Cure-on-demand wood adhesive based on the frontal polymerization of acrylates

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ABSTRACT: We demonstrated for the first time a cure-on-demand wood adhesive using thermal frontal polymerization with Southern Pine wood. Monomer structure, initiator loading, and filler loading all had an impact on the strength of the adhesive and the cure-on-demand ability. More flexible, ethoxylated monomers produced stronger adhesives; though, the ethoxylate groups reduce the ability of the system to be polymerized frontally. Addition of a highly reactive comonomer (acrylic acid) to increase molecular weight between crosslinks along with the ethoxylated triacrylate increased the propensity for frontal polymerization and made a tougher polymer. Increasing initiator loading could help ensure front propagation, but a maximum initiator loading was reached where the gaseous byproducts of the peroxide initiator made the network highly porous and thus lacking strength. Fillers such as kaolin and sawdust helped overcome decreases in strength at high initiator loadings. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44064.

INTRODUCTION

Frontal polymerization is a process, in which a localized reaction zone propagates through a system converting monomer into polymer. Three types of frontal polymerizations are thermal frontal polymerization (TFP), in which the localized reaction zone propagates through the coupling of thermal transport with the Arrhenius dependence of the kinetics of an exothermic polymerization[1–3]; photofrontal polymerization, in which the localized reaction is driven by an external UV source;[4–8] and isothermal frontal polymerization (IFP),[9,10] which relies on the Norrish-Trommsdorff gel effect to decrease the rate of termination.[11,12]

An overwhelming majority of work with thermal frontal polymerization has centered on free-radical homopolymerization, but other types of polymerizations and their corresponding monomers have been studied including anionic polymerization of ε-caprolactam,[13,14] ring-opening metathesis polymerization,[15–17] polymerization of polyacrylate-poly(dicyclopentadiene) crosslinked networks,[18] dual cure epoxy-acrylate binary systems,[19] isocyanate-alcohol polymerization of polyurethanes,[20–22] atom transfer radical polymerization,[23] thiol-ene polymerization,[24] cationic curing of epoxies,[25,26] and cyanate ester systems.[27] Work has also been performed using frontal polymerization to produce functionally gradient materials.[28] A comprehensive review of frontal polymerizations was published in 2012.[29]

Frontal polymerization allows creation of a "cure-on-demand" system, in which the formulation does not react until the external application of localized heating.[29] An example of this cure-on-demand utility is found in patents on chemical anchors.[30,31] Because curing only happens when the user is ready to cure the adhesive, unlimited time can be taken to position objects carefully and exactly.

The decomposition of the thermal initiator required for TFP is a significant step in determining the rate of polymerization, and its high activation energy allows for a front.[32] The peroxide chosen for this research was 1,1-bis(*tert*-butylperoxy)−3,3,5-trimethylcyclohexane commercially known as Luperox® 231 [L231, Figure 1(a)], because it is a liquid, soluble in acrylates and stable at room temperature. However, a potential disadvantage of peroxides is that they release gaseous byproducts although L231 produces less gas per radical produced other peroxides.[29] These gases typically give the polymers formed by TFP a porous morphology that could have a negative impact on the polymer's mechanical properties.

The front velocity is strongly dependent on the type of monomer. Acrylates react faster than methacrylates.[33–35] Acrylic acid creates the fastest fronts of the liquid monofunctional monomers[36] followed by methacrylic acid.[37] The front velocity also strongly depends on the functionality of the acrylate[35] as well as
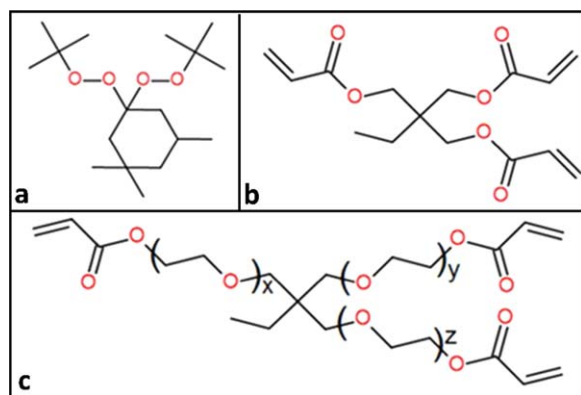
Figure 1. Structures of Luperox® 231(top left), TMPTA (top right), and TMPEOTA (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

being a function of initiator concentration and stability.[32–34] The addition of fillers also affects the front velocity.[38,39]

Fillers can be added to affect mechanical, rheological, and thermal properties.[40] Viscosity is important for acrylate adhesives; if the mixture is not viscous enough, it will flow too readily and be difficult to apply to a material's surface. Viscosity is also crucial when performing a TFP because if the reaction mixture is not viscous enough, thermal expansion caused by the highly exothermic polymerization spreads the monomer increasing the surface area and rate of heat loss to the surroundings and, in some cases, extinguishes the front.[29] Because TFP relies on the transfer of heat for propagation, the thermal conductivity of the substrate can affect propagation, which is an important consideration when binding wood because the thermal conductivity can vary greatly over a small distance on the wood.

In this study, two trifunctional acrylates were used, trimethylolpropane triacrylate [TMPTA, Figure 1(b)] and its ethoxylated form, trimethylolpropane ethoxylate triacrylate [TMPEOTA, Figure 1(c)], to develop an adhesive system for possible use in gluing wood. The high degree of crosslinking that arises from a trifunctional monomer gives the polymer a high level of strength. However, because the TMPTA network is brittle, TMPEOTA is used to minimize the brittleness because the ethoxylated portions make the network more flexible. TMPEOTA can be obtained with an average of three (1/1 TMPEOTA), seven (7/3 TMPEOTA), or fourteen (14/3 TMPEOTA) ethoxylate units per molecule: molecular weights of 428 Da, 604 Da, and 912 Da, respectively. It has been shown previously that the more ethoxylate units in the molecule, the less likely the monomer is to polymerize via TFP.[41] To counteract this decrease in reactivity, acrylic acid (AA) was introduced as a comonomer. The incorporation of a high reactivity, monofunctional comonomer such as AA decreases the molecular weight per double bond sufficiently so TFP occurs with the larger molecular weight TMPEOTA monomers.

EXPERIMENTAL

The TMPTA, 14/3 TMPEOTA, 7/3 TMPEOTA, L231, and 1 mm borosilicate solid-glass beads were obtained through Sigma-Aldrich (St. Louis, MO, USA). The 1/1 TMPEOTA was provided

by both Sigma-Aldrich and Sartomer (Exton, PA, USA). Toluene and acrylic acid were supplied by Fisher-Scientific (Waltham, MA, USA). The styrene-ethylene/butylene-styrene (SEBS) was provided by Kraton. Polygloss® 90 (kaolin) was obtained from KaMin (Macon, GA USA) and Huber (Edison, NJ, USA). The Aerosil 200 (fumed silica) was supplied by US Composites, Inc. (West Palm Beach, FL, USA).

All samples consisted of monomer, filler and initiator, with total mass of monomer being 10.0 g for every sample. The loading amount of all other components was calculated in parts per hundred resin (phr). The adhesive was applied on the face of two southern pine blocks in an area of 3.8 cm by 3.8 cm. One gram of the monomer-containing mixture was applied to each block. Borosilicate glass beads were placed on one side to ensure that the space between the two blocks was uniform and consistently the same across all samples. For a gap thicknesses less than 1 mm, fronts did not propagate reproducibly. After the two blocks were pressed together, a soldering iron or heat gun was used to initiate the polymerization front. Once the reaction finished, the sample was taken for mechanical testing (completion of reaction was defined by the observation that the front had propagated from the site of ignition through the resin to the opposite side). The ASTM D143 standard shear test was used during the mechanical testing. The shear rate was 0.60 cm min^{-1}.

Some fillers, such as SEBS, needed to have their particle size reduced for best results. Solvent dispersion was used to reduce the SEBS particle size so that it dispersed more homogenously in the monomer mixture. Toluene was used to dissolve the SEBS. After addition of the monomer(s) to the dissolved SEBS, the mixture was left uncovered as it stirred until all solvent had evaporated (minimum 6 hours).

RESULTS AND DISCUSSION

The combined TMPTA/TMPEOTA was the first comonomer system explored. Figure 2 shows the results from trials in which the filler loading and initiator loading were varied with a fixed 1:3 ratio of 7/3 TMPEOTA:TMPTA. The highest shear strength achieved with this comonomer system was 1.9 MPa. Even though the formulation with the highest shear strength contained only 6 phr silica [Figure 2(a)], that adhesive was much more brittle than the adhesive formed with both silica and kaolin, indicating that silica alone is not a viable filler system for highly crosslinked acrylate adhesives. Kaolin and other more dense fillers can help counteract the inherent brittleness of such a highly crosslinked material. Unfortunately, the large amount of kaolin in the monomer mixture helped absorbs heat too effectively, causing the front to not propagate reproducibly, which led to the large data scatter (b and c, Figure 2). Another source of the data scatter in these samples was due to the nature of the wood substrate itself. Wood varies in density and therefore thermal conductivity. Lighter, less dense parts of the wood have a lower thermal conductivity than the darker, denser regions.[42]

Pine sawdust was also tested as a filler. Each trial consisted of 10.0 g TMPTA and 5 phr silica, while kaolin, sawdust, and L231 were all varied. Figure 3a presents the shear strengths of 25 phr total of sawdust and kaolin combined in various ratios across
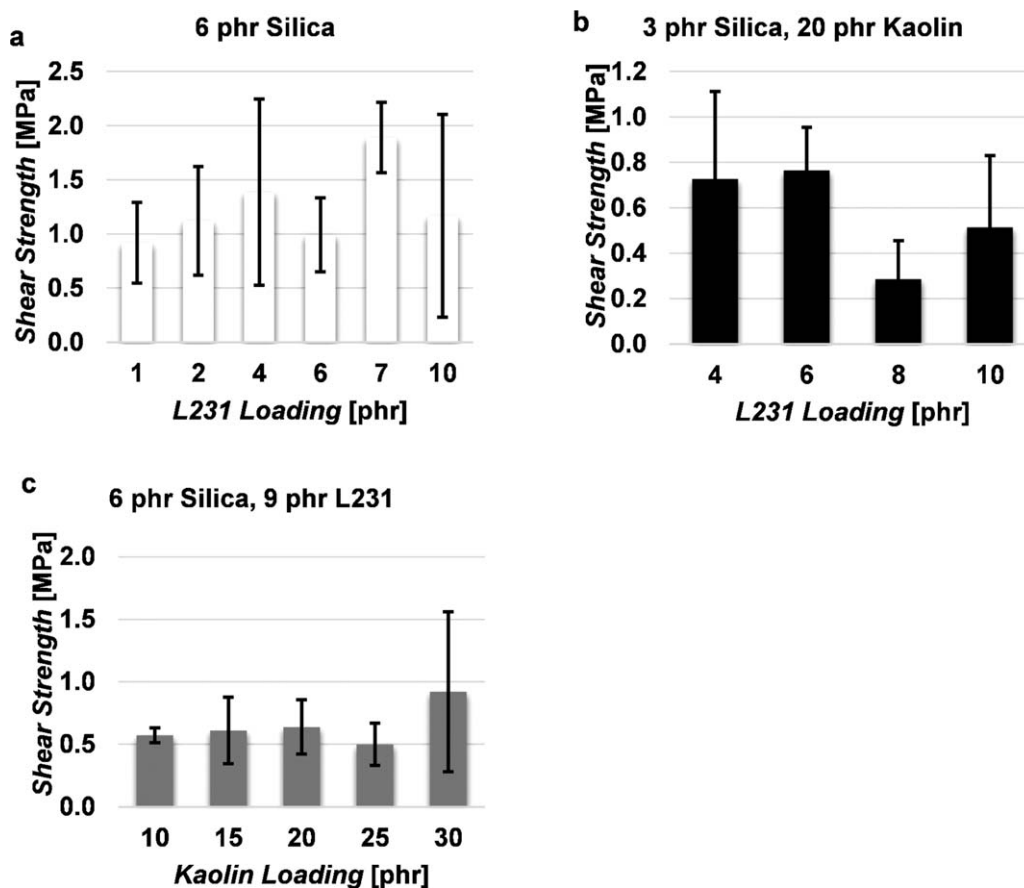
Figure 2. Shear strength as a function of initiator loading (a, b) and kaolin loading (c) for adhesives made with 3:1, TMPTA: 7/3 TMPEOTA.

several L231 loadings. A constant amount of kaolin (7.5 phr) with larger loadings of sawdust was also studied [Figure 3(b)]. Both formulations in Figure 3 exhibit behavior common to many of the samples in this group of experiments; strength tends to reach a maximum at a certain initiator loading and then decreases at higher initiator loadings. Such behavior is

believed to occur because of an increase in network porosity because of the larger amount of gaseous byproducts being released as a result of higher initiator concentration.

It is notable that filler loadings including sawdust do not need TMPEOTA as a comonomer to increase the strength beyond that of TMPTA alone. The sawdust acts as toughening agent,
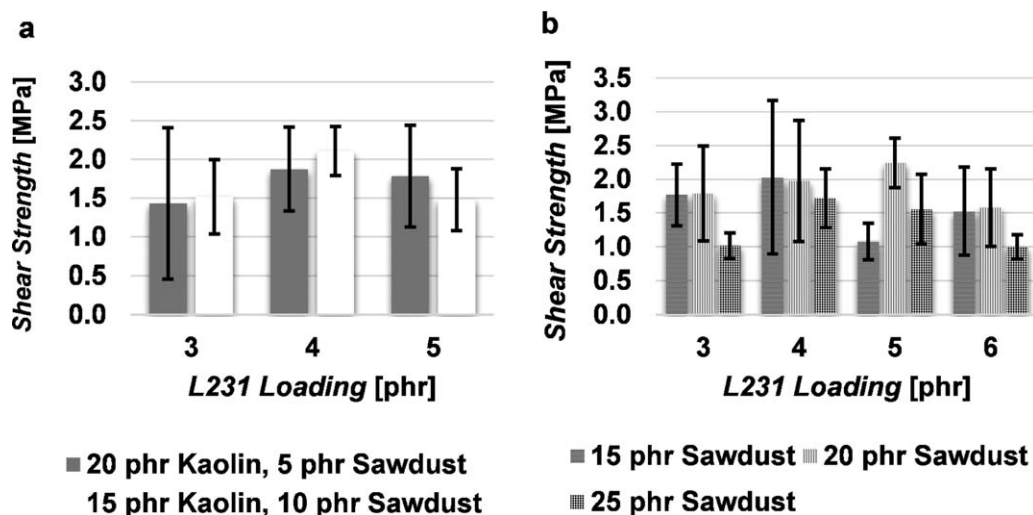
Figure 3. Shear strength of adhesive prepared with TMPTA and (a) 25 phr total filler (kaolin and sawdust) and (b) 7.5 phr kaolin and varying amounts of sawdust across multiple L231 loadings.
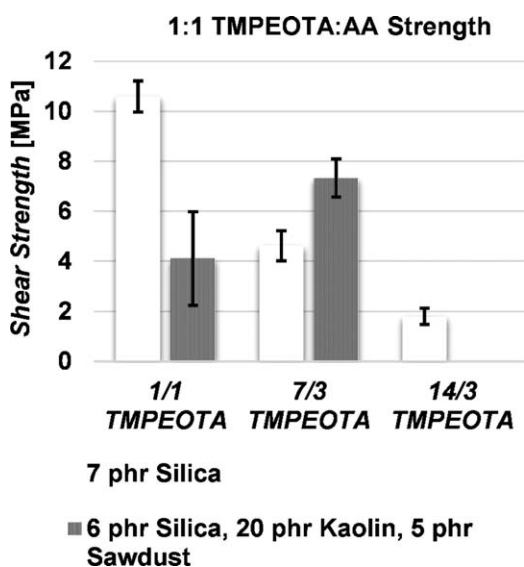
Figure 4. Shear strengths of adhesives prepared with 1:1 TMPEOTA: AA formulations.

leading to a stronger, less brittle adhesive without the need for a comonomer.

The next filler tested was poly(styrene-ethylene/butylene-styrene) (SEBS). SEBS is a linear, triblock copolymer, and so it was selected for study in hopes that it can act as an elastomeric toughener. The initial results of the SEBS as received were not promising, so SEBS was dispersed in toluene to reduce the particle size. Each sample consisted of 10.0 g TMPTA, 20 phr kaolin, 5.8 phr SEBS, and various amounts of L231 and silica. The results of the dispersed SEBS are 2.99 ± 0.43 MPa with 5 phr L231 and 2.52 ± 0.69 MPa using 8 phr silica. The trials with SEBS indicated that to reach higher strength, toughening with the incorporation of linear polymer chains is necessary.

Once it was realized that a higher amount of linear polymer in the adhesive can help achieve increased adhesive shear strength, a monofunctional comonomer was incorporated. A monofunctional monomer increases the molecular weight between crosslinks and decreases the likelihood of brittle fracture because the network is less rigid. This change in brittleness can also be seen in the difference between pure TMPTA polymer and pure TMPEOTA polymer. Acrylic acid was chosen because it has very high reactivity and could potentially help overcome the lowered reactivity of the larger TMPEOTA monomers. A 1:1 ratio of TMPEOTA:AA was determined to be the best choice for these trials, and per the previous precedent, 10.0 g of monomer mixture was incorporated with the fillers and 8 phr L231 for polymerization. Figure 4 shows the most successful formulations of the TMPEOTA/AA comonomer system.

This comonomer system was the most successful of all of the formulation sets explored. Strength greater than 10.0 MPa was obtained with the 1/1 TMPEOTA and AA. It is especially apparent in Figure 4 (as also in Figure 2) that while silica is an excellent viscosity modifier, it is severely lacking in utility as a filler for increasing mechanical properties due to the drastic decrease in strength between monomers with no filler besides silica. Also, it can be

seen that no data was obtained for the 14/3 TMPEOTA/AA with 6 phr silica, 20 phr kaolin, and 5 phr sawdust; even with the incorporation of acrylic acid, the molecular weight per double bond with that much filler is too high to obtain a reproducible front—the front quenches before polymerization is complete. While 1/1 TMPEOTA is especially useful when polymerized with AA, 14/3 TMPEOTA lowers the overall reactivity too much to be useful in this application.

CONCLUSIONS

We demonstrated for the first time a cure-on-demand wood adhesive using thermal frontal polymerization for gluing Southern Pine wood blocks. The adhesive consisted of multifunctional acrylates, fumed silica, an organic peroxide, and other fillers. The monomer structure, initiator loading, and filler loading all affect the strength of the adhesive and the cure-on-demand ability. More flexible, ethoxylated monomers produced stronger adhesives but the ethoxylate groups also had a negative effect on the ability of the system to be polymerized frontally. Addition of a highly reactive comonomer (acrylic acid) to increase molecular weight between crosslinks along with the ethoxylated triacrylate increased the propensity for frontal polymerization and produced a stronger polymer-wood bond. Increasing initiator loading can help ensure that the front propagates, but a maximum initiator loading is reached where the gaseous byproducts of the peroxide initiator make the network highly porous and lacking strength. Fillers such as kaolin and sawdust can help overcome decreases in strength at high initiator loadings. Frontal curing would only work if the gap between the wood blocks was at least 1 mm.

The monomer type and concentration was much more important than the type or filler loading. Only the triethoxylated acrylate with acrylic acid reached above 3 MPa in shear strength, and the formulation with the highest strength obtained contained only silica. Fillers can be quite useful and negate some of the lost strength caused by high an initiator loading, but too much filler can cause front quenching.

ACKNOWLEDGMENTS

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