

Supporting Information

Frontal polymerization of a thin film on a wood substrate

Karan Bansal¹, John Pojman^{2*}, Dean Webster^{1*}, Mohiuddin Quadir^{1*}

¹Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58108,
United States

²Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States

Experimental Section

Materials

Trimethylolpropane triacrylate (TMPTA) was obtained from Allnex; Fumed silica (Aerosil 202) was obtained from Sigma Aldrich. Graphene nanoplatelets were purchased from Cheaptubes, Inc (X-Y dimensions >2 μm , average thickness 8-15 nm and specific area 500-700 m^2/g) and Luperox® 231 were purchased from Sigma Aldrich. Calcium carbonate powder was obtained from Duda Energy (325 mesh, Diameter 44 μm). Oak wood panels were cut from wood sheet (1/4x2x2 Oak plywood handi-panel of red oak variant). The dimension of the purchased wood panel was 24'' x 24'' x 0.185'' from which 16 cm x 8 cm pieces were prepared for coating.

Formulation of coatings

Preparation of Base coatings. At first, base coatings were formulated using TMPTA, fumed silica and Luperox® 231. Five formulations, namely, B1-B5 were prepared using different amounts of fumed silica while maintaining the amount of TMPTA and Luperox® 231 constant (Table S1). The mixing ratio for the front to propagate completely was optimized first. Based on earlier work on frontal polymerization, we selected 1 part per hundred resin (phr) Luperox® 231, i.e., for every 100 g of resin 1 g of initiator to ensure complete propagation of thermal front.^{10, 14, 27} To obtain optimum working viscosity, fumed silica was added in 1, 2, 3, 4 and 5 phr, and the viscosities of these suspension formulations were determined with a Brookfield CAP 2000 cone and plate viscometer (ICI type). With optimized working viscosity, films with different thicknesses were prepared using drawdown bars. The wet film thickness, in this report, is considered as the gap in the drawdown bar used to draw coatings. These resin solutions with adjusted viscosity containing no filler materials were considered as base formulations. The coatings were cured with the help of a heat gun. One edge of the wood panel was heated till the front starts, after which the heating was stopped, and the front propagated by itself through frontal polymerization.

Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) test was performed using a Thermo Scientific Nicolet 8700 FTIR instrument. The sample was mixed up with KBr powder and pressed to form a KBr pellet under pressure. The sample was scanned 32 times. Spectra were collected in the range of 4000-400 cm^{-1} at a spectral resolution of 4 cm^{-1} . Resultant spectra are shown in Supporting information, Figure S1.

Coatings Containing Calcium Carbonate. To study the effect of filler types on the rate of front propagation we selected calcium carbonate first as the filler. This filler material possesses granular, macroscopic structures and is not amenable for homogenous incorporation into UV-curable resins. The base formulations were loaded at 5, 10, 15 and 20 phr. A series of resin formulations (Table S1) was prepared using varying amounts of calcium carbonate from which films of 15 mils (381 μm) wet film thickness were prepared using a drawdown bar.

Coatings Containing Graphene Nanoplatelets. The base formulation was further loaded with graphene nanoplatelets. We hypothesized that, due to enhanced thermal conduction property of graphene, the front velocity will be increased with graphene, as reported by Goli et al. for continuous conductive elements.²⁸ Graphene nanoplatelets were added in 1, 3, 5 and 7 phr in comparison to the base coating as shown in Table S1 (FPG series). A wet film thickness of 15 mils (381 μm) was prepared using drawdown bar to study the frontal properties of these formulations. As defined earlier, the wet film thickness is considered as the gap in the drawdown bar that is used to draw coatings.

Characterization of Coatings

Viscosity measurements. Viscosity was measured using a Brookfield CAP 2000 I.C.I.-type cone and plate viscometer). The viscometer used spindle 4 and was rotated at 900 RPM. The temperature at which the viscosity readings were taken was between 22° C - 23° C.

Front velocity and front temperature measurements. The front velocity and the front temperature were tracked by capturing video using an infrared (IR) camera (Seek Thermal™) coupled to an Android phone.

The reading for the front temperature was taken when the front was propagating at a constant velocity and reached the middle of the wood panel. The front velocity was calculated by plotting the position of the front versus time and determining the slope of the best-fit line. All experiments were repeated three times, the values were averaged, and the standard deviation calculated. The videos are included in the supporting information.

Computerized tomography (CT) Scan measurements. To identify surface and microstructure of the coated samples was scanned in a GE Phoenix X-ray computed tomography system (μ CT) equipped with a 180 kV nanofocus X-ray tube and a high-contrast GE DXR250RT flat panel detector (GE Sensing & Inspection Technologies GmbH, Germany). At a voltage of 600 kV and a current of 2300 μ A with a molybdenum target, 1500 projections were acquired. Detector timing was 500 msec. Sample magnification was 11.92X with a voxel size of 31.6 μ m. The acquired images were reconstructed into a volume data set using GE provided computer tomography software version 2.2 (GE Sensing & Inspection Technologies GmbH, Germany). The reconstructed volume was then viewed and manipulated using VGStudio Max (Volume Graphics, Inc., NC).

Table S1. Composition of frontally polymerizable resin. B = base film formulations, FPCC and FPG = frontally polymerized films containing calcium carbonate and graphene, respectively.

Sample	TMPTA (g)	Luperox ® 231 (g)	Fumed Silica (g)	Calcium Carbonate (g)	Graphene Nano platelets (g)
B1	10	0.1	0.1	-	-
B2	10	0.1	0.2	-	-
B3	10	0.1	0.3	-	-
B4	10	0.1	0.4	-	-
B5	10	0.1	0.5	-	-
FPCC5	10	0.1	0.3	0.5	-
FPCC10	10	0.1	0.3	1	-
FPCC15	10	0.1	0.3	1.5	-
FPCC20	10	0.1	0.3	2	-
FPG1	10	0.1	0.3	-	0.1
FPG3	10	0.1	0.3	-	0.3
FPG5	10	0.1	0.3	-	0.5
FPG7	10	0.1	0.3	-	0.7

Calculation of extent of curing

Fourier transform infrared spectroscopy (FTIR) test was performed using a Thermo Scientific Nicolet 8700 FTIR instrument. The sample was mixed up with KBr powder and pressed to form a KBr pellet under pressure. The sample was scanned 32 times. Spectra were collected in the range of 4000-400 cm^{-1} at a spectral resolution of 4 cm^{-1} . Resultant spectra are shown in below:

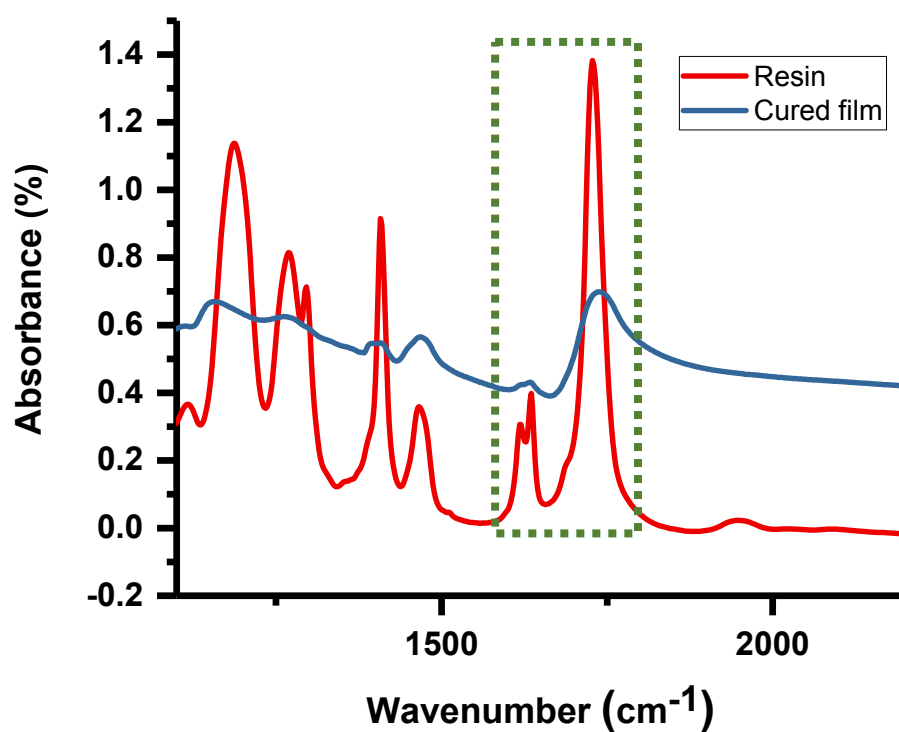


Figure S1: FTIR spectra to identify the extent of cure. While uncured resin shows strong absorption bands for C=C peaks originating from unreacted acrylates at 1630 cm^{-1} (shown in inset). After frontally polymerized (FP) curing, C=C peaks from uncured monomers were observed at $\sim 1630 \text{ cm}^{-1}$

In the highlighted areas under the peaks (Figure S1) was calculated for C=O and C=C. For the base resin, C=O band was at 1728.21 cm^{-1} , and the area corresponding to this is 49.63 units with the baseline ranging from 1660.41 cm^{-1} to 1814.69 cm^{-1} . The area corresponding to C=C bands present at 1630 cm^{-1} is 7.42 units with baseline ranging from 1602.56 cm^{-1} to 1660.41 cm^{-1} . Similarly, areas under the peaks were calculated for the cured coating. The area corresponding to C=O band was 1736.35 cm^{-1} with 25.33, and the baseline ranging from 1664.27 cm^{-1} to 1884.11 cm^{-1} . The area corresponding to C=C bands present at 1630 cm^{-1} is 0.80 units with baseline ranging from 1600.63 cm^{-1} to 1660.41 cm^{-1} .

To determine the extent of curing, the ratio of the areas under the peak for C=C to C=O was calculated. The values for the base resin and cured coating were 0.149 and 0.031, respectively. To know the extent of curing, the ratio between the base resin and cured coating was compared, which indicated $(0.031/0.149) \times 100 = 21\%$ remaining unsaturation is present in cured resin. Therefore, 79 % of initial concentration of monomers were converted into the cross-linked network initiated by frontal polymerization.

Video 1: Frontal polymerization of the base formulation.

Video 2: (a) Frontal polymerization of coating formulations containing 5 phr calcium carbonate, FPCC 5 (b) Frontal polymerization of 10 phr calcium carbonate, FPCC 10 and (c) Frontal polymerization of 15 phr calcium carbonate, FPCC 15

Video 3: (a) Frontal polymerization of coating formulations containing 1 phr graphene, FPG 1 (b) Frontal polymerization of coating formulations containing 3 phr graphene, FPG 3 and (c) Frontal polymerization of coating formulations containing 5 phr graphene, FPG 5