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Hands-On Laboratory Experience Using Adhesives for Remote Learning of Polymer Chemistry

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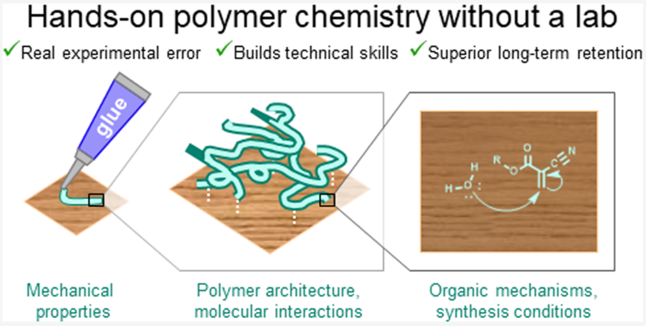

ABSTRACT: Teaching chemistry without access to a traditional laboratory space is an ongoing challenge that has become especially relevant because of the SARS-CoV-2 pandemic. While several remote learning options exist for covering general chemistry concepts (including kitchen-based experiments, online modules, and virtual reality), few options provide opportunities for hands-on learning about the chemistry of synthetic polymer materials. Here, we offer remote learning modules that use household adhesives as a platform for teaching polymer chemistry outside of the laboratory. These modules are designed for students who have taken at least one semester of organic chemistry and have varied hands-on time commitments, ranging from 2 to 10 total hours each. Concepts covered include polymer synthesis, intermolecular interactions, thermomechanical properties, structure−function relationships, and molecular design. The experiments described in these modules also give students a chance to practice research-relevant skills such as searching for primary literature sources, fabricating test samples, explaining unexpected experimental results, and revising experimental procedures to improve methodologies. Ultimately, these modules provide educators with an additional tool for teaching experimental chemistry outside of the laboratory.

KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Distance Learning/Self Instruction, Organic Chemistry, Polymer Chemistry, Laboratory Instruction*

■ BACKGROUND

Remote Learning in Chemical Education

Remote learning has been identified as both a trend and a mission for higher education in the 21st century,[1] and the COVID-19 pandemic recently forced a vast majority of the world's students and teachers to transition to remote learning.[2] Hands-on learning has been regarded as a means for students to develop a greater appreciation for chemistry and is essential for learning science.[3,4] Thus, chemical education is as strongly rooted in the laboratory as it is in the classroom, so a critical need for chemistry students is lacking for those who are learning remotely. Chemical education holds inherent challenges with remote learning by students not having access to a laboratory. Currently, this problem is not well-addressed, as students normally need to either take extra lab courses upon returning to campus or observe experiments online.[5]

Some universities offer virtual laboratory experiences, although virtual laboratories are too expensive for many schools.[1] While open-source virtual resources exist, professional virtual laboratory environments offer a richer and more encompassing experience, but at an access cost comparable to lab fees at many universities. Further, virtual laboratories do not adequately develop students' skills working with real materials. Hands-on learning in distance chemistry learning has been recently investigated with success,[6−8] although some issues can still remain regarding safety, disposal, material distribution, and variations in results.[9,10] Here, we present hands-on experiments in distance chemistry learning designed to engage a remote classroom of students, while teaching with real life experiments. This is aimed to effectively establish important principles in organic and polymer chemistry in lieu of, or in combination with, a laboratory experience. We accomplish this with adhesives, which are designed to enable organic and polymer chemistry at home to engage remote learning students.

There are two existing strategies for implementing remote learning in lieu of a physical laboratory: virtual learning experiences and kitchen chemistry (materials bought by the students or sent home as a package by the instructor). Virtual

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Table 1. Laboratory Learning Objectives and Our Approach with Kitchen Chemistry

Laboratory Course Learning Objective	How We Accomplish the Objective with Kitchen Chemistry
Applying knowledge of theoretical concepts Creating a hypothesis and making observations	Understanding concepts allows students to create and test a hypothesis. Kitchen chemistry can effectively be used in conjunction with the classroom to test hypotheses based on learned concepts.
Effectively using scientific equipment with proper technique	While advanced scientific instrumentation cannot be used at home, physically doing experiments builds technical skills. Unexpected setbacks may occur in kitchen chemistry that require the development of proper techniques.
Appreciation of science	In kitchen chemistry, the reaction seen can only be from the student's physical actions, contributing to his or her appreciation of the result.
Critique and recognize patterns in experimental data	Real (nonperfect) data is the best way to interpret results to prepare students for research, which can only come from physical expermentation.
Collaborate, summarize, and present experimental findings	Presenting experimental findings is more suitable for real data, as it is more likely to contain imperfections, allowing the student to summarize data that may not have a clear trend.
Organic chemistry[a]	Rationalize experimental results with arrow pushing mechanisms
Polymer chemistry[a]	Experience and observe structure−function relationships through polymer mechanics and viscoelasticity

[a] Organic chemistry and polymer chemistry are included as goals specific to our remote learning modules.

learning in chemistry is the practice of using computers or virtual reality to simulate laboratory work. Virtual learning with computers has been developed over the past few decades into a usable platform available commercially. There are benefits to virtual learning, such as the ease of use, absence of the need for laboratory equipment or materials, and readily repeatable experimentation.[11,12]

While there are benefits to virtual laboratories, there are several drawbacks. Students who learn with virtual laboratories do not get to experience realistic troubleshooting based on unexpected results.[13] This type of troubleshooting, an essential skill for conducting chemistry research, is lacking from virtual laboratories. Another drawback with virtual laboratories is the oversimplification of health and safety in the lab environment.[14,15]

Adhesives are safe both to use and dispose of, as well as easily transported and stored in nonfragile containers. Additionally, our experimental design allows for unexpected results so each student can actively learn from their results and develop troubleshooting abilities that will translate into traditional laboratory and research settings. This gives the use of adhesives in a remote-only hands-on course a unique advantage over other strategies.

Satisfying Laboratory Objectives with Remote Learning

Several categories of intended outcomes for laboratory learning have been outlined.[16−24] The learning objectives are meant to work harmoniously between classroom and laboratory learning, based in critical thinking, human outcomes and error, and use of resources, to refine problem-solving skills. This has been studied recently in the wake of the COVID-19 pandemic to improve virtual lab environments with these same goals.[25,26] These include the following: (1) knowledge and understanding to model theoretical concepts, (2) creation of a hypothesis and observations, (3) effective use of scientific equipment with proper technique, (4) appreciation of science, (5) critique and recognition of patterns in experimental data, and (6) collaboration, summary, and presentation of experimental findings. Using physical experimentation such as kitchen chemistry could fulfill these qualities better than a virtual laboratory in all aspects (Table 1).

Overview

As the information age has rapidly unfolded over the past 20 years, education has become more available to a growing number of students that have either opted against or simply not have had access to traditional education settings.[27] However, in-person laboratory training is critical for chemistry students, and addressing the inherent difficulty chemistry holds with remote learning has only been marginally studied. The results from these studies are promising, as they show increased comprehension by improved test scores over those of students who took the same class traditionally. Additionally, for novice chemists, kitchen chemistry may alleviate a source of anxiety by avoiding the use of hazardous chemicals.[27−29]

Kitchen chemistry involves performing chemical reactions at home. The scope, precision, and rigor of kitchen chemistry are inherently limited compared to the experience of a full laboratory, and the scope and precision can be limited compared to an advanced virtual laboratory.[30] However, kitchen chemistry has been shown to improve students' interest in chemistry as a whole, and kitchen resources can foster enhanced retention of concepts.[31] While many experiments have been developed using traditional kitchen ingredients,[32] food-based experiments are inherently limited to certain chemistry concepts. To offer students a hands-on experience in studying polymers, other household products can be explored, such as using gelatin in drug delivery, studying polysaccharide changes in caramelizing onions, and modeling freezing point depression via the colligative properties of milk.[33,34]

This work contributes to the development of hands-on remote experimentation in organic and polymer chemistry through the study of adhesives. Adhesives are readily available and packaged for safe and convenient use at home; however, many do not understand the complex organic chemistry behind these materials. Many students have used adhesives in everyday life, and research has shown that conducting chemistry experiments in a way that students can connect to real life improves their motivation and development of chemistry skills.[35,36]

Using adhesives, we can address some of the challenges discussed with other recent advances in remote hands-on chemistry learning. Recent research in chemical education has shown that an overwhelming majority of students who participate in kitchen chemistry voice satisfaction with it, even in distance courses that were rapidly forced into it from a traditional setting.[37] In order to keep students on track with the assignments, the experiments can be accompanied by a

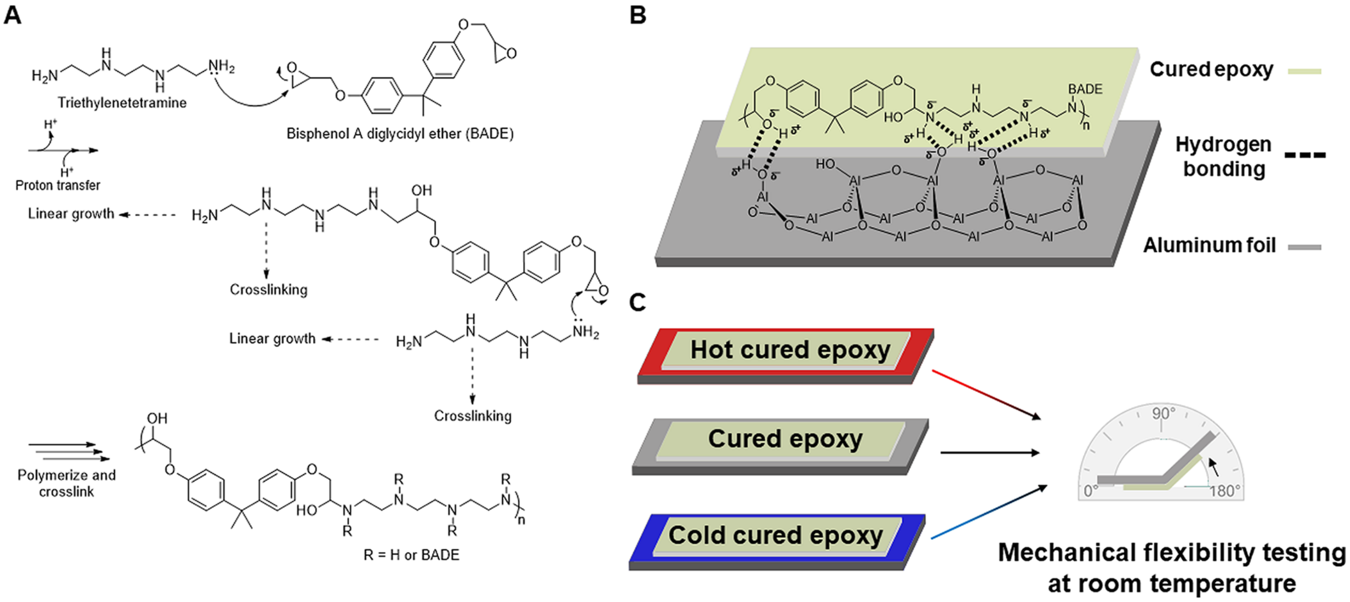

Figure 1. (A) Example of two-component epoxy ring-opening mechanism including cross-linking to create the adhesive. (B) Illustrated hydrogen bonding adhering the epoxy adhesive to aluminum foil surface. (C) Diagram of the experiment to cure the epoxy adhesive at different temperatures, followed by mechanical flexibility testing.

synchronous instruction session before each experiment, where the professor may review relevant concepts.[38] Of course, the TA and professor may be available for video conferencing during experimentation, but only if synchronous experimentation is selected for the course. Kitchen chemistry experiments can be logistically aided as well by course organization tools such as Moodle, Blackboard, or Canvas to keep due dates and experiment information easily accessible.[5,37,39] Recent studies have shown that the most effective way to get students to participate in kitchen chemistry as intended is to provide the materials for experimentation to them directly. Of course, this is most easily accomplished if all students are living in the region,[10] but the materials for our experiments are safe to handle and ship, and cost of the kits can be reimbursed to the institution in the form of a lab fee.

We have chosen several readily available adhesives for students to study: epoxies, caulk, wood glue, white glue, and cyanoacrylates. These commonplace adhesives will aid students' grasp on chemistry because of tangible and memorable results that students can connect with personal experience.[36,40] We present background information, and an experimental procedure for each material, along with pre- and postlab questions with sample answers for instructional aid. This educational tool kit provides the details necessary to teach organic and polymer chemistry concepts including the basics of arrow pushing mechanisms, polymer mechanics, and viscoelasticity to remote learning students. Thus, these modules are mainly intended for students who have taken at least one semester of organic chemistry.

■ RESULTS AND DISCUSSION

Module 1: Epoxy Adhesives (Supporting Information Handout 1)

Epoxy resins adhere to many surfaces and are frequently used as structural adhesives. They are also commonly used in sealants and coatings for surfaces. Epoxy adhesives have two main components: a resin and a hardener. These react chemically to polymerize and form the active adhesive. The resin acts as the backbone for the polymer, and the structure of the resin can dictate the adhesive's mechanical properties. For example, an aromatic group within the resin will lead to a less flexible adhesive, while an aliphatic resin will lead to a more flexible adhesive. To create the adhesive, the resin's epoxy groups act as good electrophiles for the hardener. Thus, the hardener contains nucleophilic groups, such as amines, to begin the reaction once the resin and hardener are physically combined. While the hardener is nucleophilically attacking the resin to grow the polymer linearly, the hardener also facilitates multidirectional growth, known as chemical cross-linking, due to multiple binding sites being present (Figure 1A). The adsorption mechanism depends on the epoxy used, but the adsorption interactions that contribute to adhesion are dominated by hydrogen bonds (Figure 1B). Thus, introducing external molecules that interfere with adhesive hydrogen bonding events, such as water, will decrease the adsorptive capacity. It is also important to note that a surface of pure aluminum is not capable of hydrogen bonding, but epoxy adhesives still strongly adhere to aluminum foil. This occurs because the atmosphere quickly develops a thin layer of aluminum oxide on the surface, even if the aluminum had just been cleaned or mechanically shaved.

Our results indicated two main effects on adhesive flexibility: the cure temperature and the brand used. At elevated temperatures, cross-linking density and the glass transition temperature are both higher, which led to a stiffer material compared to a room temperature cure. Conversely, at a decreased temperature cure, both the glass transition temperature and extent of reaction are lower, making the resin softer compared to a room temperature cure. The effect was so apparent that the foil itself was stiffer than the epoxy adhesive for the decreased temperature cure. Because of the thermoset nature of the epoxy adhesives, these flexibility results were obtained at room temperature, and there is no statistically significant difference between replicates. The extent of flexibility in the experiments varied between brands due to chemical composition, and as such we recommend multiple brands be used to study the differences.

Module 2: Thermomechanical Properties of Thermoplastic versus Thermoset Adhesives (Supporting Information Handout 2)

Thermoplastic Materials Have a Glass Transition Temperature (T_g) and a Melting Temperature (T_m). Thermoplastic polymer materials are made of linear polymer chains that tangle around each other. The mechanical properties of thermoplastics depend on temperature. In cold temperatures, polymer chains cannot slide past each other and are trapped in a glassy state, making the bulk material stiff and brittle. At warmer temperatures, polymer chains become more mobile in between points where they are entangled, creating a plastic material that can bend and deform some without shattering. The temperature at which a polymer material transitions from being glassy to being plastic is called the glass transition temperature, T_g. Above the T_g, thermoplastic polymers also have a melting temperature, T_m, beyond which entire polymer chains move freely and the material flows as a liquid. Melted thermoplastics can be molded, reshaped, and recycled; this property is what makes hot glue possible. T_g and T_m are higher in materials that have lower polymer chain mobility, which can be caused by more rigid chemical structures or the presence of strong intermolecular forces in the material such as hydrogen bonding between polymer chains.

Thermoset Materials Are Cross-Linked and Do Not Melt. Unlike the individual linear chains of thermoplastics, thermoset materials are made of a network of polymer segments that are interconnected by covalent bonds called cross-links, like a fish net. Thermoset materials may have a T_g, if the linear segments that occur between cross-links are long enough. However, thermoset materials do not melt because the permanent cross-links prevent the polymer segments from flowing freely. These cross-links also make thermoset materials stiffer (harder to deform), tougher (more resistant to mechanical failure like cracking), more elastic (able to return to its original shape after being deformed), and more solvent resistant (less soluble) than thermoplastics but are not recyclable and can be difficult to remove from surfaces once adhered. Most thermosets have a "sweet spot" that maximizes toughness by balancing the number of cross-links, which contributes stiffness, and the length of the linear segments between cross-links, which provides the ability to flex without cracking.

Thermoplastics and Thermosets in Adhesives. Thermoplastic adhesives are ideal for forming quick, temporary bonds that do not need to endure dramatic temperature changes, such as in crafts and household repair projects. Thermoplastic adhesives include hot glue (poly[ethylene-vinyl acetate]), washable craft glue (poly[vinyl alcohol-*co*-vinyl acetate], PVA-*co*-PVAc), and superglue (poly[ethyl cyanoacrylate], PECA). By contrast, thermoset adhesives are commonly used in industrial manufacturing because of their strength, durability, and resilience to temperature changes and solvent. Thermoset adhesives include polyurethane-based wood glues (poly[4,4′-methylenediphenyldiisocyanate]-*co*-poly[propylene glycol], PMDI-*co*-PPG, cross-linked through polyol cross-linkers), polysiloxane-based caulks (poly[dimethylsiloxane], PDMS), and epoxy resins.

This module is designed to demonstrate differences between thermoplastic and thermoset adhesives by focusing on structure−property relationships, in particular the relationships among polymer chain mobility, cross-linking, and thermomechanical properties. To illustrate these relationships, this module uses a simplified bending test, where a foil-backed thin film of adhesive is bent to a 90° angle at different temperatures. From this test, students will make qualitative observations about different adhesives, including the stiffness, toughness or brittleness, and elasticity. By making these observations at different temperatures, students can tangibly observe the effects of cross-linking, polymer chain mobility, and the glass transition on the behavior of adhesive materials (Figure 2).

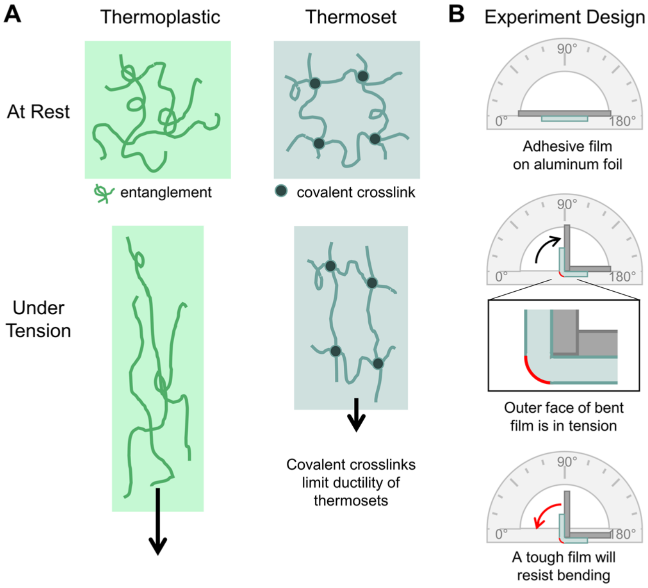

Figure 2. (A) Thermoplastic materials are made of linear polymer chains that entangle with each other. Chain entanglements give thermoplastics strength but can be overcome, especially at temperatures above the T_g. By contrast, thermoset materials are made of polymer networks with covalent cross-links that are stronger than chain entanglements, making thermosets stiffer and more elastic. (B) In module 2, students will test the differences between thermoplastic and thermoset adhesives using a simplified bending test.

When this module was performed by an undergraduate student, the student was able to observe significant stiffness changes to both the craft glue and wood glue that occur when approaching the glass transition temperature, as well as the greater elasticity of thermoset wood glue (PDMI-*co*-PPG) compared to the two thermoplastic alternatives. In terms of elasticity, wood glue at RT was the only adhesive observed to rebound after being bent to a 90° angle. In terms of T_g, the student observed a dramatic increase in the stiffness and brittleness of wood glue at −4 °C compared to RT, corresponding well with the relatively low T_g for PMDI-*co*-PPG, which falls in the range −52 to 8 °C. For thermoplastic craft glue, by contrast, the student observed a decrease in the stiffness when the adhesive film was heated to 70 °C, approaching the relatively high T_g of 80 °C, compared to when tested at RT. The final adhesive tested, PECA, was found to be relatively stiff and brittle at all tested temperatures, which is consistent with the relatively high T_g (149 °C) and low chain mobility of PECA.

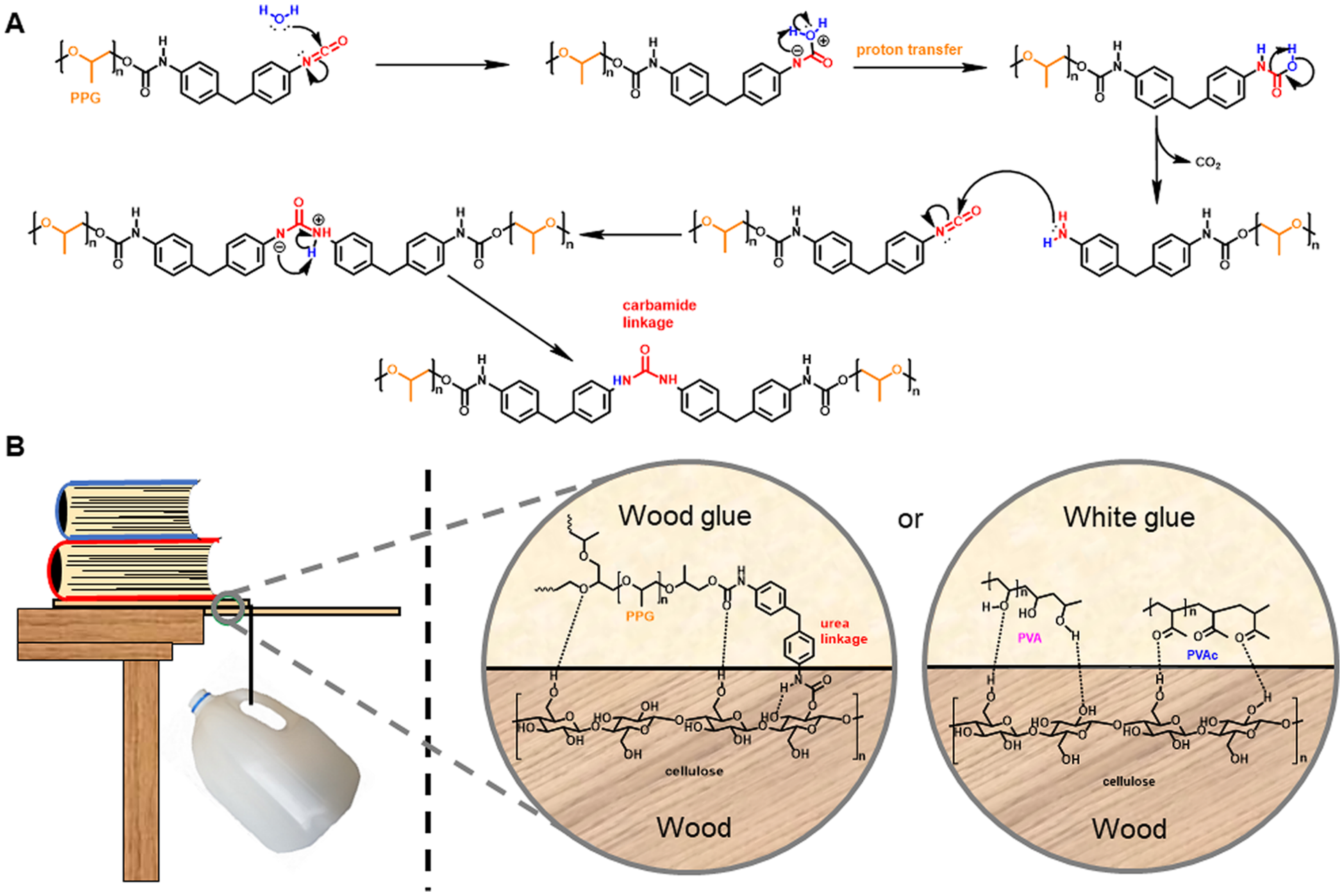

Figure 3. (A) Water attacks an isocyanate to form a nucleophilic amine to initiate the wood glue cure. Then, an amine can nucleophilically attack an isocyanate to form a urea linkage. (B) (Left) The experimental setup proposed for testing the strength of white glue and wood glue. (Right) Chemical and physical interactions between wood glue or white glue and wood. Wood glue can form urea cross-linkages with wood polymers as well as interact through hydrogen bonding, whereas hydrogen bonding is the main adhering force for white glue.

Module 3: White Glue, Such as Elmer's Glue All, and Wood Glue (Supporting Information Handout 3)

Most commercial wood glues are polyurethane-based. The liquid glue is a mixture of linear and multiarm polyols (usually polyethylene glycol or polypropylene glycol) with at least 2 isocyanate groups on each end. The isocyanate end-groups are 4,4′-diphenylmethane diisocyanate-based. These end-groups react with water to form CO_2 and a primary amine which can then react with other isocyanates, forming a urea linkage (Figure 3A). This allows the polymers to link together and form a solid 3D network. The formation of a solid network is a process known as curing. Wood is mostly composed of polysaccharides such as cellulose, xylan, and glucomannan, as well as lignan. These are hydrophilic polymers with many nucleophilic groups present, making the chemical cross-linking of isocyanate groups between the wood glue and the substrate possible. Most wood surfaces tend to be rough and porous, increasing the binding area and allowing for a degree of mechanical interlocking between the adhesive and the wood.

White glue consists of a mixture of linear poly(vinyl acetate) (PVAc), propylene glycol, and linear poly(vinyl alcohol) (PVA) in an aqueous emulsion. PVAc is good for binding porous materials, such as wood, glue, and cloth, because it can enter the pores and increase binding surface area. PVA is a protective colloid which prevents clumping and has adhesive properties. Propylene glycol is a physical cross-linking agent that also increases water solubility. Physical cross-linking occurs because white glue noncovalently adheres to surfaces as the water from the mixture evaporates, allowing the polymers to physically entangle and hydrogen bond with the substrate, rather than covalently form covalent linkages between polymer chains. The hydrophilic groups that are abundant on the polymers that make up wood make for good hydrogen bonding sites for PVA and PVAc. Most wood surfaces tend to be rough and porous, increasing the binding area and allowing for a degree of mechanical interlocking between the adhesive and the wood.

Experiment 1 (Supporting Information Handout 3) pertains to the mechanical strength of white and wood glue bonding sites, at the interface of two wooden popsicle sticks. Substrate failure was observed in many samples, illustrating that the mechanical strength of the adhesive surpassed that of the wooden popsicle stick and demonstrating that both adhesives are appropriate for bonding wood. However, student data showed all three types of failure (adhesive, cohesive, and substrate) to be possible. In this, there were noticeable differences between the breaking points of the samples. In all cases when substrate failure was not observed, the white glue samples had the highest mechanical strength when dry. Additionally, in the case of both adhesives, the mechanical properties were improved when the substrate was wet rather than dry. This was likely due to the increased cross-link density in the water activated wood glue and the enhanced permeability of the PVA and PVAc chains into the pores of

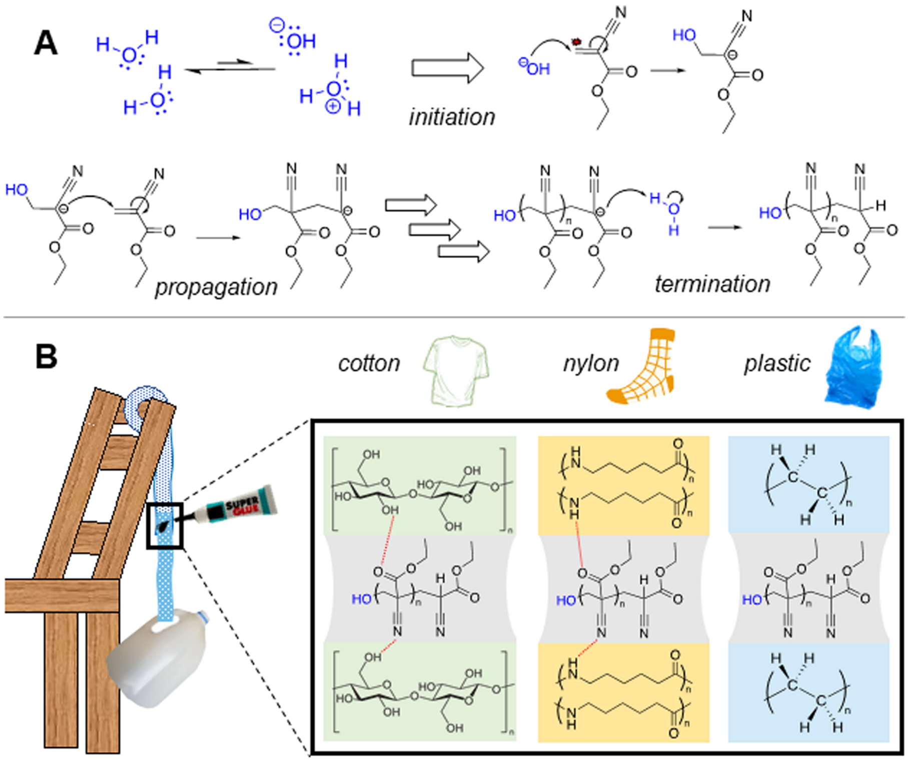

Figure 4. (A) Cyanoacrylate cure is initiated by water molecules adsorbed to the surface of the substrate. (B) The adhesive strength between a given substrate and a cyanoacrylate adhesive varies on the basis of the surface properties of the substrate. Intermolecular forces such as hydrogen bonding (depicted with red dotted lines) can affect the adhesive strength as well as the mechanical interlock, which varies on the basis of the surface roughness of the substrate. We can investigate differences in adhesive strength by performing mechanical testing with a variety of polymer substrates (cotton, nylon, polyethylene).

a wet substrate. The mechanical stability of the PVA-based white glue was not enhanced well, but an increase in average strength was observed in the wetted wood glue sample.

In experiment 2, the white glue dissolves after several hours in the water bath while the wood glue does not. The water can disrupt and replace hydrogen bonds between the PVA, PVAc, and wood, allowing the glue to redissolve. The wood glue has covalent bonds between the polymer chains and the wood, which cannot be broken by water.

Substrate failure can be observed in experiment 2 due to the weakening of the wood from water submersion. Cellulose microfibrils that make up the wood are distanced from each other with the introduction of water, creating a higher load on each fiber. Thus, if substrate failure is observed in experiment 2, a clean break is not typically seen as with dry wood, but rather, the fibrils are pulled apart from each other from excessive wetting.

Regardless of substrate wetting, white glue had the fastest cure time, followed by wood glue. The white glue samples took longer to cure when the substrate was wetted, likely due to the increased amount of water that needed to evaporate. For wood glue, wetting the substrate decreased the cure time by activating more of the isocyanate groups and increasing the rate of cross-linking.

Module 4: Cyanoacrylate Adhesive Compatibility with Various Substrates (Supporting Information Handout 4)

PECA. Cyanoacrylate adhesives (PECAs) are powerful adhesives that are capable of binding a wide variety of substrates including metals, ceramics, glass, and plastics.[41] Commercial PECAs are composed of methyl or ethyl cyanoacrylate monomers, which cure via chain-growth polymerization (Figure 4A). When the PECA is applied, it reacts with water and other functional groups on the substrate's surface to start the curing process.[42] The resulting cured PECA is a solid polymer, which creates adhesion primarily through mechanical interlock as well as weak intermolecular forces. While the polymerization can proceed through an anionic or radical mechanism, the anionic mechanism is almost always favored due to the cure conditions present during household use.[42] The mechanistic steps of chain-growth polymerizations are initiation, propagation, and termination.[43] In the anionic mechanism, a nucleophile initiates the polymerization and generates an anionic propagating chain end. In the radical mechanism, the initiator and the propagating chain end are both radicals.

Contact Angle. The strength of the bond formed by an adhesive depends partially on the surface energy of the substrate.[44] Surface energy is directly correlated with the wettability of a surface, which can be measured by contact angle,[44] the angle at which a liquid meets the surface of a material. Contact angle measurements made using water as the liquid, termed the water contact angle, are standard because these can be used to calculate a material's surface energy. Materials with a high surface energy tend to have a low water contact angle, meaning that the surface is more polar and more hydrophilic; materials with a low surface energy tend to have a high water contact angle, meaning that the surface is less polar and more hydrophobic. Thus, high surface energy materials are easier to bond with adhesives because these materials can better participate in polar intermolecular forces with the adhesive, such as hydrogen bonding, while low surface energy materials are limited to weak, nonpolar intermolecular forces.

When the experiment for this module was performed, the relationship between adhesive strength and water contact angle (WCA) was unexpected, but results could be rationalized by the macroscopic roughness of the substrates tested. From qualitative WCA observations, polyethylene had the largest WCA, followed by nylon, followed by cotton. This result was expected because cotton fabric is composed of cellulose, which contains surface hydroxyl groups, while polyethylene has no polar functional groups. On the basis of this trend, we expected that cotton would have the highest adhesive strength with cyanoacrylate due to its high wettability and abundant sites for hydrogen bonding, while polyethylene would have the lowest adhesive strength. However, contrary to our prediction based on WCA, nylon supported the most weight, followed by cotton. This reversed trend between the adhesive strengths of nylon and cotton can be explained by the thickness of the cyanoacrylate adhesive film on these materials. Cotton has a much rougher surface than nylon; therefore, the PECA film created on the cotton fabric sample was visibly thicker, compared to that on the nylon fabric sample. It is well-known that thinner cyanoacrylate films are stronger due to the surface-initiated cure, which may not extend through a thick layer of adhesive. Additionally, the site of failure is an important consideration when evaluating the results of this experiment: Both nylon and cotton failed at the site of the bond, while polyethylene experienced substrate failure, limiting the student's ability to assess the adhesive strength of the polyethylene−cyanoacrylate bond. Nevertheless, this experiment provides students with practice in critically thinking about results and a potential mismatch with their hypothesis, a consistent theme in scientific research.

Module 5: Water Effects on Caulk and Cyanoacrylates (Supporting Information Handout 5)

Most household silicone caulks are composed of a PDMS (polydimethylsiloxane) prepolymer and methyltriacetoxysilane (trifunctional cross-linker) (Figure 5A). Caulk cure results in a covalently cross-linked thermoset. To initiate the cure, hydroxyl-terminated PDMS reacts with methyltriacetoxysilane to liberate acetic acid and functionalize the PDMS with two acetoxy functional groups on each end, forming a PDMS prepolymer with reactive end-groups. From here, each acetoxy end-group can undergo one of two reactions: (1) nucleophilic attack by a hydroxyl-terminated PDMS polymer which results in either linear growth or cross-linking or (2) hydrolysis by water (from ambient humidity or adsorbed to the substrate's surface) to regenerate a hydroxyl end-group on the PDMS. Both reactions are necessary for caulk cure. Due to the release of an acetic acid molecule each time one of the aforementioned reactions occurs, the smell of vinegar signals that the caulk is actively curing. The amount of water present during the cure will impact the occurrence of acetoxy hydrolysis, which will influence the cross-linking density of the cured caulk. Higher water content contributes to a greater cross-linking density and generally leads to a mechanically stiffer material.[45]

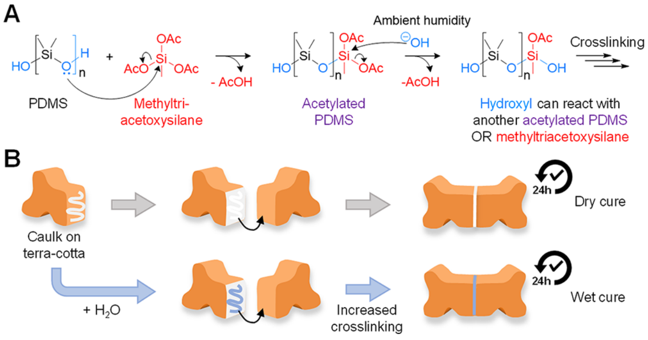

Figure 5. (A) Caulk cures when hydroxyl-terminated polydimethylsiloxane (PDMS) is covalently cross-linked by a trifunctional acetoxy cross-linker. This cross-linking reaction requires water to generate nucleophilic hydroxyl groups that are capable of reacting with the acetoxy groups. (B) We can study the effect of water on caulk cross-linking density, and thus adhesive capacity, by curing caulk on a dry or a wet terra-cotta substrate.

A bottle of superglue (PECA) primarily contains liquid cyanoacrylate monomer. When PECA is exposed to the atmosphere, water, or any other nucleophile on a substrate surface, cure of the liquid monomer is initiated. Here, the cyanoacrylate monomer reacts with a nucleophile, such as water or a nucleophile on a substrate, to generate a reactive chain end. Each nucleophile molecule initiates a new polymer chain. The reactive chain ends continue to propagate until all the monomer is consumed, eventually forming many linear poly(cyanoacrylate) polymers (detailed illustration of cyanoacrylate glue polymerization in Figure 4). The resulting cured PECA is a network of entangled poly(cyanoacrylate) polymers that adheres through mechanical interlock and weak intermolecular forces with a surface.

Terra-cotta is a ceramic material made from clay particles (aluminum silicate) that are sintered together through a firing process. Terra-cotta can absorb and retain water in its pores, making it an appropriate substrate for testing adhesives that rely on water for curing (Figure 5B).

The purpose of module 5 (Water Effects on Caulk and Cyanoacrylates) is to (1) explore the mechanical differences between a thermoset versus a thermoplastic and (2) evaluate how cure conditions (presence or absence of excess water) impact the mechanical properties of the adhesive. This module directly compares caulk, a thermoset, with PECA, a thermoplastic. The different intramolecular interactions between these materials (covalent cross-links for caulk and noncovalent entanglement for PECA) will impact the mechanical integrity of the adhesive. The experiment demonstrates that the covalent cross-links present in the caulk thermoset result in stronger adhesive properties than the noncovalent entanglement afforded by the PECA. Furthermore, this experiment allows the student to explore how the cure conditions, which impact polymer properties (molecular weight and cross-linking density), influence material properties by comparing a wet cure to a dry cure with both adhesives. For PECA, the presence of excess water during the cure ("wet cure") results in many short poly(cyanoacrylate) that cannot entangle as effectively as the longer poly(cyanoacrylate) chains that are produced in a "dry cure". As a result, it is determined that the shorter polymer molecular weight obtained from the "wet cure" of PECA leads to weaker adhesive properties. On the other hand, the presence of excess water during the caulk cure ("wet cure") had no notable effect on the adhesive properties of the caulk, compared to the "dry cure" caulk.

Data Analysis and Unexpected Results. Our experimental design allows students to collect measurements independently and provides opportunities for data analysis and workup. We anticipate that results will vary as students will use different brands and specifications of adhesive and substrate. This will provide an opportunity for students to discuss and hypothesize reasons for differences between their materials and results. The companion worksheet for each module includes tables for data collection, instructions for data workup, and accompanying questions to allow reflection.

To further emphasize and create opportunities for analysis of unexpected results, multiple conditions and experiments are included within each module to demonstrate different types of failure, the effects of humidity, and the thermal variation in response. This is especially the case in module 3 (White Glue and Wood Glue), where adhesive failure may not come before substrate failure, so multiple experiments are presented. Modules 4 (Cyanoacrylates) and 5 (Caulk and Cyanoacrylates) also include some conditions that do not always give a direct answer to the corresponding hypothesis. To contrast this, we have developed modules 1 (Epoxy) and 2 (Thermoplastics versus Thermosets) which are more straightforward tests of each hypothesis.

MATERIALS AND METHODS

Materials were purchased and used as received without further modification or purification. A comprehensive list of materials used and the supplier of each are provided in the Supporting Information (handout 6). Experimental details for each module can be found in the Supporting Information (handouts 1–5).

HAZARDS

Though adhesives are designed to be used safely at home, most adhesives can cause eye and skin irritation and may produce vapors that are harmful when inhaled. Avoid direct bodily contact with adhesives. Nitrile or latex gloves and safety glasses may be worn to provide skin and eye protection, respectively. Only use adhesives in a well-ventilated area.

PECA causes skin, eye, and respiratory irritation, may cause an allergic skin reaction, and is a combustible liquid.[46] Avoid unintentional contact with PVC, nylon, and/or cotton materials, as PECA can react rapidly and exothermically with these materials and will form permanent bonds. PECA can also react exothermically with and form permanent bonds to skin and hair.

Craft glue has no significant adverse effects upon exposure via skin contact, eye contact, inhalation, or ingestion.[47]

Polyurethane wood glue causes skin, eye, and respiratory irritation and can produce asthmatic sensitization upon inhalation, and exposure may cause an allergic reaction or asthma-like symptoms.[48] Note that warning properties (irritation, detection of odor) are not adequate to prevent overexposure from inhalation; use this adhesive only in a well-ventilated area.

Caulk causes serious eye irritation, contains combustible liquid, and may cause damage to organs or irritation to skin through prolonged or repeated exposure.[49]

Epoxy resin (reference SDS forms) such Alumilite and Art n'Glow can cause serious eye damage or irritation and is a skin sensitizer. Note that heat may be generated during the cure.[50,51]

CONCLUSION

In response to the disruption caused by the SARS-CoV-2 pandemic, we have created a set of remote learning modules that use household adhesives as a platform for teaching organic and polymer chemistry remotely. These modules were designed to provide students with an engaging, hands-on learning experience, specific to polymer chemistry, without requiring a traditional laboratory space. The experiments we describe exercise research-relevant skills such as searching for primary literature sources, fabricating test samples, explaining unexpected experimental results, and revising experimental procedures, while covering key concepts in polymer chemistry such as polymer synthesis, intermolecular interactions, thermomechanical properties, structure–function relationships, and molecular design. These modules are targeted to undergraduate students who have taken at least one semester of organic chemistry.

Undergraduate students in our research group tested and helped develop these modules remotely as summer undergraduate research projects while on-campus activities at universities across the United States were shut down. These students cited the opportunity to practice experimental reproducibility, use literature and hands-on personal experience to explain unexpected results, and modify experimental design as some of the most valuable benefits of these modules. Educators interested in utilizing these materials could implement the full collection of modules to form a remote learning laboratory course, or implement modules individually, to augment specific units in an existing polymer chemistry lecture or as the basis of polymer chemistry outreach activities. Ultimately, these modules provide educators with a valuable tool for teaching experimental chemistry outside of the laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c01374.

> Laboratory teaching modules for distance learning with and without answer keys and a comprehensive list of necessary materials along with links to purchase and current prices (PDF, DOCX)

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Notes

Any opinions, findings, and conclusions communicated in this material are those of the authors and do not necessarily reflect the views of NSF.

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