysts of triethylamine and dibutyltin dilurate used for PUF preparation were provided by Merck of Germany. All chemicals were used as received without any purification. Distilled water was used as a blowing agent.

4.2. Synthesis of Oligo-Diol from Wasted PET Glycolysis. The oligo-diol product is described in detail in our previous reports.47,48 Briefly, 48.0 g of PET flakes, 66.3 g of DEG, and 0.427 g of zinc sulfate were loaded into an Erlenmeyer flask covered with glass. The PET glycolysis reaction was conducted inside a microwave oven at a constant power of 250 W and a total operation time of 80 min. After a desirable time, the reaction mixture was allowed to cool to ambient temperature, the solid catalyst was removed by centrifugation, and the liquid mixture was obtained and kept in a dry environment to avoid moisture absorption for further applications. In this study, the oligo-diol product was then reacted with a commercial MDI in the presence of a DAP additive to fabricate fire-resistant PUFs.

4.3. Preparation of PUFs from Synthesized Oligo-Diol and Commercial Polyol Sources. PUFs were yielded by a reaction of diols and diisocyanates at a fixed ratio in an open mold. In a typical procedure, a mixture of oligo-diol or polyol with and without DAP (5−30 php), the surfactant (2 php), the blowing agent (1 php), and the catalyst (0.1 php) was evenly mixed by a mechanical stirrer at a rate of 700 rpm for 15 min. The mixture was then blended with MDI [oligo-diol or polyol/MDI:1.0/1.3 (g/g)] and stirred vigorously for 15 to 30 s before being transferred into an open mold for growth. A detailed description of the prepared samples is given in Table 1, where r-PUF and c-PUF denote the foams fabricated from the oligo-diol product of PET glycolysis and the commercial polyol, respectively.

4.4. Characterization of the Product. 4.4.1. Flammability Tests. The fire-resistance properties were evaluated by the horizontal and vertical burning and LOI tests. For horizontal burning, the specimen was held horizontally at one side, and the other side of the specimen was applied to a burner flame for 30 s. For vertical burning, the burner flame

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Figure 11. Adsorption and desorption of PUF and PUF/DAP.
was applied to the specimen for 10 s and then removed until flaming stops at which time the flame was reapplied for another 10 s and then removed. Five specimens with dimensions of 127 × 13 × 10 mm³ were tested for each sample. The burning rate and self-extinguishing time were recorded. The different efficiencies of the flammability behavior of c-PUF and r-PUF with and without DAP could be readily determined by using samples with test bar dimensions of 50 × 50 × 25 mm³ and burning them for 10 s. A LOI (Qualitest, USA) testing following ASTM D2863 was performed to determine the minimum oxygen concentration at which the materials could ignite to assess their fire resistance. Each sample was prepared with dimensions of 130 × 10 × 10 mm³. The LOI result is the average value of the five as-prepared specimens. The combustion behaviors of PUFs/DAP₁₁ were evaluated by a cone calorimeter (FTT-Fire Technology, East Grinstead, West Sussex, UK) according to ISO 5660-1 under the heat flux of 50 kW/m². Specimens with dimensions of 100 × 100 × 10 mm³ were wrapped in aluminum foil.

4.4.2. Thermal Stability Analysis. TGA was carried out on a TA instrument (TGA Q500 Universal V4.5A, New Castle, DE, USA) by heating from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

4.4.3. Cell Structure Characterization. The morphology of the foams was determined by using an optical MicroBlue MB.1152 Euromex microscope (Netherlands). The optical images were taken from different areas of each sample, and the average diameter of the cells was calculated according to ASTM D3576-98.

4.4.4. Physical and Mechanical Tests. The apparent density of foam samples with dimensions of 50 × 50 × 25 mm³ was determined as the ratio of the foam weight to its geometrical volume according to ASTM D1622, and the average value of at least three samples was obtained.

The compression test of r-PUF and c-PUF with and without a FR was measured by a universal testing machine (AG-X Plus, Shimadzu, Kyoto, Japan) according to ASTM D1621. The sample with dimensions of 50 × 50 × 25 mm³ was compressed with a loading rate of 2.5 mm/min in the direction parallel to the foam-rising direction.

Sorption isotherm tests of foam samples (50 × 20 × 10 mm³) dried in an oven at 60 °C for 24 h until reaching a constant weight were performed according to the EN ISO 12571 standard. These samples were put in a desiccator at different controlled relative humidity conditions of 33, 55, and 75%, which were prepared with different saturated salt solutions. When the moisture content of all samples reached equilibrium values, the samples were then moved to lower relative humidity conditions for the desorption test. Using this method, the adsorption and desorption isotherm curves were recorded, and the equilibrium moisture content by mass (g/g) was measured.⁴⁵,⁵⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04555.

Photographs of the foams during the combustion test and weight loss changes with the temperature of the foams during the incineration experiment (PDF)

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Notes

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