SANDIA REPORT

SAND98–2243
Unlimited Release
Printed October 1998

Final Report on Rubber Foams for Run-Flat and Off-Road Tires

Peter B. Rand and Bradley Hance

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

SAND98-2243
Unlimited Release
Printed October 1998

Final Report on Rubber Foams for Run-Flat and Off-Road Tires

Peter B. Rand and Bradley Hance
formerly with Encapsulants and Foams Division
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-1407

Abstract

Run-flat tires are a long time dream of all tire manufacturers. One of the concepts considered to accomplish this, foam-filling a tire when a puncture occurs, is explored in this report. Work on polymeric foams made from solutions of polymers and low boiling solvents has been ongoing for many years at Sandia. These one-container foams were developed for use as a dispensable barrier in DOE security systems. The marriage of our work on one-container foams and Goodyear's knowledge of tires was a logical one. Goodyear agreed to supply the compounded rubber compounds and we would foam them using our knowledge of one-container foams.

The run-flat concept would have required a very expensive development program to commercialize this concept. On the other hand, foam-filled tires for use in mines and other off-road applications provided an intermediate goal for this project. Current technology for foam-filled mine tires involved a long high temperature cure to make a usable product. If foams could be made using our one-container foam technology, this process could be greatly simplified.

Six rubber compounds were supplied by Goodyear for our foaming experiments. Foams were made with these compounds for evaluation. In addition, several low boiling solvent/foaming agents were evaluated in one of the rubber compounds. The density and foam stability were measured for all foams made.

Table of Contents

Introduction

In our proposals to Goodyear, we suggested a new run-flat and/or foam-filled tire technology based on foams generated with low boiling solvents dissolved in elastomers [1]. Sandia would do the initial foam development with input from GTR on the most suitable rubber compounds for this application. Our "paper" concept involved pre-installation of the foamable rubber compound in the tire. The foaming or blowing agent (low boiling solvent) would be introduced when the tire is pressurized. The foam would be almost instantly generated when the gas pressure in the tire dropped below the vapor pressure of the low boiling solvent. Proof of concept tests would be conducted very early in the program, with Goodyear supplied elastomers. Early tire testing, by Goodyear, would assure the viability of the concept. The smallest available tires could be used for this work. A cooperative SNL/GTR program would be required to develop pressurization gas combinations suitable for tire use. The fill gas would include both the gas from the low boiling solvent and a non-condensable gas. Diffusion of the low boiling solvent gas through the tire will be a critical issue. This concept should be usable for both run-flat tires and for permanently foamed off-road tires for heavy equipment. After successful laboratory demonstration, GTR will optimize the technology and develop a manufacturable-build concept.

DOE uses one-container sticky foams[2] as an integral part of many Safeguard access deterrent systems. Sticky foam is also an important material for our non-lethal weapon development efforts for civilian and military applications. These foams are solutions of resins in low boiling solvents that foam when released to atmospheric pressure. Our work for Goodyear involved foaming Goodyear supplied rubber compounds using low boiling solvents.

Experimental Work

Foaming the Goodyear supplied rubber compounds required containing them in a pressure vessel, introducing the low boiling solvent, allowing time for the solvent to be absorbed by the rubber compound and, finally, releasing the pressure to attempt foam formation. Our initial work was done in stainless steel pressure vessels. This allowed us to make foams and prove the validity of the concept. After this success, specially made glass pressure vessels were made to allow easy viewing of the foaming process. In all cases, the ratio of the solvent/foaming agent to the rubber compound was controlled.

The rubber compounds supplied by Goodyear are described in Table I. There was some sensitivity about the exact formulations; thus, this is the only information received. The compounds supplied by S. Jasani were compounded with polyisoprene with a paraffinic oil. D. Smith supplied compounds made with natural rubber, natural rubber blended with polybuytadiene, neoprene, and a natural rubber/polybutadiene/EPDM blend. The foaming agents (PBA's or Physical Blowing Agents) used for this work are listed in Table II. All have boiling points below 0°C.4.

Our initial experiments with all six of the rubber compounds are presented in Table III. The foaming agent in all cases was chlorodifluoro methane (HCFC-22). In all six cases, foams were made and a high proportion of the HCFC-22 was absorbed. This assured us that the basic concept for foam formation was robust. The results of our additional experiments are presented in Table IV.

We started with formulations with the natural rubber/polybutadiene/EPDM blend and HCFC-22. Our first foam in this series was formed unobserved! The bottle broke sometime during the night, leaving the foam on the lab bench. A repeat of this experiment (TF-7R) showed that a foam was slowly formed when the pressure was released. Additional foaming agent did not lower the foam density as hoped (TF-8A). All of these foams collapsed overnight as the foaming agent escaped. Our next experiments were with the natural rubber compound. Foams with much lower density and better stability were obtained (TF-10R).

In the next series of experiments, we tried excess foaming agent in several of the rubber compounds (TF-11 through 14). All these foams were high density and tended to collapse due to diffusion of the foaming agent. In the next two experiments, foams were formed by releasing the pressure to 30 psi (0.21 MPa). In both cases, foams were formed. This simulates foam formation in a pressurized tire. From here, we did a series of experiments using a variety of foaming agents.

The fluorocarbon, HFC-134a, made foams with increased volume stability, losing only 50% of its volume in six days. The best foam, TF-26, having excellent cell structure, low density, and excellent volume stability was made with chloropentafluoroethane (CFC-115). Unfortunately, the CFC's will not be allowed due to provisions of the Montreal Protocol. Also of interest is a foam made with Frigic FR-12. FR-12 is a blend of HCFC-22, HFC-134a, and butane. This blend is being marketed as a drop-in replacement for dichlorodifluoro methane (CFC-12). This experiment shows the promise of blends that could be optimized for this application.

Results

A limited number of experiments have shown that foams are easily made from tire stock rubber compounds. In general, the foams were quite high in density and collapsed overnight. The lowest density foam (TF-10R) was formed by removing the end cap from the pressure vessel. This allowed the foam to form very rapidly simulating a ruptured tire. Foams with improved stability were made with fluorocarbons and chlorofluorocarbons.

Conclusions

Foams are easily formed from stock rubber compounds. The most promising environmentally acceptable foaming agents were blends of fluorocarbons with hydrocarbons. Any future work would include optimization of a mixture to use as the foaming agent. At this point, an interactive program would be required to continue.

Rubber compounds are needed with additional oil to lower the initial compound modulus. Additionally, compounds with curing agents are needed to explore foam formation and then a low temperature cure to stabilize the foam. Another useful study to improve cell structure is the evaluation of gaseous and particulate nucleating agents. The work in this study establishes the feasibility of foam-filling tires by foaming rubber compounds with low boiling solvents. This work also advances our knowledge of the interaction of low boiling solvents with various rubbers, which is of interest to DOE defense programs. Major development programs would be required to bring either the foam-filled mine tire or a foam-filled run-flat tire to market.

Appendix A presents our initial thoughts on foam-filling tires. Appendix B lists the key technical issues that must be addressed for the successful completion of these concepts.

References

1. P. B. Rand, "In Situ Foamable Compounds for Rapid Foam-Fill of Damaged Pneumatic Tires or Foam-Fill of Off-Road Tires," SD5150, S-76~811 ~ Disclosure, 6/2/92.

2. P. B. Rand, "Sticky Foam," SD-3267, S-45, 910, Ser. No. 832,488, **Patent No, 4,202,279**, 5/13/80.

TABLE I

RUBBER COMPOUNDS FROM GOODYEAR

Goodyear ID	Source	POLYMER Type	POLYMER Parts	OIL Type	OIL Parts	CARBON BLACK Type	CARBON BLACK Parts
48396	Jasani	Polyisoprene	100	Paraffinic	25	No Data	10
48398	Jasani	Polyisoprene	100	Paraffinic	25	No Data	20
50440	Smith	Natural Rubber (NR)	100	No Data	-	No Data	low, f/color
50444	Smith	NR/polybutadiene	100	No Data	-	No Data	low, f/color
50448	Smith	NR/Neoprene	100	No Data	-	No Data	low, f/color
50452	Smith	NR/Polybutadiene/EPDM	100	No Data	-	No Data	low, f/color

TABLE II

PHYSICAL BLOW AGENTS (PBA)

Common or Commercial Designation	Chemical Formula or Composition	Boiling Point (C°)
HCFC-22	CHClF2	-40.8
CFC-115	CClF2CF3	-39.1
CFC-115	CClF2CF3	-39.1
Dimethyl Ether	C2H6O	-23.7
FIC-13I1	CF3I	-22.5
Freon 502	R22, CFC-115 blend	-45.4
Frigic FR-12	HFC-134a, HCFC-124, Butane	No Data
HCFC-124	CHCLFCF3	-11.0
HCFC-142b	CH3CClF2	-9.2
HCFC-142b	CH3CClF2	-9.2
HFC-134a	CF3CHF2	-26.5
HFC-152a	CH3CHF2	-24.7
Isobutane	C4H10	-11.7
R-406A	R22, HCFC-142b, Isobutane blend	No Data
Suva MP-39	R22,HFC-152a,HCFC-124 blend	-28.0

TABLE III

INITIAL FORMULATIONS

Formulation Number	Source	Goodyear ID	Rubber(s)	Pts. Rub. Compound	Solvent/Foaming Agent (PBA) Chemical Name	Commercial Name	Pts. PBA	Absorption of PBA	Foam
TF-1	Smith	50440	Natural Rubber (NR)	100	Chlorodifluoro Methane	HCFC-22	100	76%	Collapsed at top after valve shut
TF-2	Smith	50444	NR/polybutadiene	100	Chlorodifluoro Methane	HCFC-22	100	100%	Small Celled Foam
TF-3	Smith	50448	NR/Neoprene	100	Chlorodifluoro Methane	HCFC-22	100	71%	Good Foam, Stable
TF-4	Smith	50452	NR/Polybutadiene/EPDM	100	Chlorodifluoro Methane	HCFC-22	100	85%	Foamed
TF-5	Jasani	48396	Polyisoprene	100	Chlorodifluoro Methane	HCFC-22	100	100%	Extruded from Container
TF-6	Jasani	48398	Polyisoprene	100	Chlorodifluoro Methane	HCFC-22	100	No Data	Extruded, approximately 48 kg/m3 Density

Notes:

1. All rubber compounds had carbon black filler.
2. All foams filled container when pressure was released.
3. PBA=physical blowing agent.
4. All foams were made with equal parts by weight of the rubber compound and the PBA.

TABLE IV

TIRE FOAM FORMULATIONS AND RESULTS

FORMULATION	RUBBER COMPOUND		PHYSICAL BLOWING AGENT		RESULTS		Density
NUMBER	Goodyear ID	Polymer	Name	PBA/Rubber Ratio	Foamability	Foam	kg/m3
TF-7	50452	NR/Polybutadiene/EPDM	HCFC-22	1/1	Foaming not observed	Foam Formed	380
TF-7R	50452	NR/Polybutadiene/EPDM	HCFC-22	1/1	Foamed Slowly	Stable overnight	No Data
TF-8A	50452	NR/Polybutadiene/EPDM	HCFC-22	2/1	Foamed slowly	Some Shrink, 5-10 minutes	356
TF-8C	50452	NR/Polybutadiene/EPDM	HCFC-22	1/1	Foamed	Collapsed overnight	173
TF-9	50452	NR/Polybutadiene/EPDM	HCFC-22	2/1	Quicker Foaming, 5-10sec	Collapsed Slowly, 50% in 1.5 hr	No Data
TF-10	50440	Natural Rubber (NR)	HCFC-22	2/1	Foams quickly, popping	Good Stability	No Data
TF-10R	50440	Natural Rubber (NR)	HCFC-22	2/1	Foamed Slowly, 75% fill	Some collapse, very low density.	39
TF-11	50444	NR/polybutadiene	HCFC-22	2/1	Foamed quickly	Stable f/hours, shrank Overnight	327
TF-12	50448	NR/Neoprene	HCFC-22	2/1	Foamed	Collapsed overnight	No Data
TF-13	48398	Polyisoprene	HCFC-22	2/1	Foamed quickly. 75% fill	Collapsed in center of tube	436
TF-14	48396	Polyisoprene	HCFC-22	2/1	Foamed Quickly, 100% fill	Collapse starts in 30 seconds	298
TF-15	50440	Natural Rubber (NR)	HCFC-22	2/1	30psi, Foamed Slowly	Bleed to 30psi, 10% Shrink in hours	211
TF-16	50444	NR/polybutadiene	HCFC-22	2/1	30psi, Foamed @ 40psi	Shrank 75-80% in days	289
TF-17	50440	Natural Rubber (NR)	HCFC-22	2/1	Slow Foaming	65% fill after weekend	358
TF-18	50440	Natural Rubber (NR)	HCFC-22	1/1	Quick Foaming	Filled container	153
TF-19	50440	Natural Rubber (NR)	HFC-134a	1/1	Very slow foaming	To 50% volume in six days	200
TF-20	50440	Natural Rubber (NR)	HFC-152a	1/1	Foamed quickly, 80% fill	Slow volume loss	
TF-21	50440	Natural Rubber (NR)	FIC-13I1	1/1	Foamed slowly, large cells	Collapsed overnight	178
TF-22	50440	Natural Rubber (NR)	HCFC-124	1/1	slow, large cells	75% fill, 30% collapse overnight	210
TF-23	50440	Natural Rubber (NR)	Isobutane	1/1	Medium speed foaming	Collapsed overnight	173
TF-24	50440	Natural Rubber (NR)	Dimethyl Ether	1/1	V. Fast foaming	Collapsed overnight	163
TF-25	50440	Natural Rubber (NR)	HCFC-142b	1/1	Medium speed foaming, pops	Collapsed overnight	209
TF-26	50440	Natural Rubber (NR)	CFC-115	1/1	Removed from tube, v. slow!	Stable fine celled foam, volume stable	136
TF-27	50440	Natural Rubber (NR)	Suva MP-39	1/1	Foams & flows	Large Celled foam, collapsed overnight	202
TF-28	50440	Natural Rubber (NR)	Freon 502	1/1	Foams & Flows	Coarse Foam, Volume Stable	243
TF-29	50440	Natural Rubber (NR)	R-406A	1/1	Foams quickly & flows	Coarse foam , Collapsed overnight	212
TF-30	50440	Natural Rubber (NR)	Frigic FR-12	1/1	Foamed very slowly	Volume stable coarse foam	266

Notes: details of these experiments are in P. B. Rand's notebook entitled, "Tire Foam-1."

Appendix A

Tire Foam Disclosure

May 29, 1992

Title:

In Situ Foamable Compound for Rapid Foam-Fill of Damaged Tire or for Foam-Fill of Off-Road-Tires.

Problem:

Desire to fill pneumatic tire with foam to provide a usable tire after leak-producing damage occurs to tire or for low speed off-road applications.

Current Technology:

Off-road tires are filled with a chemically blown rubber foam. This is done in a factory and requires long high temperature cure cycles. There is no known technology to rapidly fill pneumatic tires to provide "run-flat" capability.

Features:

a. Foam must only be produced when leakage occurs for pavement applications.
b. The unfoamed material must be dimensionally stable in the tire to prevent balance problems.
c. The foamable material must be built into and/or attached to the tire and/or wheel under normal atmospheric conditions. The foaming agent will be added at time of installation of the tire onto the wheel.
d. With a large leak, foam generation must be rapid.
e. Foam must not only fill tire but also contain a pressurized gas to provide support for the vehicle.
f. Foam must be contained in the damaged tire.
g. Re-pressurization of a tire with a slow leak should allow the foam to return to the unfoamed state.
h. The foam must be easily removed from the tire to allow repair.
i. A technique for retrofitting the foam-fill capability after tire repair would be desirable.
j. For some off-road applications, the foam may be formed before the tire is used.

Solution:

A high molecular weight polymer compound that would absorb the blowing agent in place in the pressurized tire. This compound would foam when the pressure was decreased below the vapor pressure of the blowing agent/polymer combination. This system could also be used to provide foam-filled tires for off-road vehicles.

Features:

a. Foamable Compound: A variety of thermoplastic polymers or blends of these polymers are potentially suitable for this application. All thermoplastic elastomers, polyvinyl acetate, polystyrene, and all other thermoplastics which can be matched with a low boiling blowing agent. The maximum desired operating temperature of the tires will be a major factor in polymer selection. Many additives may be blended with the polymer. These could include nucleating agents, surfactants, plasticizers, fillers, stabilizers, and antioxidants.

b. Blowing Agent. The physical blowing agent (PBA) will be a low boiling liquefied gas capable of foaming the foamable compound. The gas must defuse slowly through the pressurized tire. It must also be absorbed in the foamable polymer compound in sufficient quantity to foam-fill the tire. The PBA gas will be a major constituent of the inflation gas in the tire. A mixture of two or more PBA's may be used to control the final vapor pressure and/or foamability.

Use:

a. The foamable compound would be attached to the inside surface of the tire or rim. Placement and application technique would depend on the specific application.

b. A weighed amount of the blowing agent would be added to the mounted tire. The vapor pressure of the foaming agent must be equal to or lower than the desired tire inflation pressure. Initially some liquid PBA would be in the tire.

c. Final inflation pressure would be provided by the PBA or increased using air or any other non-condensable gas.

d. The compound will foam when the pressure in the tire is less than the vapor pressure of the polymer/PBA solution.

e. A kit could be made to allow retrofit to existing tires.

f. Applications:

1. Any pneumatic tire.

2. For over-the-road vehicle and/or racing tires to enhance safety.

3. For off-road only vehicle tires to prevent flat tires. The foam would be formed in place before use.

4. For bicycle tire for safety and to allow riding on a damaged tire. Either the prefoamed or the foam on pressure loss technique could be used.

Commercial Potential:

1. This invention could provide a solution to the long sought "run-flat " tire.

2. It would allow dealer installed foam in off-road tires for low speed applications.

3. It could provide run-flat capability for bicycle tires.

4. Kits could be produced to retrofit in any pneumatic tire.

Appendix B

Sandia National Laboratories

Operated for the U.S.
Department of Energy by
Sandia Corporation
Albuquerque, New Mexico 87185-0369

date: February 14, 1994

to: DISTRIBUTION

from: Peter Rand, MS 0368 (1811)

subject: Goodyear CRADA, Fast Acting Foams, Visit #1

Summary:

Pete Rand visited the Goodyear Technical Center to discuss fast acting foams for tire applications. Goodyear will supply rubber compounds to Pete for foaming experiments for two applications:

a) Run-flat tires and
b) Foam-filled mine service tires.

Pete Rand, 1811, visited the Goodyear Tire & Rubber Company to discuss potential applications for Sandia's fast acting foams in tire applications. Two applications were discussed extensively:

a) A foam to instantly fill a leaking tire with foam (run-flat concept) and
b) Foaming tires for use in mines.

The run-flat concept is technically the most difficult but also the largest potential market. Although more questions than answers were discussed for this application, it was agreed to mutually explore the technical questions and also to try to foam some Goodyear supplied rubber compounds. The intent of the work on foam-filled mine service tires is to replace the current high temperature labor intensive foam process with a simple and potentially dealer installed, rubber foam. Goodyear agreed to supply rubber compounds for foaming experiments for this application. Foaming experiments will start when the rubber compounds arrive.

<u>Goodyear Personnel</u>

Dr. John Lawrence, Director
Dr. Frank Stuchel, Project Manager
Mike Monnot, Manager
David Smith, Senior Compounder
Sam Jasani, Senior Compounder

Agreed To Activities Include:

Goodyear:
1. Supply rubber/processing oil blends for foaming experiments for run-flat tires.
2. Supply rubber/processing oil blends for foaming experiments for mine service tires. Three uncatalized blends with varying amounts of carbon black will be supplied.
3. Determine minimum and maximum temperatures for both applications.
4. Determine experimental capability for permeability tests on rubbers and low boiling halocarbons.

Sandia:
1. Try to foam Goodyear supplied rubber compounds for both applications.
2. Do a literature search on foam-filled tires.
3. Do a literature search on the permeability of halocarbons through rubbers.
4. Discuss permeability with Sandia staff. (Gillen & Green)

Technical Issues:

Run-Flat Tires
1. Permeability of halocarbons through tire.
2. Foam stability as a function of temperature and time.
3. Compatibility of tire and foaming compounds.
4. Suitable physical blowing agent for foam.
5. Suitable rubber compounds for foam.
6. Final pressure in tire after foaming.
7. Positioning of foamable compound--on inside of tire or on wheel?
8. Installation of foamable compound.
9. Containment for foamable compound.
10. Repair of foamed tire.

Mine Service Tires.
1. All of above, except #9 & #10.
2. Long term foam stability versus foamability of the rubber compound.
3. Foam/tire bonding. (Not discussed but I think this is an issue)
4. Can we recap tire with foam-fill? (Minor issue)
5. Foam density required?

Copy to:

MS 0338	1702	D. W. Schaefer
MS 0337	1800	A. D. Romig
MS 0368	1811	R. L. Clough
MS 0368	1811	P. B. Rand
MS 0368	1811	D. Harvey
MS 9018	8940-2	Central Files (1)
MS 0899	4916	Technical Library (2)
MS 0619	12690	Review & Approval Desk for DOE/OSTI (2)
MS 1380	4212	Technology Transfer (1)

The Goodyear Tire & Rubber Co.
Goodyear Technical Center
P. O. Box 3531
Akron, Ohio 44309

Dr. John Lawrence, Director
Dr. Frank Stuchal, Project Manager
Mike Monnot, Manager
David Smith, Senior Compounder
Sam Jasani, Senior Compounder