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Project Report: Heat-labile Foams 2021

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REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

Foamable materials which can be readily decomposed to yield inert gas in a precise and moderate temperature range are desirable for applications in nuclear waste storage and securement during transportation. In the proposed work, promising lead candidates for such foams were identified from extant peer-reviewed literature, and initial samples synthesized and characterized.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
PU	Polyurethane
NCT	Normal Conditions of Transportation
TGA	Thermogravimetric analysis
IR	Infrared spectroscopy
FIP	Foam-in-place
GPC	Gel permeation chromatography
PET	Poly(ethylene terephthalate)

1.0 Introduction

In this project, the PI and co-PI worked to develop design criteria and identify material candidates from existing scientific literature for a packaging material which would mitigate existing challenges with the securement and transportation of large equipment which currently qualifies as low-level contaminated waste. The material sought was to fit the following criteria:

1. The material should be a polymer which naturally forms into a resilient foam, or which can be formed into such a foam.
2. In its final form, the foam should be subject to thermal decomposition, subliming or shrinking enough to release its contents and allow them to easily be removed from a container. This decomposition should occur at a mildly elevated temperature relative to normal conditions of transportation (NCT), with a target temperature of roughly 85°C.
3. The foam should be designed to resist radiolytic accumulation of flammable gas mixtures, through some combination of low G-values for flammables and high G-values for inert gases such as nitrogen and carbon dioxide.

The objectives of this project were stated as follows:

- Objective 1: Through a survey of literature, determine whether a foam reported in the literature has the required combination of mechanical (tensile/compressive) strength and stimulus-responsive lability. We have determined that no reported material meets the required specifications (criteria 1-2), satisfying this objective.
- Objective 2: Identify 2-3 structurally/compositionally distinct polymer or gel structures with reported properties closest to the desired combination. We have identified polyurethane (PU) foams doped with (a) azo-based diols, as a promising starting point for optimization of a material which satisfies criteria 1-3. This objective is therefore satisfied.
- Objective 3: Develop synthesis and preparation methods (expertise) for foams/gels based on these structural bases. Prepare representative samples of 2-3 materials and characterize them by TGA, GPC, and infrared (IR) spectroscopy. We have developed a standard synthesis procedure for polyurethane-based foams and prepared a standard sample using this procedure. We have also prepared the azo-based diol dopant. We have characterized these materials by IR. However, we have not yet prepared a second PU foam incorporating the azo material, nor acquired GPC or TGA data on the materials made. Therefore, this objective is incomplete.

The present report, describing our progress towards these objectives, constitutes the primary deliverable for this project. This article summarizes the current state of development of thermally degradable polymer materials.

2.0 Activities and Findings

2.1 Finding 1

A polyurethane foam material is strongly preferred for the target application. The primary driving force for this conclusion was Packaging Technology's preference for a foam-in-place (FIP) solution that could be used to secure waste equipment. FIP is a widely applicable solution for applying packaging material to custom and high value parts and provides a firm and mechanically sound molded cavity with a film lining to secure the item in question. The alternative to a FIP approach would be to formulate a polymer material into packing peanuts or a similar form which could be blown into a container to secure a load. While workable in principle, this solution would provide a less mechanically strong securement and would risk the loss of packing material chunks during packing and release.

Commercial solutions for securing packages using FIP exist as turnkey systems. Without exception, these systems are based on polyurethane two-component mixtures, which are mixed and blown into the package and form the foam securement material *in situ.* The convenience of working with these existing systems practically guarantees that it will be worth the effort to develop our material based on PU technology. Conveniently, most PU formulations are based on prepolymers which are incorporated into a reactive mixture containing the catalyst, surfactant, and blowing agent (the 'formulated polyol,') allowing a wide range of customization options for the properties of the final foam.[1]

The vast majority of polyurethane polyols are polyethers based on poly(propylene oxide) and poly(ethylene oxide),[2] .Therefore, as part of this finding, we conclude not only that a PU solution is likely to be the most practical approach. As a result of this finding, we acquired materials for preparing test samples of polyurethane foams based upon a polyether/MDI formulation common in industry. This work involved finding a replacement silicone surfactant to substitute for the surfactant named in literature, which is not available on a research scale. Using this modified procedure, we prepared bench-scale PU foam samples to serve as a reference/control sample to be compared to thermally labile materials developed during future stages of this project.

2.2 Finding 2

A small amount of work has been done on thermally decomposable PU foams.

Surprisingly, little attention in scientific journals has been paid to the deliberate design of low-decomposition-temperature PUs. The decomposition of PUs has been reviewed,[3] but efforts to deliberately design low-temperature decomposition features into PUs appear limited to the patent literature. It appears that most papers which investigate the thermal stability of PUs are concerned with *increasing* that stability, especially for purposes of fire safety. The high surface area of PU foams renders them a violent combustion hazard unless treated with flame retardant. Increasing the thermal stability of PUs also is of interest to designers of high-performance materials used in wear parts such as wheels, gears, and slides. Patents, however, describe designed PUs which degrade[4] or become flowable[5,6] under mild heat. The extant literature incorporates these properties by incorporating the labile azo bond into the backbone of the polyol. Structures containing this moiety react by bond scission through homolysis when heated, resulting in the formation of N_2 gas and the production of free radicals.

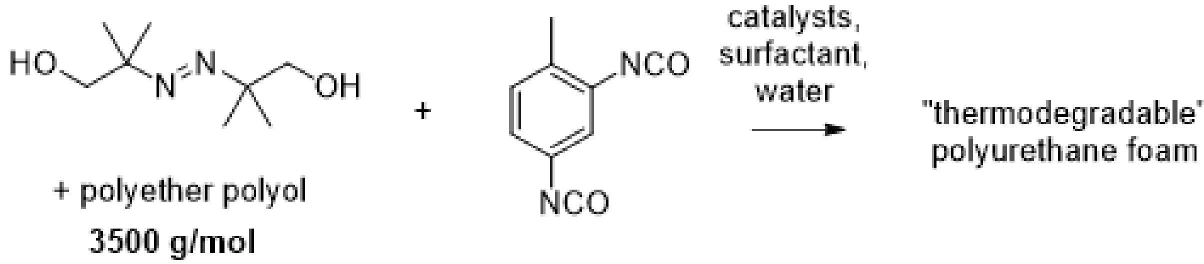

Figure 2-1. Preparation of a thermally degradable PU foam according to the Vojtova patent.

While this strategy is promising, actual results from this approach used directly in PU formulations are likely underwhelming for our purposes. The decomposition onset temperature reported for this approach is still outside our range, starting at 180°C.[4] At this temperature, the mass loss of the polymer remains below 50%, making it unlikely that a foam formulated with this approach would decompose enough to remove a packed item easily. Other strategies will need to be developed.

2.3 Finding 3

The ratio of flammable to inert volatiles released by the foam under γ-irradiation can be decreased by two strategies: (a) incorporation of unsaturated groups in the polymer backbone and (b) incorporation of azo and carbonate linkages in the polymer backbone.

All decomposition processes of candidate materials we reviewed during this project evolve inert gases as an innate part of their decomposition. As previously noted, azo diols produce N_2. Filling containers with inert gas is a common strategy to mitigate the flammability risk posed by radiolytically evolved hydrogen, raising the intriguing prospect that use of a thermally decomposable foam packaging material might also improve the fire safety profile of the package. Hydrogen (H_2) gas is by far the largest component of flammable gas evolved from most materials as a result of γ-irradiation. We thoroughly reviewed literature on the γ-ray quantum yield for H_2 of many common polymers, as expressed in G-values. Unsurprisingly, aromatic or other unsaturated polymers (which have a lower stoichiometric hydrogen content) had a lower G-value than pure aliphatics such as polyethylene (PE) or polypropylene (PP).[9,10] However, this effect is not incremental, but spans more than two orders of magnitude.

Poly(ethylene terephthalate) (PET), which has roughly one-seventh the H content of PE, has a H_2 G-value more than 100 times smaller than PE.[11] Indeed, older literature reports the H_2 G-value for this material as too low to measure, and the primary gases evolved under γ-irradiation are CO and CO_2. The effect of the unsaturated groups in PET is clearly more powerful than statistics alone explain. Conversely, the effect of 'missing' hydrogens is much less pronounced in saturated materials with non-hydrogen-containing linkages such as polyethers, which have roughly the same G-value as PE despite having half the H content. The explanation lies in the mechanism of H_2 evolution. Irradiation of a saturated polymer generates H radicals,[9] which can abstract a second H atom and form H_2 gas in a pseudo-first-order process that has no other fate to compete with it. Incorporation of double bonds from an unsaturated backbone unit creates an H radical sink in the polymer itself; radicals can add to double bonds, generating a more stable carbon-centered radical on the chain and eliminating the source of H_2 generation. This effect is so pronounced that a small amount of liquid benzene additive can suppress H_2 evolution in cyclohexane subjected to γ-irradiation. In short, the presence of any oxidizing agent (even an extraordinarily mild one, such as an aromatic ring) dramatically suppresses γ-ray-driven H_2 evolution by direct H radical quenching through addition.

This finding has immediate implications for design of a packing material for radioactive material. First, since a commercial polymer (PET) almost completely self-quenches radiolytically evolved H radicals, we should seek to maintain a similar or lower ratio (1:3) of aliphatic to aromatic carbons in candidate PU blends investigated as packaging materials. Since common isocyanates used in PU formulations are almost entirely aromatic, this design constraint may be easily met. Furthermore, as mentioned above, PET itself is commercially available as a PU polyol component (e.g., Arkema's *Realkyd* line).

Second, protective modifications need not be incorporated only through the polymer backbone itself. If more aggressive quenching reagents are needed as "pro-oxidants" to fully suppress H_2 evolution, highly active compounds such as nitroaromatics or TEMPO-based radical scavengers may be added.

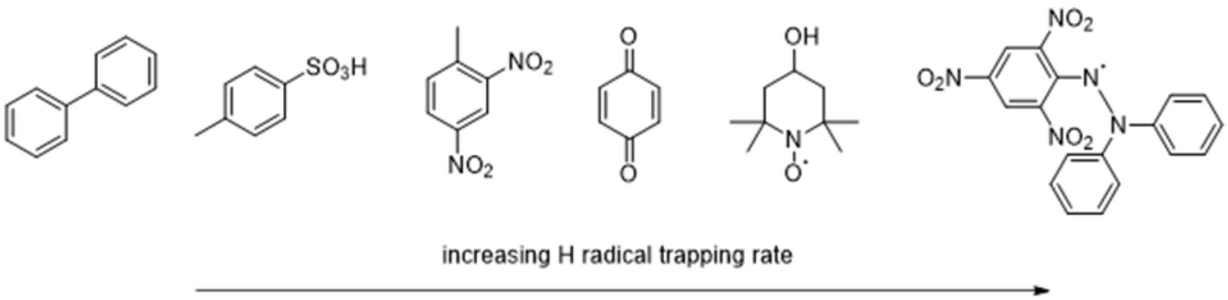

Figure 2-2. Potential radical trap stabilizers (mild organic oxidants) which could be added to suppress radiolytic H_2 evolution from a polyurethane foam.

Finally, most commercial PU foam blends contain flame retardants based upon aryl bromides and/or phosphates. These compounds suppress ignition and limit flame propagation by a near-identical process of radical scavenging and are practically certain to decrease radiolytic H_2 evolution as well. In short, a well-designed PU foam which fulfils other requirements of mechanical strength, thermal lability, and limited flammability is likely to have negligible H_2 G-values under γ-irradiation, or to be very easily tweaked to achieve this goal.

It is an open question whether the G-values of *inert* gases will be sufficient to provide an inerting function to mitigate flammability hazards (under reasonable assumptions) from flammables evolved *by the waste itself.* The answer to that question will depend on the practically achievable $G(N_2)$ of foams produced under this project.

2.4 Quality Assurance

This work was performed as a "Scoping Activity" in accordance with the Savanah River Site Quality Assurance Manual 1Q, Procedure 2-3, Control of Research and Development Activities.

3.0 Conclusions

We have prepared a clear roadmap for the preparation of thermally labile polyurethane candidate materials, toward a foam packaging material suitable for low-level contaminated waste equipment, which foam can be substantially degraded by the application of a mildly elevated temperature. This roadmap includes the formulation of custom PU blends incorporating azo labile linkers. Samples will be evaluated using mechanical testing, dynamic TGA, and RGA analysis under γ-irradiation. We have prepared one of the labile linkers (azo diol) and prepared PU foams using a standard literature procedure.

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