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Foams Produced from Sulfur Dioxide and Various Polymers

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Synopsis

A variety of polymers have been foamed with sulfur dioxide. Properties of the foams could be varied by choice of polymer to produce rigid, semirigid, flexible, rubbery, fibrous, self-extinguishing, and/or heat-resistant materials.

INTRODUCTION

Some years ago, it was noted in these laboratories that rigid foams could be produced by soaking an acrylonitrile–methyl acrylate polymer in liquid sulfur dioxide followed by evaporation of the sulfur dioxide. These results were of interest since others had used sulfur dioxide to prepare foams, but generally had to use autoclaves to accomplish the foaming.[1] In the experiments to be described, no autoclaves were necessary.

A variety of polymers have been foamed with sulfur dioxide during this investigation. Properties of the foams could be varied by choice of polymer. Thus, rigid, semirigid, flexible, rubbery, fibrous, self-extinguishing, and/or heat resistant foams could be produced.

EXPERIMENTAL

Preparation of Acrylonitrile (AN)-Methyl Acrylate (MA) Copolymers

Since the first foam produced by dissolving a polymer in liquid sulfur dioxide was composed of 90 parts of acrylonitrile and 10 parts of methyl acrylate, initial efforts involved determination of the mole ratios of each monomer which could be used to make polymers capable of being foamed by the sulfur dioxide procedure. The preparation of the AN–MA copolymers is described below.

Various ratios of monomers (Table I) were charged to a three-necked, round-bottomed flask along with 11.1 ml. of 3.03*N* hydrochloric acid and 1429 ml. of deionized water. The flask was fitted with a condenser, stirrer, addition funnel, thermometer, and nitrogen inlet and placed in a constant temperature water bath. The reaction mixture was heated to 30 ± 0.5°C. in a nitrogen-purged atmosphere for $1^1/_2$ hr.

TABLE I
Monomer Charge

Approximate AN/MA weight ratio desired	Monomer charge, g. AN	Monomer charge, g. MA
90:10	144	16
80:20	128	32
60:40	96	64
50:50	80	80
40:60	64	96
20:80	32	128
10:90	16	144

The calculated quantities of sodium sulfite and sodium chlorate (catalysts) were dissolved in deionized water, diluted to 150 ml., and charged to the addition funnel. The first catalyst addition consisted of 60 ml. or 40% of the total volume of feed. After 25 min. an additional 25 ml. of catalyst solution was added. An exotherm of 3–4°C. generally occurred during the above addition and was checked by adding ice to the water bath. The remaining catalyst was added at 25-min. intervals in volumes of 25, 25, and 15 ml. Additions were complete in $1^2/_3$ hr. The reaction mixture was maintained strongly acid (pH 2) throughout the polymerization. Generally, an adjustment was made after the second catalyst addition with 5 ml. of 3.03*N* hydrochloric acid. The reaction mixture was agitated for one hour after the final catalyst addition. The polymer was collected by filtration using a Buchner funnel.

Some difficulties were encountered in the separation of the polymer latex from the aqueous phase with increased ratios of MA to AN. In these cases, the emulsion was broken by the addition of 300 ml. of isopropyl alcohol and 200 g. of sodium chloride after the catalyst addition was completed, and the reaction mixture was agitated for 1 hr. The polymer was collected in a Buchner funnel, reslurried with deionized water in a Waring Blendor, filtered, reslurried with 60–65°C. deionized water, filtered, and dried in an oven overnight at 60°C.

The dried polymers, which ranged from a powder to a gummy substance depending upon the increase of MA to AN, were mixed with Dry Ice, put through a Bantam micropulverizer with the use of a $^1/_{16}$-in. screen, and air-dried. Polymers containing more than 60% methyl acrylate would revert back to a gummy state when placed in an oven at 40°C. to eliminate carbon dioxide (from the Dry Ice).

Foaming Technique

The dry polymers, depending upon the ratios of MA to AN, would either form a gel or a solution when immersed in liquid sulfur dioxide. Foams were prepared through the elimination of sulfur dioxide by quenching the gel or solution in water at room temperature.

When it became apparent that not only the gel but the solution foamed, the following standard quantitative control test procedure was adopted. A quantity of polymer was sprinkled into liquid sulfur dioxide contained in a Dewar vessel and stirred for 2 hr.; the gel mass or solution was quenched in a volume of water at room temperature. The initial volume, the final volume of foam and the type of foam were noted. Conditions adopted were as follows: polymer charged, 12 g.; liquid sulfur dioxide charge, 300 g.; dissolution time, 2 hr.; quenching water volume, 500 ml.

Foaming Results

In addition to the AN–MA polymers, several other copolymers of acrylonitrile were investigated. As shown in Tables II and III all acrylonitrile copolymers or terpolymers which were tried yielded foams.

Table IV lists some other polymers which produced foams using the techniques described. The polymers were thermoplastic materials of either aromatic (polystyrene, polycarbonate) or aliphatic types [poly(methyl methacrylate), poly(vinyl acetate)].

Experiments conducted to determine the limits of polymer concentration in liquid sulfur dioxide are summarized in Table V.

Polymers which did not foam under the conditions described for these experiments were: polyethylene, poly(vinyl chloride), polytetrafluoroethylene, nylon, polyacetal, polyacrylamide, melamine–formaldehyde or phenol–formaldehyde.

The 90 AN–10 MA polymer could be suspended in other liquefied gases such as nitrogen, ammonia, dichlorodifluoromethane, chlordifluoromethane, or ethyl chloride. These suspensions did not produce foams.

Properties of AN–MA Foam

The density of the AN–MA foams could be varied over wide ranges. For example, a 90 AN–10 MA foam could be made with a density ranging between 2 and 40 lb./ft.^{3}. Usually foams of 20 lb./ft.^{3} were produced. The 90 AN–10 MA foam was relatively flame-resistant, having a burning rate of 2 in./min. as compared with commercial polystyrene foams having a rate of 7–8 in./min. and commercial rigid polyurethane foams having a rate of 8–10 in./min.

The cold gels of 90 AN–10 MA containing sulfur dioxide are elastic. In many respects they are similar to gum rubber, that is, they can be stretched several hundred per cent before breaking.

DISCUSSION

Dissolution of a polymer in liquid sulfur dioxide followed by evaporation was found to be an effective means of preparing foams from a variety of polymeric materials. In the techniques used in this work, it appeared that almost any copolymer of acrylonitrile could be foamed using this procedure.

TABLE II
Copolymers of Acrylonitrile

Copolymer	Copolymer composition	Copolymer weight, g.	Type of mixture	Foam volume, ml.		Type foam
				Initial	Final	
Acrylonitrile–methyl acrylate	95% AN–5% MA	12	70% gel–30% Solution	496	200	Rigid foam
	90% AN–10% MA	12	Very viscous solution	600	300	Semirigid foam
	80% AN–20% MA	12	Solution	1000	500	Fluffy fibrous foam
	60% AN–40% MA	12	Solution	500	150	Semirigid fibrous foam
	50% AN–50% MA	12	Solution	1000	150	Fibrous semigummy foam
	40% AN–60% MA	12	Solution	900	125	Fibrous gummy foam
	20% AN–80% MA	12	Solution	900	90	Gummy foam
	10% AN–90% MA	12	Solution	900	75	Very gummy foam
Acrylonitrile–acrylamide	90% AN–10% MA	12	Solution	400		Foamed but disintegrated
Acrylonitrile–allylethyl ammonium bromide	90% AN–10% AEAB	12	Solution	200	75	Rigid flaky foam
Acrylonitrile–allyl 3-ketobutyl ether	90% AN–10% AKE	12	Solution	700	100	Semirigid fluffy foam

Acrylonitrile–dimethylamide	90% AN–10% DMAM	12	Solution	600	300	Fluffy foam, self-extinguishing
Acrylonitrile–ethyl acrylate	85% AN–15% EA	12	Very viscous solution	1000	500	Semirigid fluffy foam
Acrylonitrile–3-hydroxy-4-pentenenitrile	90% AN–10% HPN	12	Solution	150	30	Semirigid flaky foam
Acrylonitrile–isobutylene	80% AN–20% IB	12	Solution	900	700	Semirigid fluffy foam
Acrylonitrile–methacrylamide	90% AN–10% MAM	12	Solution	300	75	Fluffy foam
Acrylonitrile–methyl methacrylate	70% AN–30% MMA[a]	12	60% Solution, 40% granulars	450		Foamed but disintegrated into granulars
Acrylonitrile–*N*-phenyl *N*-allyl-*O*-methylisourea	90% AN–10% PAMIU	12	Solution	150	35	Rigid flaky foam
Acrylonitrile–vinylidene chloride	95% AN–5% VIC	12	Gel particles in solution	200	20	Rigid-flaky foam, self-extinguishing
Acrylonitrile–vinyl chloride	30% AN–70% VC	12	Viscous solution	1500	1000	Fluffy foam, self-extinguishing
Acrylonitrile–vinylisobutylene ether	90% AN–5% VIB	12	Gel particles in solution	200	20	Rigid flaky foam

[a] Sample obtained from a cast sheet.

TABLE III
Terpolymers of Acrylonitrile

Copolymer	Copolymer composition	Copolymer weight, g.	Type of mixture	Foam volume, ml.		Type foam
				Initial	Final	
Acrylonitrile–ethyl acrylate–acrylamide	40% AN–40% EA–20% AM	12	Solution	1000	250	Gummy foam, rigid when dry
Acrylonitrile–ethyl acrylate–glycidyl methacrylate	40% AN–40% EA–20% GMA	12	Solution	150	50	Rigid flaky foam
Acrylonitrile–vinyl acetate–methylvinylpyridine	85% AN–8% VA–7% MVP	12	Gel mass	75	100	Rigid foam
	85% AN–8% VA–7% MVP	12	Gel mass	75	100	Rigid foam with suspended PVC particles
Poly(vinyl chloride)		6				

Sulfur dioxide, carbon dioxide, nitrogen, fluorohalocarbons, and other "inert" gases have been used previously to prepare polymeric foams. In one of the earliest reports of such products, Miles melted polyamides while under pressure of an inert gas.[1] The preparation, thus, was usually carried out in an autoclave. The foam was produced by a rapid reduction in pressure, such as extrusion of the polymer from a vessel under pressure into the open atmosphere.

TABLE IV
Dry Polymers That Foamed

Polymer composition	Polymer weight, g.	Type of mixture	Foam volume, ml. Initial	Foam volume, ml. Final	Type of foam
Poly(methyl methacrylate) beads	12	Solution	800	250	Flaky foam
Poly(methyl methacrylate) powder	12	Solution	900	400	Flaky foam
Polycarbonate beads	12	Solution	1000	500	Flaky foam
Polycarbonate powder	12	Solution	1000	500	Flaky foam
Polystyrene	12	Gel mass	500	150	Rigid foam
Poly(methyl acrylate)	12	Solution	1000	75	Very gummy foam
Poly(vinyl acetate)	12	Solution	400	100	Gummy foam

TABLE V
Polymer Concentration Limits in Liquid Sulfur Dioxide

Copolymer	Polymer composition	Type of solution	Absorption, %
Acrylonitrile–methyl acrylate	90% AN–10% MA	Gel	19.5
Acrylonitrile–methyl methacrylate	92% AN–8% MMA	Viscous solution	11.6
Acrylonitrile–vinyl acetate–methylvinylpyridine	85% AN–8% VA–7% MVP	Gel mass	17.4
Acrylonitrile–vinyl chloride	70% VC–30% AN	Viscous solution	9.8
Polycarbonate		Viscous solution	30.6

Miles[1] also prepared foams by forming a film from a 25% solution of a polyamide (hexamethylene diammonium adipate with caprolactam) dissolved in chloroform–methanol. The film containing unevaporated solvent was heated under slight pressure to yield a light spongy product.

More recently, Peticolas[2] has prepared foams by supersaturating a polymer with a substantially inert gas under pressure followed by reduction in pressure. He indicates that the polymer should have a low transmission rate for the gas being used. Thus, he gives examples of foaming a poly(vinylidene chloride)–acrylonitrile polymer using argon, carbon dioxide, or nitrogen at 500–1500 psi. Polycarbonate was foamed with carbon dioxide at 400 psi. Polytetrafluorethylene was foamed with carbon dioxide, nitrogen, or chlorotrifluorethylene at 450–2100 psi and temperatures of 170–250°C.

Both Miles and Peticolas obtained best results by use of heat and fairly high pressures. The present work did not require pressure, other than that exerted by the liquid sulfur dioxide in a Dewar vessel. The only heat used was that involving the heat of solution developed by pouring liquid sulfur dioxide into water.

In retrospect, the foaming technique appears to succeed because of the solubility characteristics of the solvent, sulfur dioxide.

Liquid Sulfur Dioxide as Solvent

Liquid sulfur dioxide has a low dielectric constant (17.27 at −16.5°C.). Thus, covalent solutes are more soluble in it than are ionic compounds.[3] Katz and Sheft[3] indicate that most organic compounds are very soluble in liquid sulfur dioxide, including alcohols, esters, amines, phenols, aromatic hydrocarbons, nylon, and poly(L-aspartic acid). A detailed discussion of various theories of the chemistry of solutions in liquid sulfur dioxide has been presented by Elving and Markowitz.[4]

From the data enumerated by Katz, it is expected that the following polymers would be soluble in liquid sulfur dioxide: acrylonitrile copolymers, polyaromatics as polystyrene or polycarbonate, and polyesters as poly(methyl methacrylate) or poly(vinyl acetate). The lack of solubility of polyethylene, polytetrafluoroethylene, and the crosslinked melamine and phenolic materials also is expected. However, the results with nylon, polyacrylamide, or poly(vinyl chloride) were surprising in this light, since Katz's data would indicate them to be soluble.

The plasticization of the soluble polymers by the liquid sulfur dioxide presumably permits good foaming. The change in pressure obtained by going from −10°C. (liquid sulfur dioxide) to 25°C. (room temperature) accompanied by the decrease in solubility of sulfur dioxide in water at increased temperatures leads to the rapid release of the gas and to the formation of discrete cells, thus a foam.

In many respects, the general procedure for producing foams was similar to that used to form resilient poly(vinyl chloride). A dissolved gas was held in the plasticized polymer until pressure was suddenly released.

These experiments suggest that it should be possible to prepare foams by use of low-boiling compounds having low dielectric constants with resultant high solvent powers for covalent polymeric solutes.

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Résumé

Différents polymères ont été transformés en mousse au moyen de dioxyde de soufre. Les propriétés de ces mousses peuvent être variées par le choix du polymère à produire des matériaux rigides, semi-rigides, flexibles, caoutchouteux, fibreux, auto-extincteurs ou résistants à la chaleur.

Zusammenfassung

Eine Vielfalt von Polymeren wurde mit Schwefeldioxyd geschäumt. Durch Auswahl der Polymeren konnten die Eigenschaften der Schaumstoffe variiert und starre, halbstarre, biegsame, kaut-schukartige, faserartige, selbstlöschende oder hitzebeständige Stoffe erzeugt werden.

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