

Pulverized Polyurethane Foam Particles Reinforced Rigid Polyurethane Foam and Phenolic Foam

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ABSTRACT: Polyurethane consumption has been increasing in recent years, raising concerns about how to deal with the polymer waste. Post-consumer rigid polyurethane foams or polyurethane foam scraps (PPU) ground into particles were utilized to strengthen mechanical properties of rigid polyurethane foam (PUF) and phenolic foam (PF). Viscosity of prepolymer with PUF was measured and PPU was well dispersed in prepolymer, as observed by optical microscope. Microstructures and morphologies of the reinforced foam were examined with scanning electron microscope (SEM) while cell diameter and density were measured by Scion Image software. Universal testing machine was employed to optimize compressive properties at various weight ratios of PPU. Both PUF and PF with 5 wt % PPU, respectively, exhibited considerable improvement in mechanical properties especially compressive property. The compressive modulus of PUF with 5 wt % PPU was 12.07 MPa, almost 20% higher than pure PUF while compressive strength of PF with 5 wt % PPU reached 0.48 MPa. The thermal stability of the reinforced foam was tested by thermal gravity analysis (TGA) and the result shows no obvious impact with PPU. The decomposition temperatures of PUF with PPU and PF with PPU were 280°C, because PPU has relatively weak thermal stability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39734.

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INTRODUCTION

Polyurethane foam (PUF) synthesized from polyol and polyisocyanate exhibits excellent properties such as heat insulation, sound absorption, shock proof, good mechanical properties, simple process, low density, low weight, etc. Thus, it is widely used in construction, transportation, military, and other manufactures.^{1–3} As per Research and Markets, the global consumption of polyurethanes was estimated at 13,650.00 kilo tons in 2010 and expected to reach 17,946.20 kilo tons by 2016 and the service life of PUF is 5–10 years based on the application environment. So the waste of PU became a serious environmental problem since PUF is a thermosetting plastic which could not be recycled by simply melting and re-molding.⁴ With the increasing consumption of PUF, the disposal of PUF wastes draw public attention as traditional disposal methods such as landfill, incineration, and chemical degradation all have their apparent drawbacks, such as landfill occupies too much land because the density of PUF is low (0.02–0.05 g/cm³) and the natural degradation duration of common PUF is over 100 years⁵; incineration will produce polluted gas and smoke while chemical degradation costs large amount of money to reuse the foam, which is the main obstacle to the application.^{5–7} Scientists tried various novel methods to recycle polyurethanes. For instance, Howard et al. investigated a

soil microorganism for its ability to degrade polyurethane.⁸ Ghose and Isayev put recycled foam into a continuous ultrasonic reactor and used high-power ultrasound to decrosslink polymer, then blended the powder with the virgin polyurethane rubber.⁹ Asahi et al. conducted methanolysis investigation of a model polyurethane.¹⁰ But still mechanical recycling process was more practical due to low cost, high efficiency, and applicable to all kinds of PUF.⁵ Normally, PUF was ground into particles and then incorporated into some other materials as thermoset,¹¹ polyvinylchloride,¹² polypropylene,¹³ and rubber vulcanizate.¹⁴ However, there are still unsolved problems which blocked recycled PPU's adhibition. The particle of PUF possesses high polarity and agglomeration of these particles weakens the properties of composite materials. Although some researchers tried to modify the particles to avoid agglomeration, the high cost of modification once again became an obstacle. Compared to the limited improvement of properties with the increment of cost, these methods could never put into mass production and currently, the only method that makes widely use of the recycled PUF is preparation of low quality composite materials with unmodified PUF particles.

Unlike PUF, phenolic foam (PF) had good flame resistance, for instance, low flammability, low peak heat release rate, no

dripping during combustion, low smoke density, and nontoxicity, but its mechanical properties particularly brittleness restricted PF's application and scientists devoted to improve its toughness. Yuan et al. introduced polyurethane prepolymer as modifier mixed with phenolic resin and prepared modified PF, which enhanced mechanical strength of PF.¹⁵ This work motivated us to utilize PPU to improve compressive strength of PF at low cost. Thus, the application of reinforced foam could be more extensive and the service life of foam may be extended.

For our research, post-consumer rigid polyurethane foams (PPU) were utilized to reinforce PUF and PF. Since the composition of PPU is similar to PUF, there will be no difficulties in dispersion without modification of PPU particles. Thus PPU is added into prepolymer of PUF and after foaming, uniform composite foam should be prepared. PF also has high polarity, and the interaction between PPU particles and PF may lighten agglomeration that indicates PPU particles may be a good reinforcement for PF. Based on the above theories, PPU was recycled, ground to fixed size (80–150 μm) powder, and then mixed with prepolymer of polyurethane foam and phenolic resin respectively, the viscosity of mixture was tested and the dispersion of PPU was also studied by optical microscope. After foaming, the microstructure of foam was examined by SEM and also macro-defects were observed under optical microscope. Universal testing machine was employed to optimize compressive properties at various weight ratios of PPU. TGA was utilized to study their thermal properties. All the results show that our method not only solved the recycling problem of post-consumer rigid polyurethane foams or polyurethane foam scraps but also made significant improvement of PUF and PF in mechanical strength without sacrificing other performance. The advantages of our preparation of composite foam were simple, high efficiency, and low cost.

EXPERIMENTAL

Materials and Sample Preparation

Polymethylene polyphenylisocyanate (PAPI), polyether polyol GR-4110G [OH] = 420 mg KOH/g, surfactant H-310A, and catalyst DMCNA were all supplied by Shanghai Plastics Co. (Shanghai, China). Phenolic resin was purchased from Shanghai Flat Glass Factory, China. *N*-Pentane, which was used as blowing agent for polyurethane foam and PF, paratoluenesulfonic acid, and phosphoric acid were all analytical grade. The curing agent used for PF was a mixture of phosphoric acid, paratoluenesulfonic acid, and deionized water with a weight ratio of 1 : 2 : 2. PU particles were obtained by grinding post-consumer rigid polyurethane foam on emery cloth in laboratory, and the average size was 80–150 μm .

Pulverized rigid polyurethane foam scraps (PPU) were blended with polyol with a mechanical stirrer at 1000 rpm for 10 min. Then catalysts, surfactant, and blowing agent were added dropwise into the mixture and kept the stirrer speed at 2500 rpm for 5 min. After that, PAPI was added and stirred strongly at 4000 rpm for about 20 s and finally the mixture was poured into a mold and cured at 40°C for 2 h. The formulation for rigid polyurethane foam filled with PPU is listed in Table I and

Table I. Formulation for Polyurethane Foam with PPU

Ingredients	Weight ratio
Components A	
Polyol	100
PPU	0, 5, 10, 15
Catalysts	3.0
Surfactant	5.0–6.0
Blowing agent	10
Component B	
PAPI	130

the weight ratio of PPU is based on the total of polyol and PAPI is proportionate to polyol only. The density of the polyurethane foams was controlled at $55 \pm 2 \text{ kg/m}^3$.

Procedures for the preparation of PF were similar to those for rigid polyurethane foam. PPU was mixed with phenolic resin at 1000 rpm for 10 min. Then surfactant, curing agent, and blowing agent were dripped into the mixture and stirred at 2000 rpm for 5 min. Finally, the mixture was poured into a mold and cured at 80°C for 2 h. The formulation for PF filled with PPU is listed in Table II, in which the mass fraction of other ingredients is directly related to phenolic resin. The density of the PFs was controlled at $75 \pm 2 \text{ kg/m}^3$.

CHARACTERIZATION AND MEASUREMENT

Various amounts PPU mixed with prepolymers of PUF and PF and their viscosities were measured by SANSE rotary viscometer according to GB/T 12008.8-92.¹⁶ 201AD optical microscopy was employed to study the morphology of PPU's dispersion in both PUF and PF's prepolymers. Microstructure of foam was examined by Hitachi S-529 SEM using Scion Image software (Scion Corporation) to obtain the average cell size and cell density.¹⁷ Macro-defects were observed by optical microscope. The compressive strength and modulus of foams were determined by a universal testing machine (Sans CMT6104) at room temperature according to GB/T 8813-88¹⁸ test standard. All measurements were performed perpendicular to the foam's rise direction. The cross head speed was set at 2 mm/min and the foams were pressed up to 15% deflection. The thermal stability of various specimens was carried out using a Shimadzu DTG-60H thermo gravimetric analyzer with samples being heated from 50°C to 600°C under nitrogen atmosphere at a rate of 10 °C/min.

Table II. Formulation for Phenolic Foam with PPU

Ingredients	Weight ratio
Phenolic resin	100
PPU	0, 5, 10, 15
curing agent	8–9
Tween-80	4.0–5.0
pentane	6.0

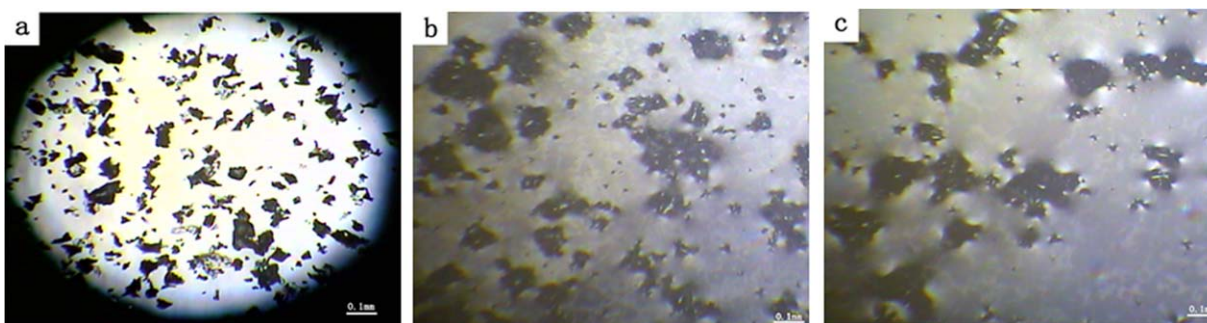


Figure 1. Morphology of PPU (a) dry powder, (b) in PUFs prepolymer, (c) in PF's prepolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Morphology of PPU

Optical microscope was employed to inspect the morphology of PPU, as shown in Figure 1. The size of dry PPU particles is about 100 μm , but the scale of PPU particles in polyol and phenolic resin is obviously much larger than the dry, due to good compatibility between particles and polymers. Polymers such as polyol and resin permeate into particles causing swelling of particles, which means the enlarging of particles' scale. Excellent dispersion of PPU particles in polyol and phenolic resin is also observed in Figure 1(b,c).

Viscosities of Polyol/PPU Blends and Phenolic Resin/PPU Blends

As we could expect, the more fillers mixed with resin, the viscosity increased dramatically, which will affect foaming process. A series of experiment was designed to measure the viscosity of the mixture of different weight ratios of PPU and resin under fixed temperature 25°C by a rotary viscometer. The results are shown in Tables III and IV, viscosity of polyol and phenolic resin increased intensively with the increasing PPU, especially when the weight ratio of PPU is 10%, the viscosity of polyol with PPU increased to 5480 mPa s from 1900 mPa s compared with polyol without PPU. And also when the amount of PPU was 15 wt %, viscosities of both polyol blends and phenolic resin blends exceeded 10,000 mPa s. With the increasing of viscosity, the flowability of mixture decreased and this may cause the macro-defects due to uneven foaming.¹⁹

Effect of PPU on Microstructures of the Foams

Figure 2(a–d) shows the morphologies of PUF with various amount of PPU. The cell diameter and density were measured by Scion Image software and the results are listed in Table V.¹⁷ All the cells represent polyhedral whether PPU was added or not but the scale of cell decreased due to addition of PPU. The cell diameter decreased as PPU amount increased until the amount exceeded 10 wt % and after that, the cell diameter

Table III. Viscosity of Polyol with Different Amount of PPU at 25°C

Sample	Polyol	Polyol/ PPU5wt%	Polyol/ PPU10wt%	Polyol/ PPU15wt%
Viscosity (mPa s)	1900	3400	5480	>10,000

remained virtually unchanged, which proved that the morphology of foam was affected by the addition of PPU dramatically. The reason is when foaming, the added PPU as nucleating agent generated more cells thus the cell density increased while after 10 wt %, the decomposing rate of blowing agent became the control step of foaming, thus the cell density remained unchanged, around 6×10^5 cells/cm³. The areas of triangle sections among the cell edges, marked in Figure 3, were also calculated and the results are listed in Table V. The area of triangle section was proportional to cell wall thickness and the thicker wall formed larger triangle area.²⁰ With the increasing of cell density, the cell wall became thinner due to the increase of superficial cell wall area and unchanged total amount of PUF. The scale of cell affected the performances of foam severely which will be discussed in the following part. And with the increasing of PPU, more defects of foams were observed under optical microscope due to the remarkable increase of viscosity of the mixture. The macro appearance of PUF with different amount of PPU is shown in Figure 4 and much more little holes can be observed in PUF with 15 wt % PPU than PUF with 5 wt % PPU.

PF with PPU represents the same properties as PUF with PPU and Figure 5 shows numerous defects in PF with 15wt% PPU compared with pure PF.

Compressive Properties

The compression test results of PUF (density: 55 kg/m³) are shown in Figure 6 and Table V. As the stress increases, the linear curve follows the Hooke's Law until the yield point, which defines the compressive modulus of the foam. After the yield point, the curve falls abruptly and this indicates that materials began to compress. The next was a sustained plateau region, which demonstrates the collapse of the foam.²¹ As shown in Figure 6 and Table V, the compressive strength values σ_m , compressive modulus E , and compressive stress at 10% strain σ_{10} of

Table IV. Viscosity of Phenolic Resin with Different Amount of PPU at 25°C

Sample	PR	PR/ PPU5wt%	PR/ PPU10wt%	PR/ PPU15wt%
Viscosity (mPa s)	500	1620	4900	>10,000

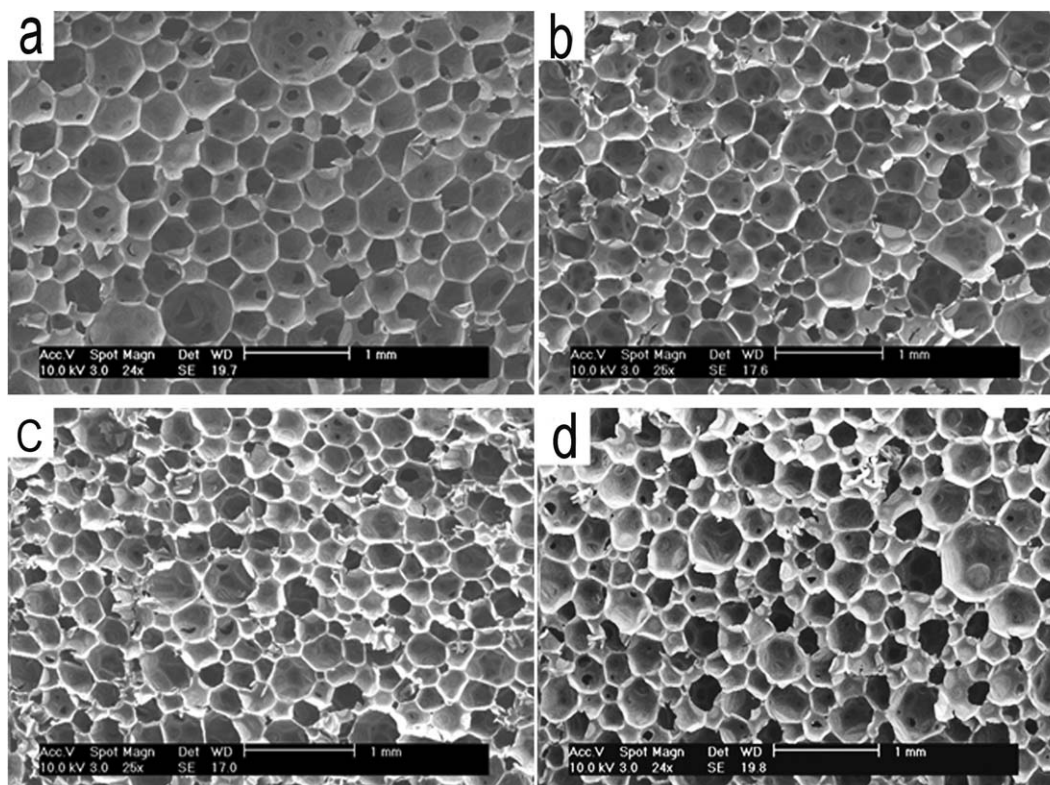


Figure 2. Micromorphology of PUF with various content of PPU by SEM (a) 0 wt % ($\times 24$), (b) 5 wt % ($\times 25$), (c) 10 wt % ($\times 25$), (d) 15 wt % ($\times 24$).

PU/PPU increased at the addition of 5 wt % PPU but decreased remarkably when the addition amount was above 5 wt %. For instance, compressive strength (σ_m) increased 12.4% at the addition of 5 wt % PPU but decreased to 0.31 MPa with 15 wt % PPU, compared with pure PUF and compressive modulus (E) increased slightly, by about 5%, when PUF mixed with 5 wt % PPU but decreased from 10.91 MPa to 10.34 MPa at 15 wt % PPU. These results can be explained by the microstructure and macromorphology of PUF, which was discussed in the previous part. Comparing cell diameter or cell density with compressive strength, as sample PUF with no PPU and 5 wt % shows, the increasing of cell density caused the increment of compressive strength, which indicated that the cell density affected mechanical property, while sample PUF with 10 wt % PPU and 15 wt % shows the compressive strength decreased even the cell diameter remain almost the unchanged. Triangle sections area which indicated the thickness of wall shows the same result. With the addition of PPU, the cell density did increase but the thickness of wall became thinner, which

decreased its mechanical property. This micromorphology also has macroscopic evidence that more macro-defects were observed with the increasing of PPU. So it was concluded that although the cell density do affected its mechanical property, the main enhancement mechanism should be the synergistic effect between PPU and PUF.

PF (density: 75 kg/m^3) with various amount of PPU were also tested and the results were pretty much exactly the same as PPU except there was no obvious yielding point observed during the experiment and fluctuate curve was recorded where PPU's curve sustained plateau region after the supposing yielding point. As shown in Figure 7 and Table VI, the optimum amount of PPU mixed with PF was 5 wt % where σ_m reached 0.48 MPa compared with pure PF and PF with other amount of PPU. The reason is because the addition of PPU induces better cells but increases defects simultaneously which agrees with the explanation on compressive test results of PUF with PPU.

Table V. Cell Diameter, Cell Density, and Compressive Properties of Different Amounts PUF Filled with PPU

Sample	Cell diameter (μm)	$N_c \times 10^{-5}$ (cells/ cm^3)	Triangle sections area (μm^2)	σ_m (MPa)	E (MPa)	σ_{10} (MPa)
PUF	378.4	1.53	914	0.36	10.91	0.31
PUF/PPU5wt%	325.6	2.34	582	0.41	12.40	0.33
PUF/PPU10wt%	246.2	6.15	435	0.34	11.03	0.29
PUF/PPU15wt%	252.4	6.07	421	0.31	10.34	0.26

N_c , cell density; σ_m , compressive strength; E , compressive modulus; σ_{10} , compressive stress at 10% strain.

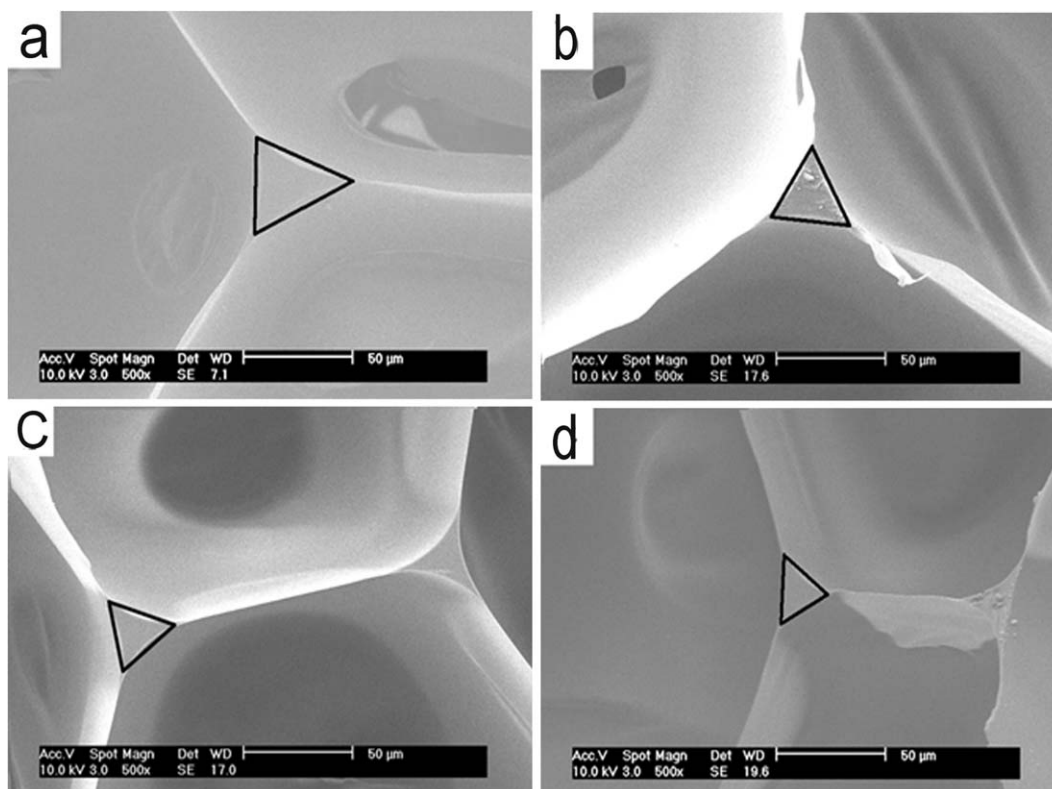


Figure 3. Micrographs of cell edges of PUF with different contents of PPU by SEM (a) 0 wt % ($\times 500$), (b) 5 wt % ($\times 500$), (c) 10 wt % ($\times 500$), (d) 15 wt % ($\times 500$).

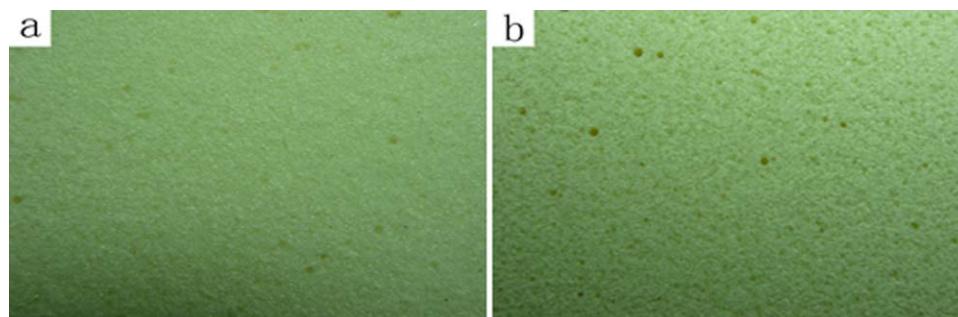


Figure 4. Macro appearance of PUF with different contents of PPU (a) 5 wt %, (b) 15 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

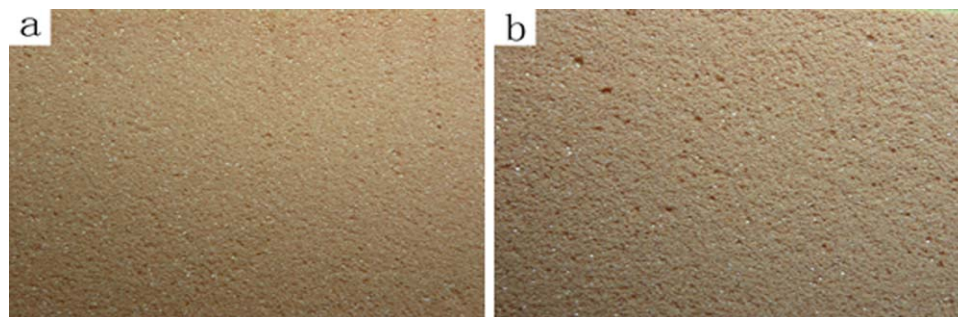


Figure 5. Macro appearance of PF with different contents of PPU (a) 0 wt %, (b) 15 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

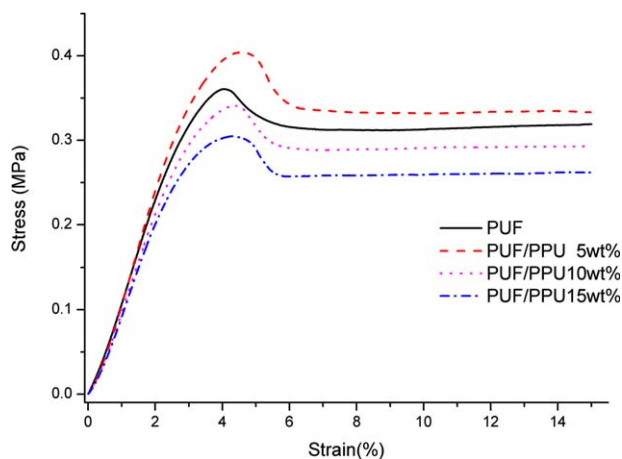


Figure 6. Compressive stress–strain curves of PUF with different contents of PPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

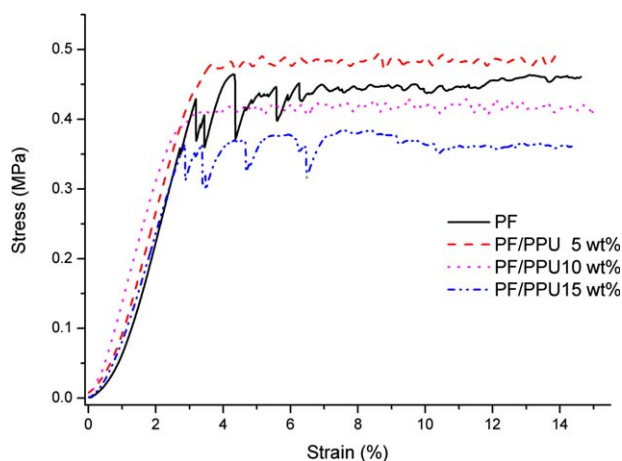


Figure 7. Compressive stress–strain curves of PF with different contents of PPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties

TGA measurements were carried out to obtain information on the thermal stability of PUF and PF with and without PPU, and the results are shown in Figures 8 and 9. From Figure 8, PUF with various amounts PPU were stable until 280°C, whose weight loss was no more than 5%. When the temperature was over 280°C, the foam began to degrade. Since PPU and PUF have same composition, the degradation curve did not have any

Table VI. Compressive Properties of PF with Different Contents of PPU

Sample	σ_m (MPa)	E (MPa)
PF	0.43	18.37
PF/PPU5wt%	0.48	17.44
PF/PPU10wt%	0.41	17.28
PF/PPU15wt%	0.36	15.7

σ_m , compressive strength; E , compressive modulus.

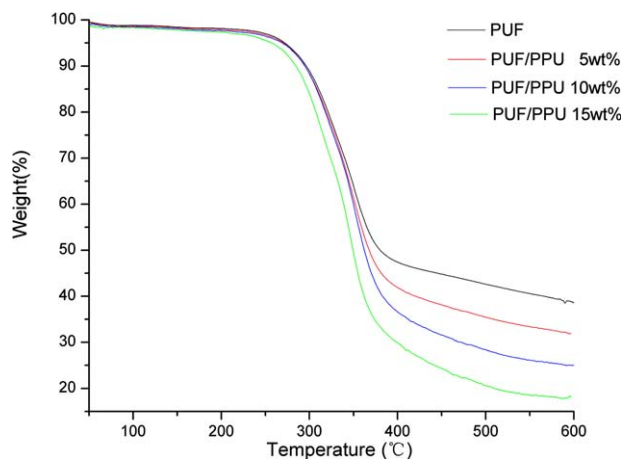


Figure 8. TGA of polyurethane foams with different amount PPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

steps. So it was proved that the addition of PPU did not affect thermal stability of PUF and the added PPU was mixed with PUF to form a homogenous phase, which indicated that there was strong interaction between PPU and PUF.

Pure PF was relatively thermally stable up to 530°C, as shown in Figure 9, while PF with different amount PPU firstly degraded at 330°C–430°C due to the decomposition of polyurethane component (PPU), and the maximum decomposition temperature was at 527°C just slightly lower than 530°C, which indicated there was no obvious interaction between phases of phenolic and polyurethane.

CONCLUSIONS

To recycle polyurethane and improve mechanical properties of polyurethane foam and PF, the post-consumer rigid polyurethane foams or rigid polyurethane foam scraps (PPU) were ground into particles and then mixed into polyurethane foam and PF, respectively. PPU was well dispersed in phenolic resin

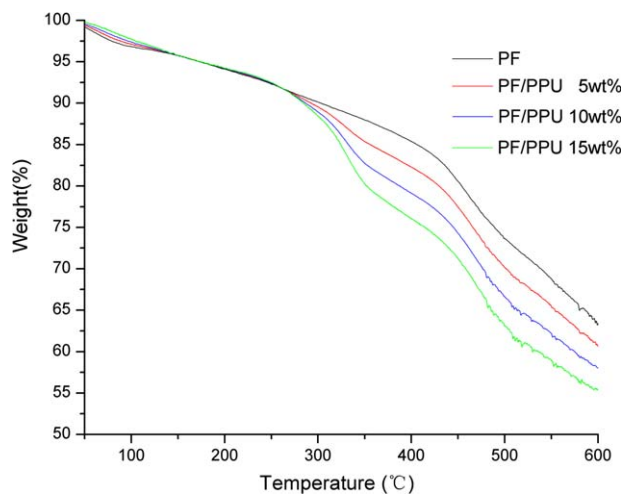


Figure 9. TGA of PFs with different amount PPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and polyol and the addition of PPU increased the compressive property and did not have significant negative impact on the thermal stability. However, the excessive addition of PPU resulted in the increase of prepolymer viscosity dramatically, affected the foaming process, caused macro-defects, weakened cell structure, and finally reduced the mechanical properties. The optimum amount of PPU with PUF and PF is 5 wt % whose microstructure exhibits best cell and the morphology exhibits less macro-defects. The reinforced foams show not only good compressive property but also thermal stability.

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