

Highly flame retardant green composites using seashells

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Using ground seashell as a biofiller in an acrylonitrile butadiene styrene copolymer increases flame retardance.

Increasing seafood consumption has led to generation of a large volume of seashell waste that is essentially treated as useless and dumped onto reclaimed land or into coastal waters. Seashells are mainly composed of calcium carbonate (CC), mineral oxides, and organic materials.^{1,2} When decomposing, seashells produce gases whose odor and toxicity are hazardous to human health. Because CC is one of the most commonly used inorganic fillers, recycling seashells offers a means of using this material productively, for example, as soil conditioners, low-cost absorbents, and as biofiller in polymers. The aim of the work described here is to develop a green composite from acrylonitrile butadiene styrene copolymer (ABS) using a ground biofiller derived from seashells collected from the seashore. ABS is a widely used thermoplastic polymer because of its good chemical resistance, mechanical properties, and processing advantages. However, the polymer is easily flammable. Consequently, we decided to investigate the flame-retardant properties of ABS composites containing CC produced from seashell waste.³ To our knowledge, these properties have not yet been reported in the literature.

We made the biofiller by washing the seashells to remove any residual meat, soaking them in 4% sodium hydroxide solution for 48h to remove any further impurities, further washing with distilled water, drying, and finally grinding with a high-speed mill. The resulting seashell particles had a diameter of around 2.5–3.2 μ m. We then dried ABS, commercially supplied CC (CaCO₃), ground seashells, and tannic acid in a cycling oven for 4h prior to mixing. Finally, we blended ABS with the filler powder at various contents by melt compounding to obtain the composites.

We determined the composition of both the filler and the composites, and we examined the effect of adding the filler to ABS in terms of dynamic mechanical, tensile, and flame-retardant properties. The composition of the biofiller was determined by x-ray fluorescence (XRF) to be largely composed of CC (~96.2%), the remainder being other mineral oxides such as iron oxide (Fe₂O₃). We also fabricated

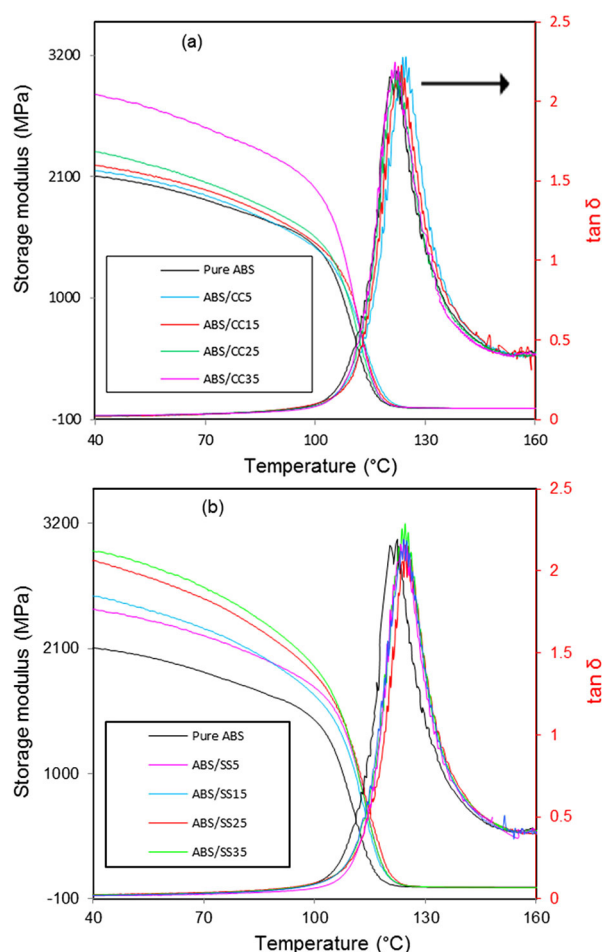


Figure 1. Evaluation of storage modulus and loss modulus/storage modulus ($\tan \delta$), which is a measure of energy dissipation potential of a viscoelastic material. (a) Composites of acrylonitrile butadiene styrene copolymer (ABS) and calcium carbonate (CC). (b) ABS and seashell (SS) composites in terms of the filler content obtained by dynamic mechanical analysis (DMA) in tension mode. Addition of a ground seashell biofiller increases the storage modulus and glass transition temperature.

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Table 1. Combustion data of ABS/CC and ABS/SS composites obtained by cone calorimetry at a heat flux of 35kW/m². ABS/SS25, a sample with 25% SS filler, showed the best combination of flame-retardant properties. TTI: Time to ignition. Av. HRR: Average heat release rate. PHRR: Peak heat release rate. The percentage reduction of PHRR compared to pure ABS is also given. THR: Total heat release. AMLR: Average mass loss rate. FPI: Fire performance index, which is the ratio of TTI to PHRR. Seashell-derived composites are better than both pure ABS and those containing CC, due to trace mineral oxides, which can enable the formation of a heat-insulating ceramic layer when burned.

Sample	TTI (s)	Av. HRR (kW/m ²)	PHRR (kW/m ²) (% reduction)	THR (MJ/m ²)	AMLR (g/s m ²)	FPI (s m ² / kW)
Pure ABS	22 ± 4	254 ± 7	696 ± 10 (0)	77	17.6	0.03
ABS/CC5	30 ± 3	218 ± 5	569 ± 8 (-18)	75	16.6	0.05
ABS/CC15	31 ± 5	207 ± 8	450 ± 11 (-35)	81	16.8	0.07
ABS/CC25	32 ± 3	208 ± 6	419 ± 7 (-40)	74	14.3	0.08
ABS/CC35	24 ± 5	202 ± 8	430 ± 9 (-38)	73	14.1	0.06
ABS/SS5	32 ± 4	237 ± 5	532 ± 6 (-24)	94	20.5	0.06
ABS/SS15	34 ± 4	226 ± 9	506 ± 10 (-27)	72	17.7	0.07
ABS/SS25	46 ± 3	234 ± 6	385 ± 8 (-45)	85	12.6	0.12
ABS/SS35	33 ± 5	252 ± 5	368 ± 7 (-47)	96	11.9	0.09

composites using commercial CC as a comparison. Dynamic mechanical analysis (DMA) was used to determine the viscoelastic behavior of the composites. DMA data showed that addition of low amounts of seashell biofiller to ABS increases the storage modulus (E'), and the glass transition temperature (T_g): see Figure 1. This improvement in E' and T_g values may be attributed to a restriction of chain mobility, which could be due to good matrix-filler interactions.

We also examined the mechanical properties of ABS/CC and ABS/seashell (ABS/SS) composites with different filler concentrations using a tensile testing machine (see Figure 2). The tensile strength of

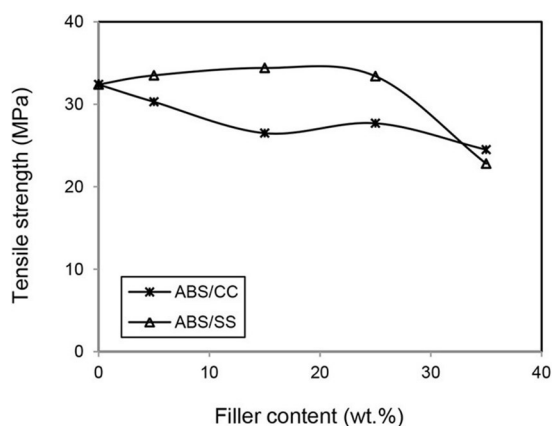


Figure 2. Tensile strength of ABS/CC and ABS/SS composites as a function of filler content.

the ABS/CC composites decreased with addition of the CC filler. For example, at 35wt% of CC the tensile strength was 24% lower than the value recorded for pure ABS. We attribute this to particle aggregation and poor interfacial adhesion of the filler-polymer matrix. In contrast, tensile strength improved by addition (up to 25wt%) of seashell-derived CC filler. We attribute this improvement to the good dispersion of SS powder in the polymer matrix, and a strong interaction between the ABS matrix and SS particles. However, the lower tensile strength of ABS/SS above 25wt% SS loading may be associated with inevitable aggregation of the SS powder at higher filler concentrations. We observed a good correlation between the tensile strength and the storage modulus data in the case of ABS/SS composites.

We evaluated the flame-retardant properties of the ABS/CC and ABS/SS composites by cone calorimetry (see Table 1). The heat release rate (HRR) curves obtained with an external heat flux of 35kW/m² are shown in Figures 3 and 4 for CC and SS composites, respectively. The time to ignition (TTI) is the time to sustain ignition of the sample. Pure ABS has the shortest TTI (22s), making it easy to ignite under the correct heat flux.⁴ We find a rather sharp peak heat release rate (PHRR) value of 696kW/m² after 135s for pure ABS, indicating that there is little char remaining (see Figure 3). The ABS/SS composites have a longer time to ignition compared to the ABS/CC composites. A significant reduction in PHRR (45%) and the longest TTI measured (46s) was observed for the ABS/SS25 composite, although the total heat release (THR) increased. The reduction in PHRR indicates formation of a ceramic layer as the

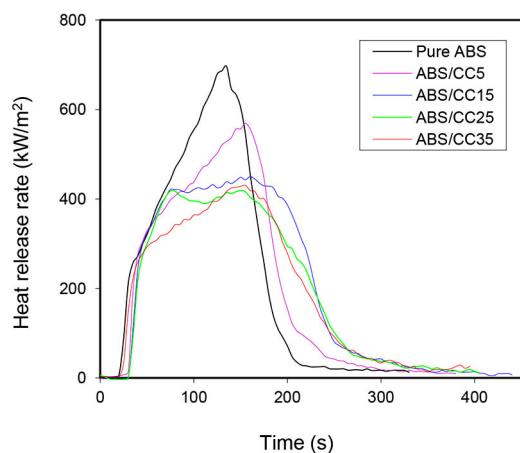


Figure 3. HRR curves of ABS/CC composites at a heat flux of 35kW/m^2 . Formation of a cracked insulating ceramic layer lowers the HRR slightly.

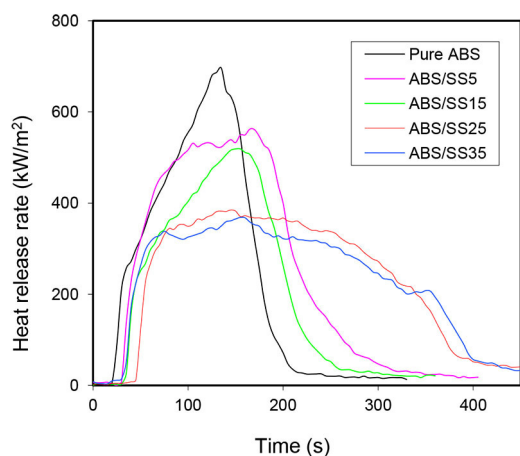


Figure 4. HRR curves of ABS/SS composites at a heat flux of 35kW/m^2 . Formation of a compact and crack-free insulating ceramic layer lowers the HRR for samples containing 25 or 35% SS.

material burns that acts as an insulating barrier between the fire and composite, preventing the exchange of heat and flammable polymer fragments.⁵ We find this ceramic layer to be much more cohesive, very compact, and lacking in surface microcracks in ABS/SS25 samples. This may be attributed to the presence of both organic and mineral oxides such as Fe_2O_3 in the seashell, as demonstrated by XRF analysis. These impurities play a significant role in the suppression of polymer oxidation during combustion by aiding the formation of the ceramic layer.⁶

Composites containing 25wt% CC have less useful properties. The ABS/CC25 composite exhibits a reduction on peak HRR of 40% with a time to ignition of 32s. The fire performance index, defined as the ratio of TTI to PHRR, is used to measure the flame efficiency of materials. The largest value, indicating the highest flame retardancy for the CC composites, is 0.12, observed for the ABS/SS25 composite. The reduced PHRR suggests that a cohesive char layer is formed during combustion. However, it contains surface cracks.

In summary, we have produced a set of composites consisting of acrylonitrile butadiene styrene copolymers combined with either CC or ground seashells as fillers. The best material properties were found for 25wt% filler, and the SS composites outperformed the CC composites, due to formation of a heat-insulating crack-free surface ceramic upon heating. Our next steps are to develop more novel green composites from other natural biofillers combined with different polymers.

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