Soy Flour Substitution in Polymeric Methylene Diphenyl Diisocyanate Resin for Composite Panel Applications

Osei Asafu-Adjaye
Brian Via
Sujit Banerjee

Abstract

Partial substitution of polymeric methylene diphenyl diisocyanate (pMDI) resin by 10 to 15 percent soy flour for the manufacture of strand board improves board properties while decreasing cost. For particleboard and medium-density fiberboard the soy-substituted resin performs as well as the control pMDI. The reaction of soy flour with pMDI occurs over several hours as tracked by CO_2 evolution. The soy-amended resin must be used within about 30 minutes of formulation. Uniform mixing of soy flour with pMDI is critical because unreacted soy flour tends to retain water, which degrades the wet properties of the board. The soy flour increases the tack of pMDI resin, which increases the surface coverage and the relative bonded area at the glue line.

Soy-based products were used as binders for plywood and related products (Lambeth 2003) but were replaced by petroleum-based binders such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) because of cost–benefit considerations. However, recent concerns with formaldehyde emissions have prompted reconsideration of soy binders for indoor applications. Several attempts have been made to extend soy adhesives to wood composites, most often in combination with hydrocarbon-based adhesives (Vnucec et al. 2017). Soy proteins have been functionalized to improve their native performance (Qi and Sun 2011) and some of these perform as well as PF or UF resins. However, commercialization has been challenging because of cost considerations. The only significant commercial use of soy adhesives has been in products such as decorative veneer where exposure to water is relatively low (Li et al. 2004, Li 2010).

Polymeric methylene diphenyl diisocyanate (pMDI) resin is increasingly used as a formaldehyde-free resin for bonding wood but is costly and sometimes requires synergistic extenders to be cost effective (Narron et al. 2020, Wan et al. 2020). In previous work we have shown that partial (~15%) substitution of soy flour in pMDI resin for the manufacture of strand board and particleboard improves cost–benefits without deteriorating board properties (Cheng et al. 2019). These properties have a strong dependence on how the soy flour and pMDI are mixed and applied. At room temperature, the soy flour raises resin viscosity to the point where it impedes spraying. This increase does not occur if the mixture is prepared at 40°C (Cheng et al. 2019, Via et al. 2019). Also, soy flour increases the cold tack of pMDI, which is especially useful for particleboard, in which the mats tend to disintegrate while being conveyed to the press (Asafu-Adjaye et al. 2020). We have previously discussed the interaction of soy flour and pMDI resin at press temperatures (Hand et al. 2018). In this article we study the mechanism of the interaction of soy flour with MDI resin and illustrate the effect of uniform mixing of resin and soy flour on board properties. We also identified where partial soy flour substitution actually improves product performance.

Materials and Methods

Defatted soy flour (7B) was provided by Archer Daniels Midland (Chicago, Illinois); its dry-basis moisture content (MC) was 6.2 percent. The pMDI resin was MONDUR 541

The authors are, respectively, Graduate Student and Director, School of Forestry and Wildlife Sci., Auburn Univ., Alabama (oaa0014@auburn.edu, brianvia@auburn.edu [corresponding author]); and Emeritus Professor, School of Chemical and Biomolecular Engineering, Georgia Tech, Atlanta (sb@gatech.edu). This paper was received for publication in March 2020. Article no. 20-00014.

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from Covestro (Leverkusen, Germany). Screened wood strands (MC 7% to 8%) were donated by J.M. Huber (Edison, New Jersey), Louisiana-Pacific (Nashville, Tennessee), and Norbord (Toronto, Canada) Corporations. Fiber for medium-density fiberboards (MDFs) was obtained at an MC of 9 percent from Kronospan (Jihlava, Czech Republic). Wood sawdust particles were provided by West Fraser (Vancouver, Canada) and dried to 6 to 7 percent MC. Emulsified wax (Hexion Bord'N-Seal FMH-XD) was obtained from Huber Corp.

Wax was first sprayed on the wood products at a loading of 1 percent (ovendried weight) for flakeboard and particleboard and 0.2 percent for MDF. MDI or mixtures of MDI and soy flour were then sprayed on the wood products with a paint sprayer powered by an air compressor. Strand board was made with a resin load of 3 percent of wood weight; a 4 percent resin load was used for particleboard. The same resin loading was applied to both face and core layers.

Mats were formed in a 43 by 43 cm frame without orientation and then hot pressed for 3 minutes at 213°C and 2 MPa. The nominal thickness of the board was 1.1 cm. The target density was 641 kg/m^3 (40 lb/ft^3), 689 kg/m^3 (43 lb/ft^3), and 650 kg/m^3 (41 lb/ft^3) for strand board, particleboard, and MDF, respectively. For MDF, to see the additional effect of density, we tested 560 and 650 kg/m^3.

For MDF, we had difficulty in blending the resin with the fiber. In industry the resin is added at the blow line, a procedure that cannot be easily reproduced in the lab. These difficulties were resolved by using a cement mixer–like blender with the orifice covered with clear plastic. A 3-cm-diameter hole was cut out from the center of the plastic to accommodate the spraying gun. Fibers were dispersed by hand.

The moisture cycle test for bonding performance (single cycle or D4 test) was run according to American Plywood Association PS2 (2004). Specimens (152 by 152 mm) were soaked in 66°C water under about 506 mbar. The vacuum was released after 30 minutes and the samples were kept soaked at atmospheric pressure for an additional 30 minutes. They were then dried at 80°C for 15 hours. Internal bond, water absorption, and thickness swell were measured according to ASTM D1037-12 (ASTM International 2012).

CO_2 measurements were made with a Neulog NUL-260 instrument. Mixtures of MDI (30 g) and either soy flour (3 g) or water (190 μL) were stirred at a Reynolds number of about 47 and the headspace CO_2 measured. The amount of water added was equivalent to the water contained in 3 g of soy flour. The stirring speed was kept at 3,000 to 3,200 revolutions per minute across all the measurements at room temperature.

Contact angle was measured on a metal coupon with the sessile drop method using an OCA-50 system equipped with a 6.5-fold zoom lens. Measurements were taken after 30 seconds of application at room temperature.

For statistical analysis, we ran an analysis of variance to test if at least one of the groups differed from the other groups. All of our tests were significant to $\alpha = 0.05$ (not shown) and Fishers least significant difference (LSD) was used to determine if treatments differed. The total range was listed and in all cases the LSD was less than the range, which indicated significance.

Results and Discussion

Mixing soy flour and MDI resin

CO_2 evolution.—pMDI resin can react with the water contained in soy flour or with functional groups in components of the flour. The reaction of pMDI with water proceeds according to Equation 1 (Yakabe et al. 1999):

$$\mathrm{Ar-N=C=O+H_2O \rightarrow Ar-NH-C(=O)OH \rightarrow ArNH_2+CO_2} \tag{1}$$

pMDI and water do not mix well; they tend to form two layers, and the rate of reaction is partly governed by physical processes such as mixing efficiency. Allport et al. (2003) reported that the half-life for the reaction of water and pMDI is less than 2 hours, although this value is very approximate. Because the reaction of pMDI with either water or soy flour releases CO_2, the measurement of CO_2 evolution over time can provide insight into the reaction.

CO_2 emission profiles measured under various conditions are illustrated in Figure 1. The ''water only'' curve corresponds to the amount of water contained in the two ''soy'' curves. The maximum CO_2 that would be evolved if all the water were to react with pMDI is 8,150 parts per million (ppm) over and above the baseline value of 360 ppm. The terminal value for the water only curve in Figure 1 is 2,800 ppm, which represents 31 percent conversion. Hence, the reaction should continue slowly for several hours. However, water is not the only source of the CO_2. The ''dry soy'' curve where bone-dry soy flour was mixed with pMDI also reflects appreciable CO_2 release. Also,

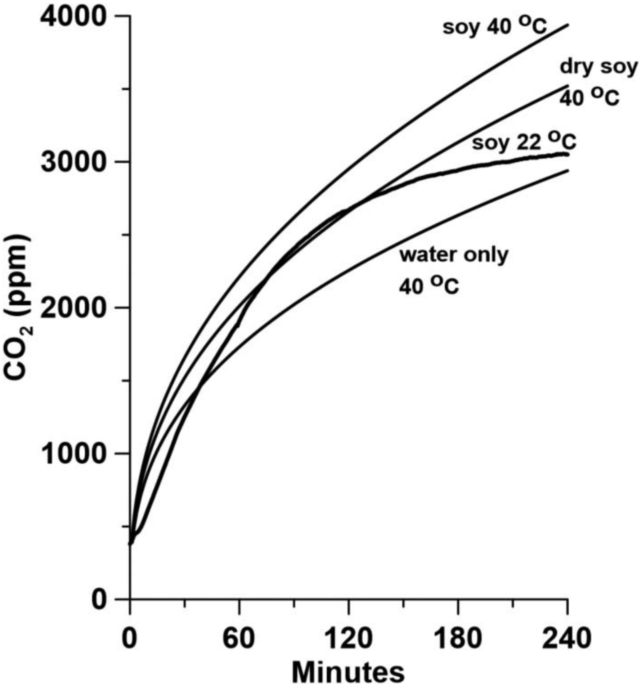

Figure 1.—CO_2 evolution from the reaction of methylene diphenyl diisocyanate resin with soy flour or water. ppm = parts per million.

some of the CO_2 was trapped as bubbles or dissolved in the resin and was released slowly.

The rates of all the processes in Figure 1 are quite similar. Their interpretation is difficult because CO_2 evolution depends on both the pMDI reaction rate and on the rate of CO_2 release from the resin. The CO_2 values are higher at 40°C than at 22°C because the reaction should be faster at 40°C, and also because the viscosity of pMDI is almost three times lower at 40°C than at 22°C (Cheng et al. 2019). The lower viscosity at 40°C facilitates the escape of CO_2 bubbles trapped in the resin. The rate for dry soy is higher than that for water only, which implies that the functional groups in soy flour react faster than does water. He and Yan (2005) reported the opposite situation for pMDI reaction with wood of varying MC. They found the rate to double going from dry wood to 7 percent MC wood. However, the water in wet wood is bound water at these low levels, which is different from our case where the water added to MDI is free water. Nevertheless, both studies indicate that the reaction rate of pMDI with water or soy flour is quite similar.

Our results seemingly conflict with those of Yakabe et al. (1999), who found the reaction of MDI with water to take several hours. However, Yakabe et al. (1999) noted that the reaction was mass transfer limited because the two liquids are effectively immiscible. In our measurements water was stirred into excess MDI, where mass transfer limitations would be less severe. The practical aspect of our findings is that gas is evolved for an extended period from soy/MDI mixtures. The viscosity increases as a result, so the mixture must be used within about 30 minutes at 40°C before spraying is impeded. However, this issue may be moot if inline mixers are utilized (Thakur et al. 2003).

Strand board applications

In previous work we noted that wet properties degraded when soy flour substitution exceeded 10 percent. The average edge swell increased, but this was caused by high values in a small subset of the samples; most of the samples were unaffected by the soy (Cheng et al. 2019). This would be the outcome if the soy flour was not fully dispersed; small clumps of soy flour present in just a few samples would tend to attract moisture. It follows that more uniform mixing should reduce edge swell. Two modes of blending were used to evaluate the importance of uniform mixing: stirring soy flour into pMDI by (1) hand stirring with a glass rod, and (2) with a blender with a whip fixture. About 0.3 to 0.5 g of the soy powder was added at a time to the pMDI over 5 minutes. Results from D4 tests are presented in Table 1. Blender mixing gives better results than hand mixing ($P < 0.05$), and all the soy values are lower than those of the control pMDI. Strength properties (both dry and wet) are illustrated in Figure 2. Although the dry properties are relatively unaffected by the mode of mixing, there is a clear improvement in wet strength. For modulus of elasticity and modulus of rupture the values from the blended soy resin are better than those from pMDI alone. These results have been confirmed in industrial pilots (personal communication 2020).

Table 1.—Edge swell results of polymeric methylene diphenyl diisocyanate (pMDI) substituted with 12 and 15 percent soy flour with different blending techniques.[a] *Note that treatments/control that do not overlap were significantly different as confirmed through least significant difference.*

Treatment	Edge swell (%)
pMDI (control)	50 ± 6
12% Soy hand	43 ± 3
12% Soy blender	35 ± 2
15% Soy hand	33 ± 4
15% Soy blender	30 ± 2

[a] $n = 6$.

An operational concern with the use of soy is its potential effect on board quality if the production line goes down and the resinated flakes need to be stored before pressing. The effect of storage was measured by resinating the flakes and pressing immediately and after a delay of 6 hours. The results are provided in Table 2. As expected, the properties of the control boards (pMDI only) degrade upon storage, but surprisingly, the properties of the soy-treated boards are, for the most part, better than those of the pMDI controls.

Particleboard applications

Results from soy-treated particleboard were similar to those obtained with strand board as shown in Figure 3 in that there was no statistical difference between the control and soy-treated boards. Hence, in the absence of spraying issues, at least 20 percent soy flour can be substituted for particleboard. However, as described earlier, the main benefit of soy flour is its ability to increase cold tack, which is important for both particleboard and plywood (Hogger et al. 2018, Wan et al. 2020). At 12 percent soy

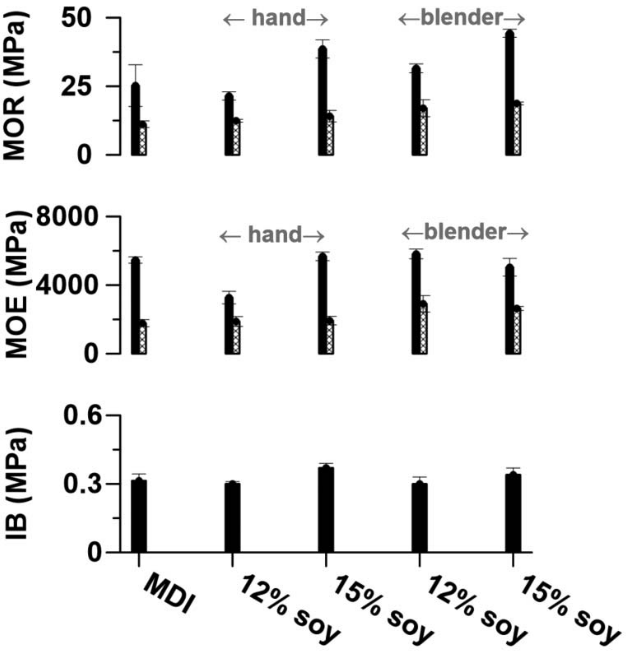

Figure 2.—Effect of soy substitution on strand board properties. The hatched bars represent wet properties; n = 8. *MDI = methylene diphenyl diisocyanate; IB = internal bond; MOE = modulus of elasticity; MOR = modulus of rupture.*

Table 2.—Properties of boards made from flakes prepared immediately after resination and after 3 and 6 hours.[a,b] *Note that treatments/control within a column that do not overlap were significantly different as confirmed through least significant difference.*

	TS inner (%)	TS edge (%)	WA inner (%)	Dry MOE (MPa)	Wet MOE (MPa)	Dry MOR (MPa)	Wet MOR (MPa)	IB (MPa)
0 h								
Control	15 ± 1	21.2 ± 0.4	30 ± 7	5,400 ± 900	1,500 ± 60	40 ± 5	15 ± 2	0.77 ± 0.03
Soy	14 ± 1	20 ± 1	22 ± 1	6,200 ± 700	1,550 ± 50	43 ± 5	16 ± 1	0.9 ± 0.1
3 h								
Control	11 ± 2	17 ± 1	22 ± 4	7,400 ± 900	1,900 ± 300	53 ± 9	19 ± 2	0.8 ± 0.1
Soy	13 ± 1	19 ± 1	22 ± 3	6,500 ± 300	1,960 ± 60	45 ± 3	21 ± 2	0.9 ± 0.2
6 h								
Control	17 ± 2	20 ± 2	30 ± 1	3,000 ± 100	1,000 ± 100	24 ± 3	12 ± 1	0.6 ± 0.1
Soy	13 ± 1	21 ± 2	23 ± 3	3,300 ± 200	1,120 ± 60	27 ± 2	12 ± 1	0.7 ± 0.1

[a] Three percent resin loading, 10 percent soy flour substitution, $n = 6$.

[b] TS = thickness swell; WA = water absorption; MOE = modulus of elasticity; MOR = modulus of rupture; IB = internal bond.

flour substitution, the cold tack approximates that provided by UF resin. Higher soy flour substitution may lead to excessive tack (Asafu-Adjaye et al. 2020).

The increase of pMDI tack by the addition of water has been noted by Moriarty (2017a, 2017b), but there was no discussion of the effect of board properties. Zhang et al. (2018) has reported a fivefold increase in lap shear strength when water is added to pMDI at a level of 30 percent. However, the lap samples were cured at 160°C for 5 hours under 50 kPa pressure, which bears no resemblance to industrial practice. Also, wet properties, which are especially sensitive to changes in resin formulation, were not reported.

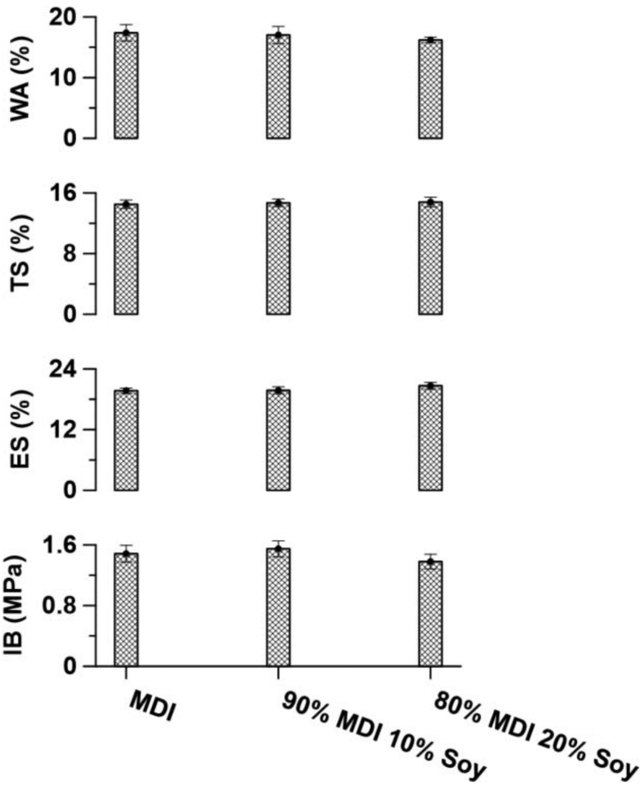

Figure 3.—Effect of soy substitution on particleboard properties; n = *12. MDI = methylene diphenyl diisocyanate; IB = internal bond; ES = edge swell; TS = thickness swell; WA = water absorption.*

MDF applications

Boards were prepared with various resin formulations and tested for various strength properties. The results from two separate runs (a and b) are shown in Figure 4. The properties of boards from run b are better than those from run a because of the higher density used in run b. The properties of the soy-treated and control (MDI) boards are broadly equivalent. There appears to be a trend for the soy flour to slightly improve dry properties while degrading wet properties to a small extent, but these differences are in the neighborhood of the 1σ uncertainty.

Mechanism

The effect of soy flour substitution on flakeboard, particleboard, and MDF are similar in that the wet and dry properties either improve or remain unchanged. Kowalski et al. (2013) noted that an effective adhesive immediately wets a surface upon contact. Wetting increases surface coverage and promotes surface penetration, which fills in microscopic surface irregularities. Tack is defined as the adhesive failure energy of adhesive joints formed with low contact pressure during a short contact time (Zosel 1985). It is likely that the higher tack of the soy-amended resin improves resin spread at the bond line, thereby increasing the interfacial contact area. The contact angle measurements support this position. The contact angle of pMDI on a metal surface is 42.5°; the corresponding value for the soy-amended MDI is lower, at 32.6°. Thus, a single mechanism is proposed for increasing the prepress stability of particle mats and for strength enhancement in strandboard panels.

Conclusions

The wet and dry properties for 10 to 15 percent soy flour–substituted boards are equivalent or superior to those of control (pMDI only) boards for both strand board, MDF, and particleboard. For particleboard, the soy flour provides the added benefit of increased cold tack. The 15 percent substitution level is probably a practical maximum because higher levels could lead to excessive cold tack as well as to higher resin viscosity. The higher tack of the soy-treated resin likely increases the relative bonded area at the glue line.

Acknowledgment

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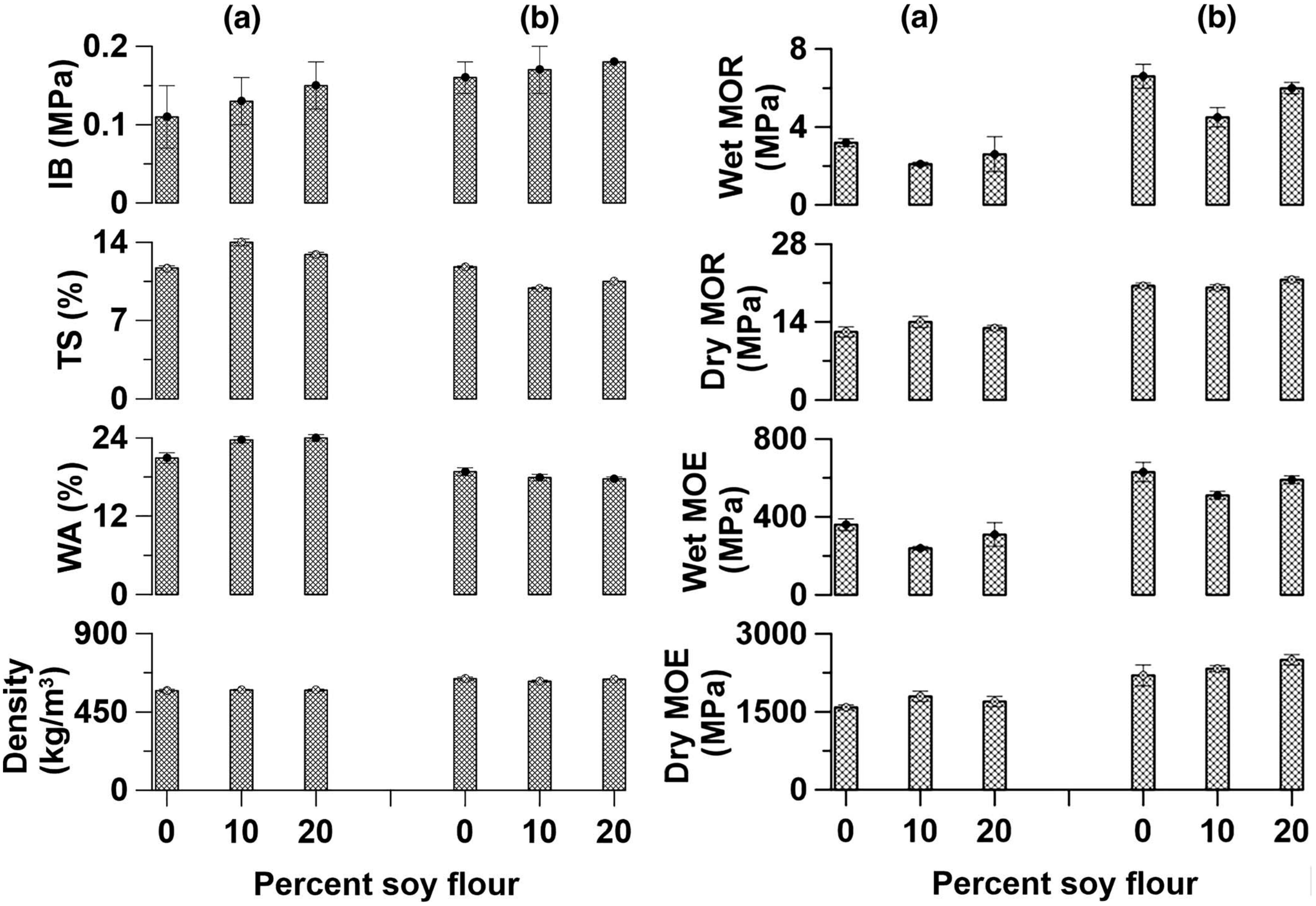

Figure 4.—Effect of soy substitution on medium-density fiberboard properties at two different densities; n = 8. *WA = water absorption; TS = thickness swell; IB = internal bond; MOE = modulus of elasticity; MOR = modulus of rupture.*

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