

Functionalizing gum arabic for adhesive and food packaging applications

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A new bio-based hydrophobic gum arabic-based copolymer is an excellent adhesive and improves the properties of polylactic acid for potential food packaging applications.

In recent years, bio-based polymers such as cellulose, chitosan, and gum arabic have attracted substantial interest because they are environmentally friendly, non-toxic, biodegradable, and have low carbon footprints. Currently, the potential applications for bio-based polymers are limited as they tend to be hydrophilic in their natural forms. However, if the polymers can be converted to hydrophobic materials, their potential applications increase dramatically. Here, we discuss our recent work on the modification of gum arabic (GA)—a natural polymer sourced from various acacia tree species—with oligo(L-lactic acid) (OLLA) using an in situ polycondensation reaction that does not require a catalyst or initiator, and produces a hydrophobic bio-based polymer suitable for adhesive and packaging applications.^{1,2}

We synthesized the gum arabic-*graft*-oligo(L-lactic acid) (GA-g-OLLA) copolymer by microwave irradiation (240W) of gum arabic and lactic acid in an inert atmosphere at 130°C for 45min, resulting in the grafting of OLLA chains onto ~40% of the GA polymer backbone. This method converts the hydrophilic GA polymer into a hydrophobic GA-g-OLLA copolymer through capping of the hydrophilic amino and hydroxyl functional groups present in GA molecules, which was confirmed using proton nuclear magnetic resonance spectroscopy: see Figure 1(a,b). Furthermore, the GA-g-OLLA copolymer has a number average molecular weight of ~1140Da and a weight average molecular weight of ~2470Da. These values were used to calculate a polydispersity index of ~2.16 for the copolymer, consistent with an increase in functionality and, therefore, formation of GA-g-OLLA.

Gum arabic is a good adhesive for soft substrates such as paper, but the adhesive nature of this polymer as it pertains to its hydrophilicity is yet to be understood. Hence, we tested the adhesive properties of GA-g-OLLA with various porous and nonporous substrates including

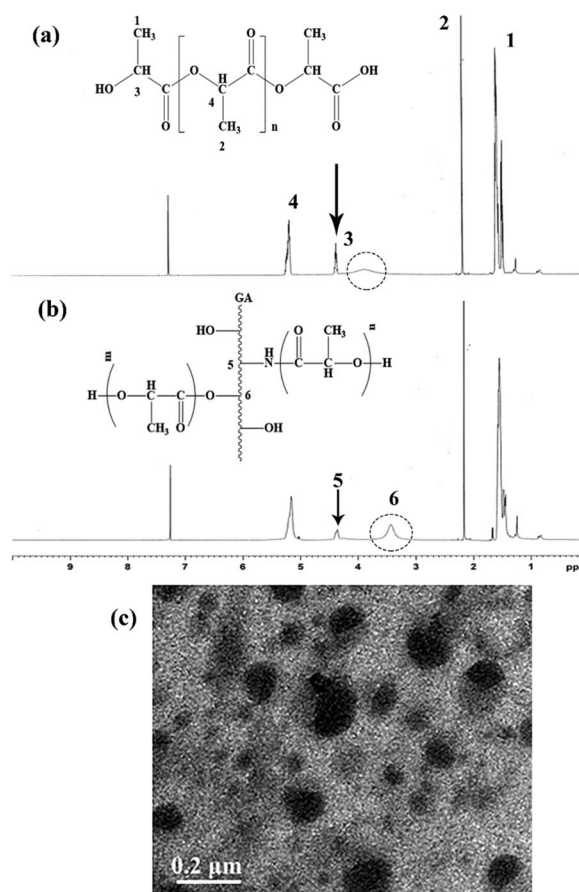


Figure 1. Proton nuclear magnetic resonance spectra of (a) oligo(L-lactic acid) (OLLA) and (b) gum arabic-*graft*-oligo(L-lactic acid) (GA-g-OLLA). The reduction in intensity of the peak at 4.37ppm and the shift of the broad peak at 3.8ppm to 3.4ppm confirms OLLA grafting onto the amino (NH) and hydroxyl (OH) groups, respectively. (c) A transmission electron micrograph of a poly(lactic acid) (PLA)/GA-g-OLLA(5%) bionanocomposite film. n,m: OLLA repeat unit.

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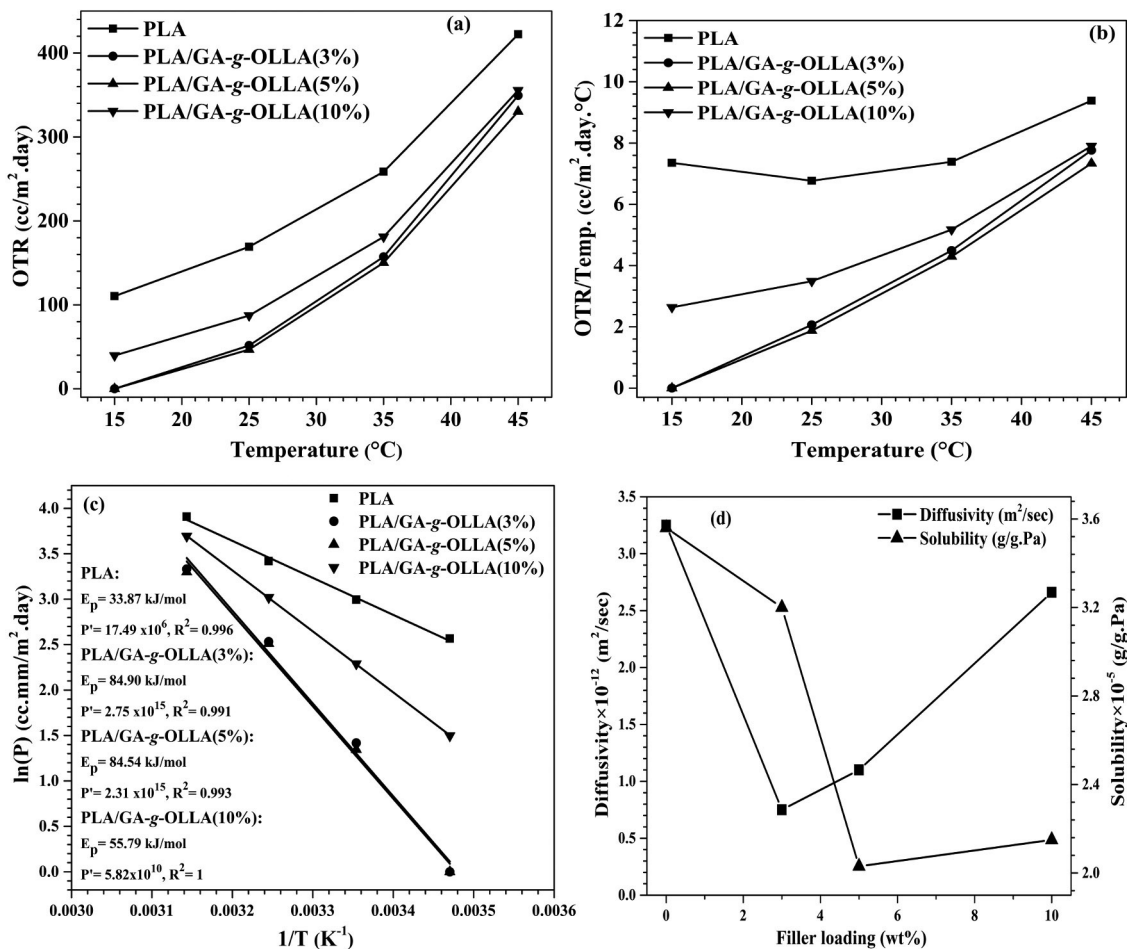


Figure 2. (a) Oxygen transmission rates (OTR) for PLA/GA-g-OLLA bionanocomposite films at various temperatures, (b) rate of change in PLA/GA-g-OLLA OTR with respect to temperature, (c) temperature dependence of the oxygen permeation rate for PLA/GA-g-OLLA films, and (d) oxygen diffusivity/solubility of PLA/GA-g-OLLA films at 25±0.1°C and 0% relative humidity. P , P' : Oxygen permeability. E_p : Activation energy for permeation of oxygen molecules. R^2 : Coefficient of determination.

paper, aluminum, polyethylene terephthalate, wood, glass, granite, and iron. Using a lap-shear test (in which two pieces of substrate are bonded and then pulled apart), we found that GA-g-OLLA selectively binds silica-containing substrates such as glass and granite, and no adhesion was observed for the other substrates. Thus, we carried out a detailed investigation at optimal conditions (15% by weight GA in the GA-g-OLLA copolymer, 2000N compression load, and 10min compression time) with glass and granite substrates. We found that as the shear stress increases, shear cracks develop on the substrate and the substrate eventually fails, leaving the adhesive bond line intact with no observed deformation. The maximum loads experienced by the glass and granite substrates before failure were 1082±220MPa

and 3803±291MPa, respectively. Hence, we consider GA-g-OLLA to be a promising bio-based adhesive.

The non-toxic and biodegradable nature of GA-g-OLLA suggests its possible use in food packaging. Thus, we synthesized poly(lactic acid) (PLA)/GA-g-OLLA bionanocomposite films with a range of compositions (3, 5, and 10% by weight GA-g-OLLA filler). The single observed glass transition temperature (T_g)—the temperature at which a material changes from a hard, glassy state to a rubber-like state—for these films shows the two polymers are compatible, and transmission electron microscopy analysis confirms the presence of homogeneously dispersed nanoscale GA-g-OLLA particles in the PLA matrix: see Figure 1(c).

Adding GA-g-OLLA filler to the PLA matrix reduces T_g by up to 24°C (owing to enhanced mobility in the molecular segments), a favorable result for food packaging applications. The water vapor transmission rate is also reduced by 27% with the addition of 5% filler, a result of the absence of available OH groups on the GA backbone.¹ Furthermore, the oxygen transmission rate (OTR) reduces with added GA-g-OLLA filler (caused by decreased molecular motion of the polymeric chains), although at 10% GA-g-OLLA the OTR is higher than with other filler loadings, potentially a result of aggregation of the GA-g-OLLA particles: see Figure 2(a). However, there is an increase in OTR with increasing temperature (15–45°C) in all cases, with the rate of change in OTR significantly higher for the bionanocomposite films—see Figure 2(a–c)—which may be caused by a combination of reduced diffusion rates and increased oxygen solubility.

The activation energy for oxygen permeation through the PLA/GA-g-OLLA films increases with filler loadings up to 5% (resulting in improved gas barrier properties). Moreover, there is a significant drop in oxygen diffusivity and solubility in the bionanocomposite films when compared with PLA: see Figure 2(d). This data clearly indicates that solubility is the prime factor in the significant oxygen permeability reduction in the PLA/GA-g-OLLA films. Indeed, the reduced solubility coefficient is primarily responsible for the decrease in OTR in these films because the presence of the filler restricts the availability of active sites in the PLA matrix. Hence, the unavailability of functional sites restricts the physical interaction between the polymer and oxygen molecules, which also helps increase the resistance to oxygen diffusion through the PLA matrix.

We also conducted a kinetic study of the bionanocomposite films to help predict the behavior of the material in high-temperature situations such as processing and recycling. The degradation pathways of the films were interpreted by thermogravimetric analysis/Fourier transform IR spectroscopy (which identifies gaseous products and new molecular groups produced by material deterioration). Peaks associated with hydrocarbons, water, carbon dioxide, and cyclic oligomers were observed, along with a new N–H degradation peak (at 1517cm⁻¹).³ In addition, we calculated the activation energies for thermal degradation of these films using several models and found that increases in activation energy occurred with increases in fractional decomposition of the PLA/GA-g-OLLA films,² which confirms that the bionanocomposite films have complex degradation pathways.

In summary, we have synthesized a bio-based hydrophobic graft copolymer from GA and lactic acid. The GA-g-OLLA copolymer displays excellent adhesive strengths for glass and granite substrates. We also explored the application of GA-g-OLLA as a filler to produce bionanocomposite films with PLA that improve on the structural, thermal, and gas barrier properties of PLA for potential food packaging applications. Our future work in this area will include thoroughly

investigating the mechanism of GA-g-OLLA adhesive bonding and exploring the toxicity, migration, biodegradation, and recycling of the PLA/GA-g-OLLA bionanocomposite films.

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