

Sound Attenuation of Interpenetrating Polymer Network Foams

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Synopsis

Interpenetrating polymer networks (IPNs) composed of polyurethanes and epoxies were prepared by the simultaneous technique. Modifications of the polymer structures resulted in a series of IPNs exhibiting semimiscible behavior, as evidenced by broad glass transitions in the dynamic mechanical spectra. Since this indicates materials with potentially good sound attenuation properties as a function of temperature and frequency, foams were prepared from these IPN systems. Enhanced sound absorption occurred in these foams when measured using the impedance tube method.

INTRODUCTION

Interpenetrating polymer networks (IPNs)¹⁻⁶ (Ref. 1 is a comprehensive monograph in the field; Ref. 2 cites early works on one-component IPNs) are unique blends of crosslinked polymers containing essentially no covalent bonds, or grafts, between them. True IPNs are also homogeneous mixtures of the component polymers.

IPNs possess several interesting characteristics in comparison to normal polyblends. Formation of IPNs is the only way of intimately combining crosslinked polymers, the resulting mixture exhibiting (at worst) only limited phase separation. Normal blending or mixing of polymers results in a multiphase morphology due to the well-known thermodynamic incompatibility of polymers. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains.

IPNs synthesized to date exhibit varying degrees of phase separation, dependent principally on the compatibility of the polymers. With highly incompatible polymers, the thermodynamic forces leading to phase separation are so powerful that it occurs substantially before the kinetic ramifications can prevent it. In these cases, only small gains in phase mixing occur. In cases where the polymers are more compatible, phase separation can be almost completely circumvented. Complete compatibility is not necessary to achieve complete phase mixing, since the permanent entanglements (catenation) can effectively prevent phase separation. With intermediate situations of compatibility, intermediate and complex phase behavior results. Thus IPNs with dispersed phase domains ranging from a few micrometers (incompatible) to a few tens of nanometers (intermediate)⁴ and finally, to those with no resolvable domain structure (complete mixing)⁷⁻⁹ have been reported.

Incompatible polymer alloys¹⁰⁻¹² display different separated T_g 's and therefore exhibit several damping ranges corresponding to the glass transition temperatures of the components. Homogeneous polymer alloys⁸ show only one damping (T_g) which may be slightly broader than those of individual components. Semicompatible polymer blends¹³ where the mixing between the polymers is extensive have a very broad damping range and lead to a wider temperature (frequency) use range.

In the present study, it is this intermediate situation (semicompatibility) which is desired. Polymer systems with broad transitions (over a wide range of temperature and frequency) will be the most effective acoustical absorbing materials. When polymers are at their glass transition, the time required to complete an average coordinated movement of the chain segments approximates the length of time of the measurement. If dynamic or cyclical mechanical motions are involved such as vibrational or acoustical energy, the time required to complete one cycle, or its inverse, the frequency, becomes the time unit of interest. At the glass transition conditions, which involve both temperature and frequency effects, the conversion or degradation of mechanical or acoustical energy to heat reaches its maximum value. Thus, in this study, IPNs of low and high T_g polymers were prepared in an effort to obtain this "semicompatible" behavior, to thus achieve the desired broad range acoustical energy absorption.¹⁴ These IPNs are based on polyurethane and epoxy networks prepared via the one-shot, simultaneous polymerization technique (SIN or simultaneous interpenetrating polymer network).⁶ These polymers were studied because previous studies of IPNs of similar polymers resulted in homogeneous morphologies (an unusual phenomenon), and it was felt that the simplest approach would be to somewhat "decompatibilize" the polymers.^{15,16} This research focused on the maximizing of the dynamic mechanical properties of the resulting IPNs, i.e., synthesis of IPNs which have a high and broad $\tan \delta$. IPN systems that looked the most promising were used to prepare foams.

In principle, noise contacts the foam structure in the form of sound pressure waves. The pressure wave within the foam structure is partially converted to heat energy and is dissipated. The common types of damping materials are foams^{17,18} and homopolymers or copolymers, which exhibit efficient damping only in narrow temperature (frequency) ranges corresponding to the glass transition of the polymer.¹⁹⁻²¹ In this paper, we present the synthesis of foams composed of IPNs of semimiscible behavior, thus taking advantage of both the cellular structure of foams, as well as the broad damping behavior of the IPNs.

EXPERIMENTAL

Preparation of Materials

Elastomers

All polyols were vacuum dried overnight at 80°C. All other materials were used as received (Table I).

For preparation of polyurethanes (PU), ethylene oxide capped

TABLE I
Material

Material	Supplier	Chemical composition
Isonate 143L	Upjohn	Carbodiimide modified diphenylmethane diisocyanate
Niax 31-28	Union Carbide	Graft copolymer of poly(oxypropylene)-oxyethylene adduct of glycerol with 21 wt % polyacrylonitrile
Isonol 100	Upjohn	<i>N,N'</i> -bis(2-hydroxypropyl)aniline
DER 330	Dow Chem.	Bis-phenol A-epichlorohydrin epoxy resin
T-12	M & T Chem.	Dibutyltin dilaurate
Niax A-1	Union Carbide	70% Bis(2-dimethylaminoethyl)ether solution in dipropylene glycol
XU-213	Ciba-Geigy	BCl ₃ -amine complex
DMP-30	Rohm and Haas	2,4,6-Tris(dimethylaminomethyl)phenol
Freon 11A	E.I. DuPont	Trichlorofluoromethane
DC-193	Dow Corning	Silicone copolymer surfactant
L-540	Union Carbide	Nonhydrolyzable surfactant
L-5303	Union Carbide	Silicone surfactant
L-5614	Union Carbide	Hydrolyzable surfactant

poly(oxypropylene) glycerol containing 21 wt % grafted polyacrylonitrile (Niax 31-28, Union Carbide), MW = 6,000 was blended with a carbodiimide modified diphenylmethane diisocyanate (Isonate 143L, Upjohn), *N,N'*-bis(2-hydroxypropyl) aniline (Isonol 100, Upjohn), and dibutyltin dilaurate (T-12, M&T Chemicals). The IPN elastomers²² were synthesized by the mixing of two components. One part included Isonate 143L and the epoxy resin, a bisphenol A-epichlorohydrin adduct (DER 330, Dow Chemical). The other part contained Niax 31-28, Isonol 100, T-12, and epoxy catalyst (BF₃-etherate, Eastman Chemical).

The blend was mixed for 30–40 s at room temperature. It was poured into a hot mold (100°C) and cured for 30 min at 100°C on a platen press under a pressure of ca. 400 psi. The elastomers were then post-cured in an oven at 100°C for 16 h and conditioned at 25°C and 50% relative humidity for 3 days prior to testing.

Foams

PU foams were prepared by the one-shot, free-rise method. A homogeneous liquid mixture consisting of Niax 31-28, Isonol 100, surfactant DC-193 (Dow Corning), T-12, Niax A-1 (Union Carbide), trichlorofluoromethane (Freon 11A, E. I. DuPont), and water was mixed thoroughly with Isonate 143L. It was put into a cold mold and allowed to free rise.

It was necessary to prepare IPN foams using a hot mold method. One component contained Niax 31-28, DC-193 and three different surfactants (L-540, L-5303 and L-5614) from Union Carbide, T-12, 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30, Rohm and Haas), BCl₃-amine complex (XU-213, Ciba-Geigy), Freon 11A, and water. The other included Isonate 143L, DER 330, and Freon 11A. The two components were mixed and poured into a hot mold and cured at 90°C for 2–3 h. The foams were

post-cured at 90°C for 16 h, and conditioned at 25°C and 50% relative humidity for 3 days.

METHODS OF ANALYSIS AND TESTING

Dynamic Mechanical Spectroscopy. A Rheovibron (DDV-II, Toyo Measuring Instrument Co.) was used to measure the dynamic mechanical properties of the elastomers. The sample is a rectangular film with the dimensions of $2.4 \times 0.2 \times 0.1$ cm. It was carried out from -60 to 180°C with a heating rate of $1-3^\circ\text{C}/\text{min}$ at 110 Hz.

Density of Foams

The density was determined gravimetrically according to ASTM D 1622.

Sound Absorption of Foams (Impedance Tube)

The measurements were carried out using the impedance tube technique. It was run on the standard Bruel and Kjaer equipment (Standing Wave Apparatus Type 400Z, Beat Frequency Oscillator Type 1014, and Frequency Spectrometer Type 2112). Two measuring tubes with diameters of 3 and 10 cm were employed. The larger tube was used for frequencies from 100 to 2000 Hz, the small one from 1250 to 6300 Hz. All samples were 2 in. in thickness, except for IPN foam #9, which was 1.5 in. (due to difficulties in synthesis).

Ultimate Mechanical Properties

The tensile strength and elongation, and hardness were determined according to ASTM methods D-412 and D-2134, respectively.

TABLE II
Formulations and Properties for Polyurethane/Epoxy IPN Elastomers

Sample no.	1	2	3	4
Polyurethane				
Isonate 143L (g)	5.19	3.7	4.31	5.27
Niax 31-28 (g)	64.8	37.12	33.08	38.59
Isonol 100 (g)	0.0	0.0	0.68	0.79
T-12 (g)	0.012	0.036	0.06	0.06
Epoxy				
DER 330 (g)	0.0	26.6	24.8	21.02
BF ₃ etherate (g)	0.0	0.072	0.6	0.6
PU/epoxy weight ratio	100/0	60/40	60/40	70/30
Shore A hardness	46	16	84	45
Tensile stress, 22°C (psi)	838	337	1,025	500
Elongation, 22°C (%)	343	580	84	1,300

RESULTS AND DISCUSSION

IPN Elastomers

The ability of elastomers to absorb mechanical and acoustical energy is indicated by their dynamic viscoelastic properties, as seen from Rheovibron studies. The presence of a broadened glass transition indicates the semi-compatible morphology in the elastomers, and is the desired behavior for sound absorption applications. The formulations, properties, and Rheovibron curves of PU and IPN elastomers are shown in Table II and Figures 1-4.

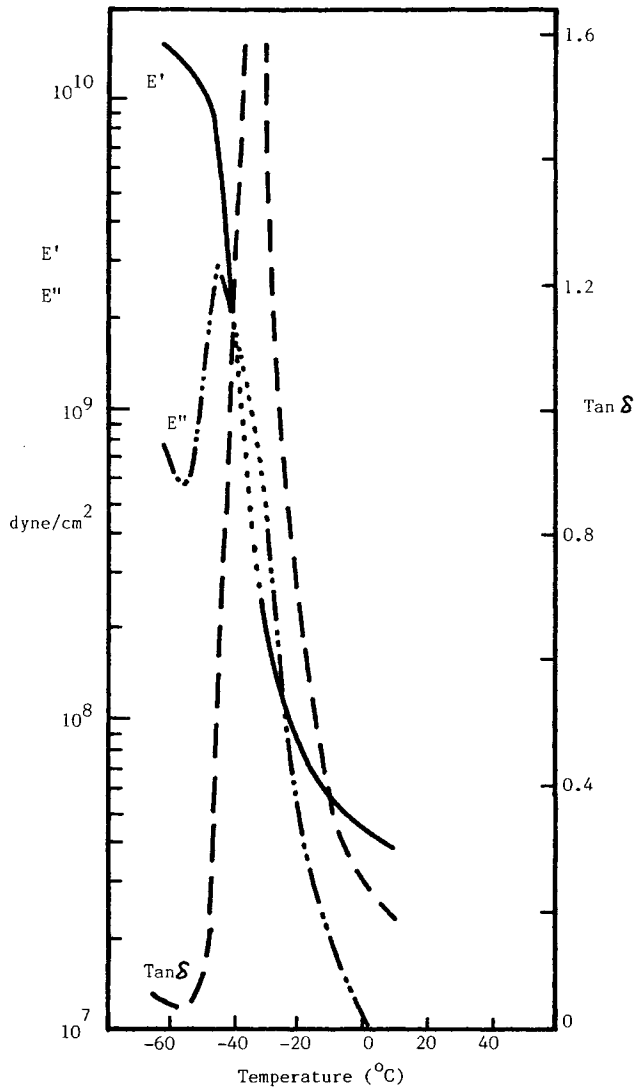


Fig. 1. Temperature dependence of dynamic modulus E' , loss modulus E'' , and loss tangent for elastomer #1.

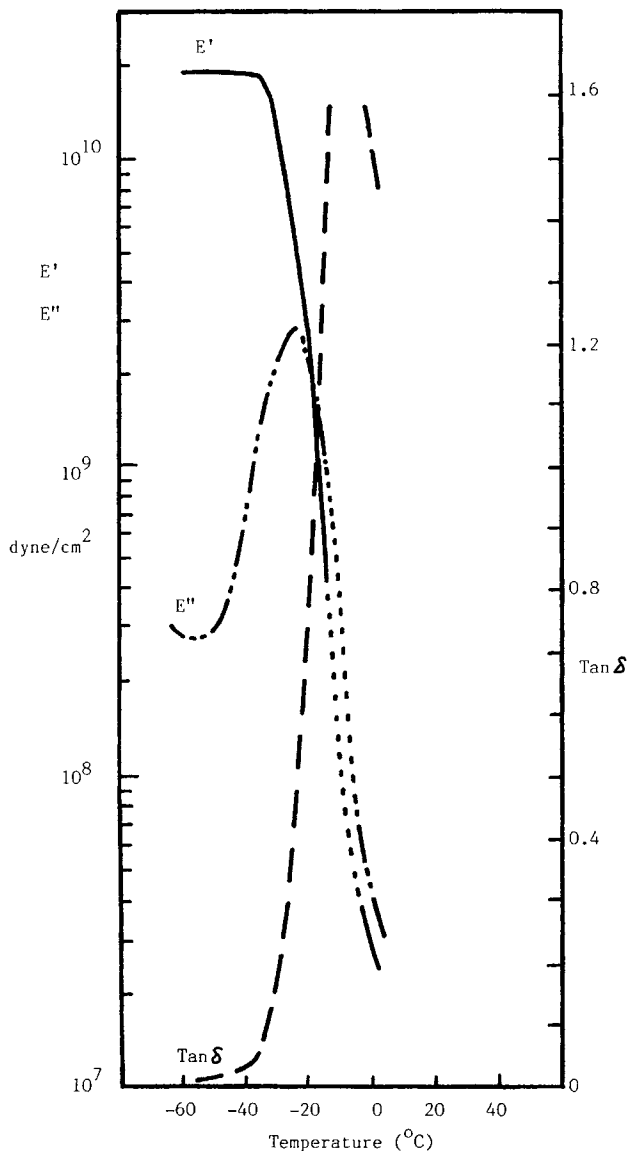


Fig. 2. Temperature dependence of dynamic modulus E' , loss modulus E'' , and loss tangent for elastomer #2.

Comparison of the Rheovibron spectra of 100% polyurethane (Fig. 1) with those of the IPNs (Figs. 2–4) shows the presence of a “semimiscible” morphology, as indicated by the broadening of the single $\text{tan } \delta$ and E'' peaks. The T_g 's also shift to higher temperature (close to 25°C), due to the presence of the rigid epoxy component. This latter behavior is desirable for a successful sound and vibration absorber. A number of other IPNs of varying compositions were prepared, but the systems discussed are with the broadest and highest loss peaks, centered around 25°C , with the greatest success in foaming. In other words, this study was not performed to determine explic-

itly morphologies of IPNs, structure–property relationships, etc. It was to combine two of the most fundamental features of a good sound attenuator, i.e., a leathery, broad transition polymer with a cellular structure. The foam formulations were based on these elastomers (some modifications did have to be made to obtain a proper foam). However, a few comments on the morphology with regard to structure can be made. Addition of Isonol 100 [an amine-containing short diol as chain extender (see Figs. 2–4)] resulted in a broadening of the loss peaks as well as a decrease in magnitude and shift to slightly higher temperature (due to the increased amount of hard

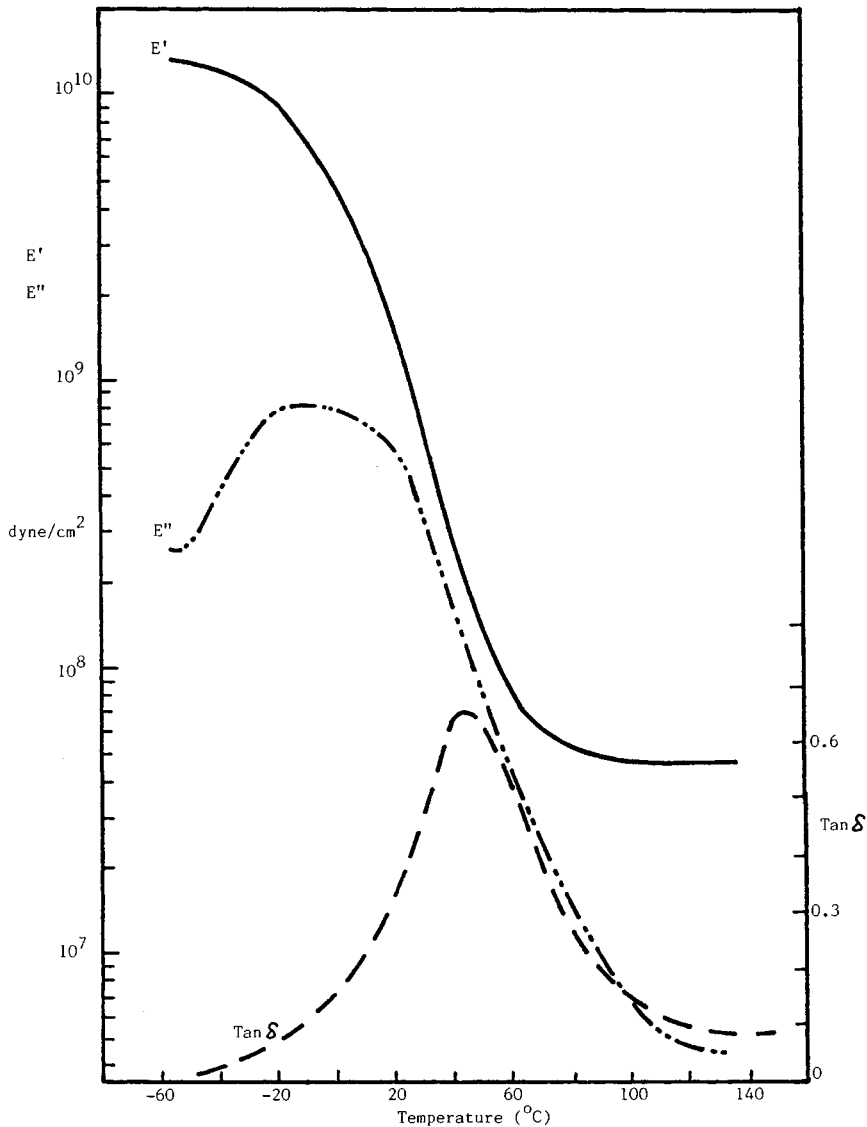


Fig. 3. Temperature dependence of dynamic modulus E' , loss modulus E'' , and loss tangent for elastomer #3.

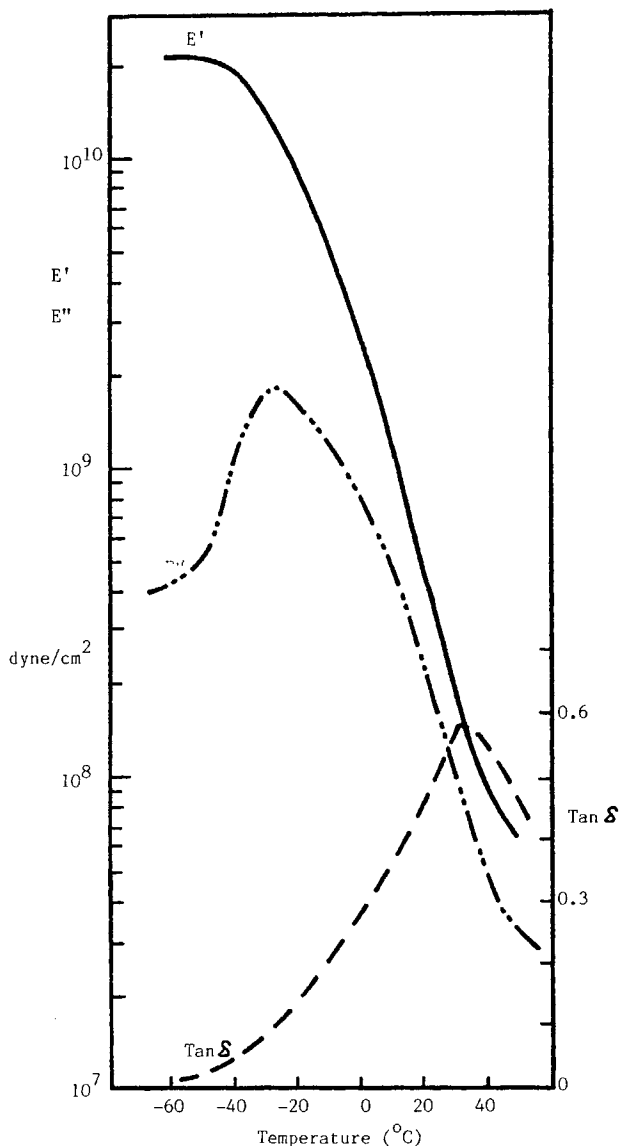


Fig. 4 Temperature dependence of dynamic modulus E' , loss modulus E'' , and loss tangent for elastomer #4.

blocks in the segmented polyurethanes). Addition of Isonol 100 apparently resulted in a decrease in miscibility of the polymers, due most likely to the increase in polarity of the polyurethane, resulting in greater differences in solubility parameters between the polyurethane and the epoxy. The broadening also resulted in a decrease in magnitude of the $\text{tan } \delta$ peak.

IPN FOAMS

After synthesizing a number of IPN elastomers with the desired dynamic mechanical properties (i.e., broad $\text{tan } \delta$ centered near 25°C), IPN foams were prepared using the basic formulations of elastomers having the broadest

tan δ peaks. The formulations, properties, and sound absorption of PU and IPN foams are shown in Table III and Figures 5–11. The G.M. PU reference, fiberglass, and 100% PU foams were selected as the controls in order to compare with the IPN foams. The G.M. reference is a standard, 2 pcf density flexible PU foam (formulation not available).

The G.M. polyurethane reference and our 100% polyurethane foam exhibited similar sound absorption (see Figs. 5 and 7), except for our PU at 400 and 500 Hz. All the IPN foams showed superior sound absorption at all frequencies compared to the two polyurethane foams, indicating that the morphology of the polymer in the cell walls is contributing to the attenuation. When compared with fiber glass, the IPN foam showed much greater absorption in the low frequency domain (100–300 Hz), where good sound absorption is traditionally difficult, but less in the high frequencies. The higher density IPN foam (Fig. 8) did not show absorption characteristics

TABLE III
Formulations and Properties for Polyurethane/Epoxy IPN Foams

Sample no.	7	8	9	10	11
Polyurethane					
Isonate 143L (g)	47.92	34.08	34.6	43.79	29.91
Niax 31-28 (g)	109.61	264.6	66.7	88.8	100.3
Isonol 100 (g)	2.19	5.4	1.33	0.89	1.0
T-12 (g)	0.96	0.14	0.14	0.36	0.48
Niax A-1 (g)	0.22	0.0	0.17	0.12	0.072
Epoxy					
DER 330 (g)	0.0	84.06	47.69	25.72	25.4
XU-213 (g)	0.0	0.91	0.72	0.72	0.72
DMP-30 (g)	0.0	0.36	0.36	0.36	0.36
Freon-11A (g)	43.84	91.0	35.0	45.0	35.0
Water (g)	2.19	0.0	1.33	1.67	1.0
DC-193 (g)	1.1	4.8	1.0	0.0	0.0
L-5303 (g)	2.19	0.0	1.0	0.0	0.0
L-5614 (g)	0.0	0.0	0.0	0.9	1.2
L-540 (g)	0.0	0.0	0.0	0.9	1.2
Density (lb/ft ³)	1.61	9.1	2.16	2.47	2.37
PU/epoxy ratio	100/0	70/30	70/30	85/15	85/15

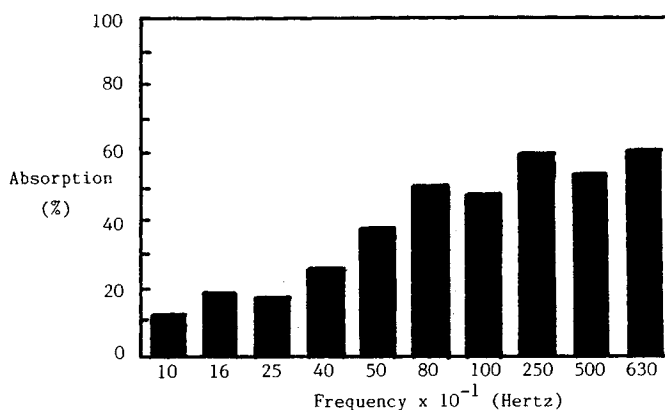


Fig. 5. Normal incidence sound absorption of foam #5.

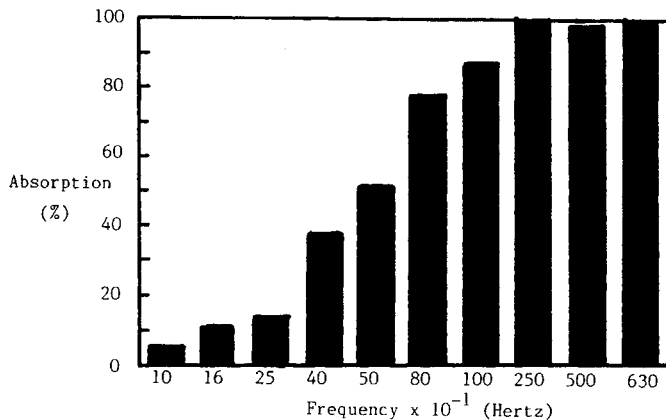


Fig. 6. Normal incidence sound absorption of foam #6.

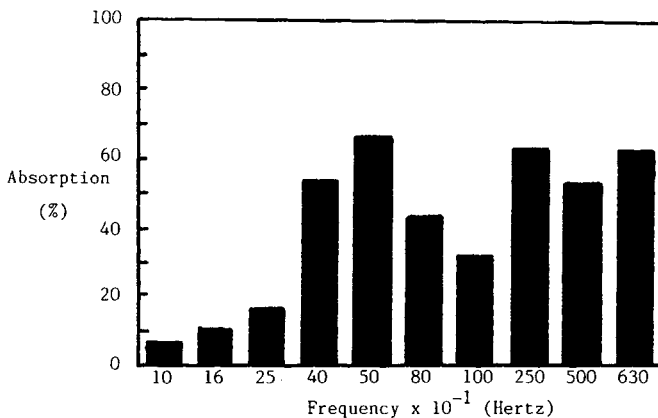


Fig. 7. Normal incidence sound absorption of foam #7.

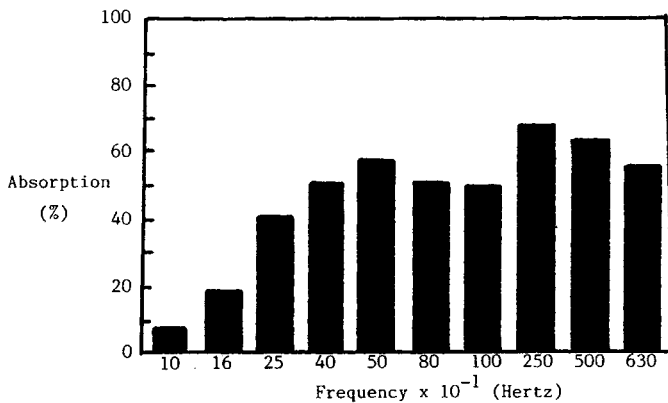


Fig. 8. Normal incidence sound absorption of foam #8.

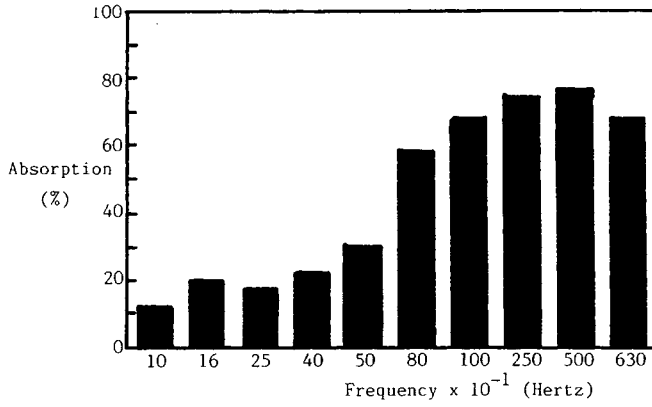


Fig. 9. Normal incidence sound absorption of foam #9.

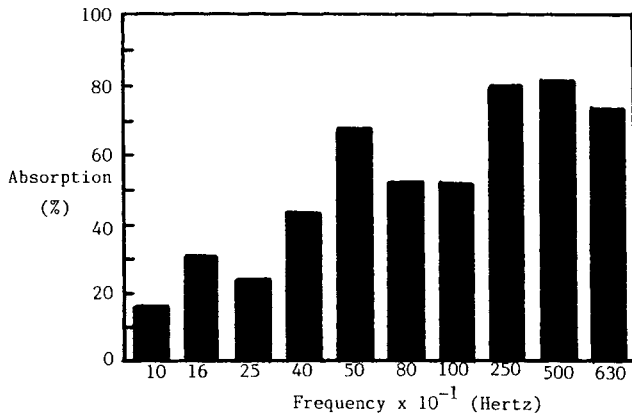


Fig. 10. Normal incidence sound absorption of foam #10.

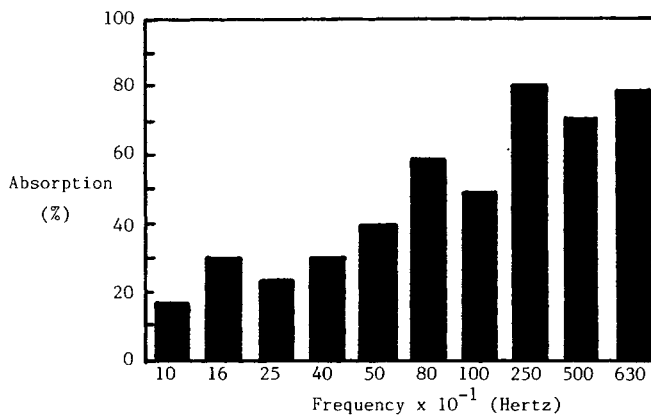


Fig. 11. Normal incidence sound absorption of foam #11.

quite as good as the lower density foams, indicating that the cellular structure is also important in sound absorption. It should be noted that IPN foam no. 9 (Fig. 9) was only 1.5 in. in thickness, as opposed to 2 in. for all the other specimens. Thus, the actual sound absorption properties of this foam would be expected to be about 33% better, when compared to the other 2-in. samples.

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