

Studies of Polymeric Systems for Damping of Vibrations in the Sonic Range

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Synopsis

Closed-cell foams based on rigid polyurethanes blended with more viscoelastic polymers possess good vibration-damping properties. The damping characteristics of the various polymers differ, indicating that the chemical nature has an influence on the acoustical performance of the blend. Damping is also temperature dependent. By selection of polymers, foam effective for damping at various service temperatures and over various frequency ranges can be made. The damping characteristics of polymers can be changed by adding fillers. Such methods may be employed to achieve a broader damping peak at the desired service temperature. The damping of vibration of an aluminum strip could be increased by one to two orders of magnitude between 20°C to 60°C when the strip was coated with the experimental materials in comparison with commercial open-cell, elastic foams of comparable density. A dynamic resilience of only 9% was achieved.

INTRODUCTION

Vibration damping is of environmental and industrial importance^{1,2} since noise is radiated by the vibration of an object, especially metallic. The application of damping materials to the vibrating surface will convert the energy into heat which is dissipated within the damping materials rather than being radiated to the air as airborne noise. Amorphous viscoelastic polymers are good damping materials under certain conditions. The viscoelastic properties of polymers are temperature dependent. A decrease in temperature has an effect similar to an increase in the frequency of the applied sinusoidal force. With increasing temperature, viscoelastic polymers change from a glassy state to a rubbery state and finally to a viscous liquid.

Since at transitions, such as the glassy transitions, a material absorbs energy and then dissipates it as heat, the cyclic kinetic energy of vibration will be converted into heat by the polymer at that temperature, resulting in rapid decay of the amplitude of vibration. The greater the ability of a polymer to convert the energy into heat, the faster will be the rate of decay of the amplitude. The damping peaks for polymers are narrow normally; and in order to broaden the damping peaks, copolymers or blends of two or more homopolymers may be used. However, attention must be given to the compatibility of the polymers and their ability to show a high degree of overlapping of the damping peaks. The glass transition of a copolymer usually occurs at a temperature intermediate between

those of the homopolymers making up the copolymer, so that the rule of mixtures applies.

The application of a homogeneous dissipative layer of a stiff viscoelastic material to a metal was first studied by Oberst.³ The damping performance of a vibrating structure may be expressed by the complex modulus⁴

$$E^* = E' + iE''$$

or

$$E^* = E'(1 + id)$$

where d is the damping factor. Then,

$$d = \tan \delta$$

where δ is the phase shift by viscous friction. The damping is also defined as the inverse of the quality factor of the resonances produced by the materials:⁵

$$d = 1/Q$$

The specific damping capacity ψ of a material is defined as the ratio of energy dissipated per cycle to the maximal strain energy stored per cycle in a free or forced vibration. It is related to the damping factor as follows:¹

$$\psi = 2\pi d$$

The dynamic resilience R' of a material is defined as the ratio of the energies stored in two cycles of a free damped vibration and is also related to the damping factor by the following equation:¹

$$R' = e^{-\psi}$$

Therefore, the damping efficiency of viscoelastic polymeric materials may be described by their damping factor d , specific damping capacity ψ , dynamic resilience R' , and the corresponding elastic modulus E' . In addition, the data can be used to calculate the relaxation time,⁶ $\theta = 1/\omega d$, in which ω is the frequency; the dynamic tensile viscosity,⁶ $\eta' = E'd/\omega$; and the velocity of sound,^{1,7} $c = (E'/\rho)^{1/2}$, in which ρ is the density.

EXPERIMENTAL

Materials

Polyester, unsaturated phthalic anhydride, propylene glycol, maleic anhydride type dissolved in styrene (32%); Reichhold Chemicals PolyLite 31000.

Epoxy resin, diglycidyl ether of bisphenol A (DGEBA), Epon 828, Shell Chemical Co.

Hydroxyl-terminated polybutadiene (PB_{HTS}), Phillips Petroleum Co., Butarez-HTS, viscosity 80 poises at 25°C.

Copolymer of butadiene and acrylonitrile (NBR), 34% acrylonitrile Krynac 34-35, Polysar Ltd.

Poly(ethylene oxide), Baker Chemical Co., average molecular weight 3000-3700.

Polyester urethane foam, Blachford Ltd., Aquaplas F.70.100 foam, a com-

bination of a vibration damping layer over an open-celled polyester urethane sound-absorbing foam.

Copolymer of styrene and butadiene (SBR), 80% butadiene and 20% styrene, $\bar{M}_n = 2300$, Richardson Co. Ricon 100.

Poly(vinyl chloride) (PVC), Goodrich Chemical Geon 121.

Poly(vinyl chloride)/butadiene-acrylonitrile copolymer blend (PVC-NBR), Goodrich Chemical Geon Latex 552, 50% solids suspension with an anionic emulsifier which after curing contains 50% PVC, 30% NBR, and 20% plasticizer.

Poly(methyl methacrylate) (PMMA), Fisher Scientific Co.

Polyurethane foam, reticulated, Scott Paper Co., Coustex Acoustical Foam.

Novolac epoxy resin, CIBA ECN 1235, molecular weight about 540.

Polysulfone, Union Carbide, p-1700 natural 11.

Methyl ethyl ketone peroxide, Chinook Chemicals MEEKO 60.

Epon curing agent T-1, polyamine, Shell Chemical Co.

Silicone surfactant, Dow Corning foam stabilizer, DC-190.

Triethylamine, Eastman Chemical.

Toluene-2,4-diisocyanate, du Pont Hylene T.

Castor Oil, Fisher Scientific Co.

Glycerol, Fisher Scientific Co.

Diethyl phthalate, plasticizer, Eastman

Tricresyl phosphate, plasticizer, Monsanto.

2(2'-Hydroxyl-5'-methylphenyl)benzotriazole, ultraviolet absorber, CIBA-Geigy Tinuvin P.

Stannous octoate, M & T Chemical Corp.

Trichlorofluoromethane, BDH.

Cobalt naphthenate, Chinook Chemicals.

Piperidine, Fisher Scientific Co.

Lead powder, 200 mesh, and **lead foil**, 1.6 mm thick, Fisher Scientific Co.

Glass fiber, chopped strands, 6 mm, Fiberglas Canada Ltd.

Lead alloy, Canada Metal Co., Cerrolow-117, melting point 47°C, composed of 44.7% bismuth, 22.6% lead, 8.3% tin, 5.2% cadmium, and 19.1% indium.

Preparation

Polyester and its Composites, Polyblends. The polyester was cured using methyl ethyl ketone peroxide (2% based on the resin) at 100°C for 1 hr. The composites and polyblends of polyester were cured in the same way, except that a promoter such as cobalt naphthenate (0.5% based on the resin) was added before the addition of methyl ethyl ketone peroxide to shorten the gel time. The following fillers were used: lead powder (200 mesh), lead foil (1.6-mm thick), lead alloy, glass fiber, poly(vinyl chloride) 100/diethyl phthalate 70, poly(vinyl chloride) 100/copolymer of butadiene and acrylonitrile 60/diethyl phthalate 40, poly(methyl methacrylate), and styrene-butadiene copolymer. In all cases, the well-mixed (30 min) components were degassed before casting into molds and cured for acoustical tests.

Epoxy Resins and Polyblends. The epoxy resin (DGEBA) and Novolac epoxy resin were used as base resins. The DGEBA was cured with Epon curing agent T-1 at 100°C for 1 hr. The amount of curing agent used was 30 parts based

on 100 parts of resin. DGEBA/polybutadiene (hydroxyl-terminated) blend (3/1) was cured at 100°C for 18 hr, and DGEBA/NBR blend (100/10) at 65°C for 3 hr. The Novolac epoxy resin was cured with piperidine (60 parts per 100 of resin) first at 90°C for 24 hr and then at 150°C for another 24 hr. Polyblends of Novolac epoxy resin were cured in the same way.

Poly(vinyl chloride)/Butadiene-Acrylonitrile Copolymer and Polyblends. Mechanical blends of poly(vinyl chloride)/butadiene-acrylonitrile copolymer with poly(methyl methacrylate), Aquaplas F.70, and lead powder, respectively, were prepared. The components were mixed for 1 hr and heated at 50°C for 2 hr.

Plasticized Poly(vinyl chloride). Poly(vinyl chloride) was plasticized using dioctyl phthalate (70 parts based on 100 parts of resin). The well-mixed components were heated at 180°C for ½ hr.

Polyether Urethane Foam. The foams were prepared with the following composition (in parts by weight): poly(ethylene oxide) 4000, 100; lead powder, 200 mesh, 2.0 (in making a base foam, no lead powder was used); Dow Corning silicone surfactant 190, 1.0; triethylamine, 0.2; water, 3.6.

To the well-mixed ingredients, 46.0 parts by weight of toluene-2,4-diisocyanate was added and the mixture stirred. Vigorous foaming occurred in about 10 sec. The foams were tack free after 25 min.

Rigid Polyurethane-Based Foams. The polyurethane-based foams were prepared using the following formulations (parts by weight):

Component A: castor oil, 100; glycerol, 28.6; stannous octoate, 0.286; D.C. silicone surfactant 190, 0.286.

Component B: tricresyl phosphate, 6.13; 2(2'-hydroxy-5'-methylphenyl)-benzotriazole, 0.214.

Component C: 10.7 parts by weight of *one* of the following modifiers: 1) poly(vinyl chloride)/butadiene-acrylonitrile copolymers (PVC-NBR) plasticized; (2) Hydroxyl-terminated polybutadiene (PB_HTS); (3) styrene-butadiene copolymer, SBR, (20/80); (4) plasticized poly(vinyl chloride); (5) poly(methylmethacrylate); (6) glass fiber; (7) lead powder, 200 mesh; (8) lead alloy.

Component D: toluene-2,4-diisocyanate, 85.7; trichlorofluoromethane, 34.3.

In each of the experiments, component A was blended for 2 min. The solution of component B was added and the mixture blended for 2 min followed by the addition of the modifier, component C. The mixture was blended for 3 min. Component D ingredients were added last and the mixture blended for 5 sec. The resulting mixture was immediately poured into a mold or container where it was allowed to foam (about 25–30 sec) and was aged at room temperature for a period of 24 hr. Most of the foams became tack free after a few minutes. The aging process could be accelerated by heating at 100°C for 10 min or at 60°C for 30 min. Some of the foams contracted after aging, for example, those containing plasticized poly(vinyl chloride)/butadiene-acrylonitrile copolymer (modifier 1). To overcome this, it was necessary to concentrate modifier 1 from 51% solids to 71.4% solids and increase the amounts of stannous octoate and Dow Corning 190 silicone surfactant (1.5 times the tabulated quantity). In another formulation, the same amount of SBR (modifier 3) was added to the mixture containing modifier 1 (71.4% solids) to give dimensional stability to the foams. These steps overcame what was probably a deleterious effect on the curing system of the water in the concentrated Geon latex.

Test Procedures—Complex Modulus and Damping Measurements

The internal damping and dynamic modulus of elasticity E' were determined using a Bruel and Kjaer Complex Modulus Apparatus Type 3930.^{5,8} The test samples were bar shaped with dimensions $13 \times 1.1 \times 0.42$ cm, and the foam samples were coated on an aluminum bar with the dimensions $13 \times 1.1 \times 0.15$ cm.

Measurements were made at the different resonant frequencies of the sample bar. Usually, two to five successive resonances modes were used depending on the polymeric material and the temperature, because some materials at certain temperatures and frequencies did not resonate. The mode numbers n of the resonances were determined by considering the succession of resonant frequencies obtained. The theory of bending waves in bars indicates that constant ratios exist between the different frequencies of resonance:⁵ f_1, f_2, \dots, f_n , the frequencies of the 1st, 2nd, and n th resonant modes, and K_n , the coefficient used for the calculation of the elastic modulus E' .⁵ The resonant frequencies were read from the frequency response curve.

The damping factors at n modes of resonance were calculated from the resonance peaks. Since the frequency response curve was recorded with logarithmic frequency scanning, the direct reading of $f_n/\Delta f_n$ was made using the Bruel and Kjaer Q-Rule Type BM 1001.⁵ When a resonant peak was too narrow to allow the bandwidth to be measured accurately, a reverberation decay method was used.⁵

Experimental Errors

In the complex modulus experiment, a magnetic transducer (Bruel and Kjaer Type MM 0002) was used to pick up the vibration. The velocity sensitivity was reported by the manufacturer to be independent of the frequency (less than $\pm 10\%$ up to 2000 Hz).

The frequency calibration of the beat frequency oscillator was accurate to $\pm 2\%$ over the frequency range of 20 to 20,000 Hz. The temperature was measured by a thermocouple and was accurate to $\pm 1.5\%$ over the temperature range of -50°C to 180°C .

The reproducibility of the samples (i.e., different batches of the same composition) depended on the technique of preparation. In general, when the samples were prepared under identical conditions, the confidence was 90–95%.

RESULTS AND DISCUSSION

Vibration Damping by Solid Polymers

Vibration Damping by Polyester, Epoxy Resin, and Polysulfone

The damping of substrate-borne sound depends on the glass transition temperature of the polymeric materials.^{9,10} Figure 1 shows the damping, or loss factor, for polyester, epoxy resin, and polysulfone at second-mode resonance frequencies (310–460 Hz). Polysulfone, which has a high T_g at 188°C , did not dampen vibrations at temperatures below T_g . However, a rather prominent damping peak occurred at about 10°C , and this may be due to a low temperature

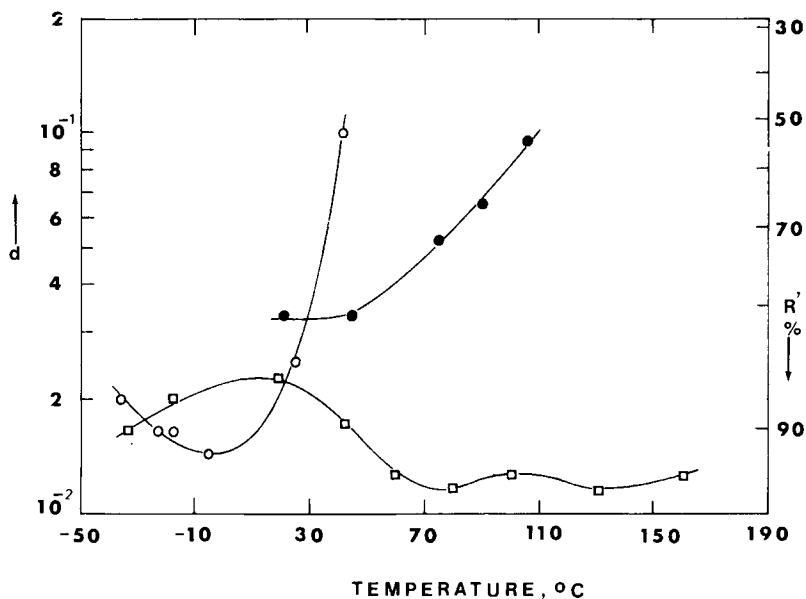


Fig. 1. Damping of substrate-borne sound by polymers at second-mode resonance (310–460 Hz): (○) polyester; (●) Novolac epoxy resin; (□) polysulfone; d = damping factor; R' = dynamic resilience.

relaxation process such as a motion of the phenyl rings of the polysulfone molecules. On the other hand, the epoxy resin with $T_g = 108^\circ\text{C}$ showed considerable damping above 70°C , and up to about 110°C . The polyester with a much lower T_g at 55°C , had a high loss factor at temperatures above 30°C .

The magnitude of the damping factor can be related to the stiffness of the damping material. According to Ruzicka¹¹ and Oberst,¹² the higher the stiffness or the elastic component of the complex modulus for the damping material, the greater the damping. However, this was found to be true only for certain materials and over certain temperature ranges. Figure 2 shows the dynamic elastic modulus E' of the polyester, epoxy resin, and polysulfone at various temperatures. At temperatures below 50°C , the value of E' for polyester was the greatest, followed by that for epoxy resin and finally polysulfone. This sequence was not the same as for the damping efficiency (Fig. 1). At temperatures higher than 50°C , the elastic modulus for polyester decreased rapidly and was lower than that for epoxy resin at the same temperatures, but the damping factor of the former was greater than that of the latter. Thus, the damping characteristics of a material are not affected solely by the stiffness of the material. Other factors such as the viscous component of the complex modulus have to be considered. In a good damping system, the ratio of the viscous component E'' to the elastic component E' of the complex modulus should be large, the damping factor $d = E''/E'$ should be large.

To achieve good vibration damping, it is necessary to increase the hysteresis by increasing the viscous component in a system resulting in greater heat dissipation. The relative amount of heat dissipated in two cycles of a freely damped vibration can be related to the relative energy stored in the two cycles by the dynamic resilience R' . A good damping system should dissipate a larger amount of energy as heat, and less energy should be recovered, in the successive cycles

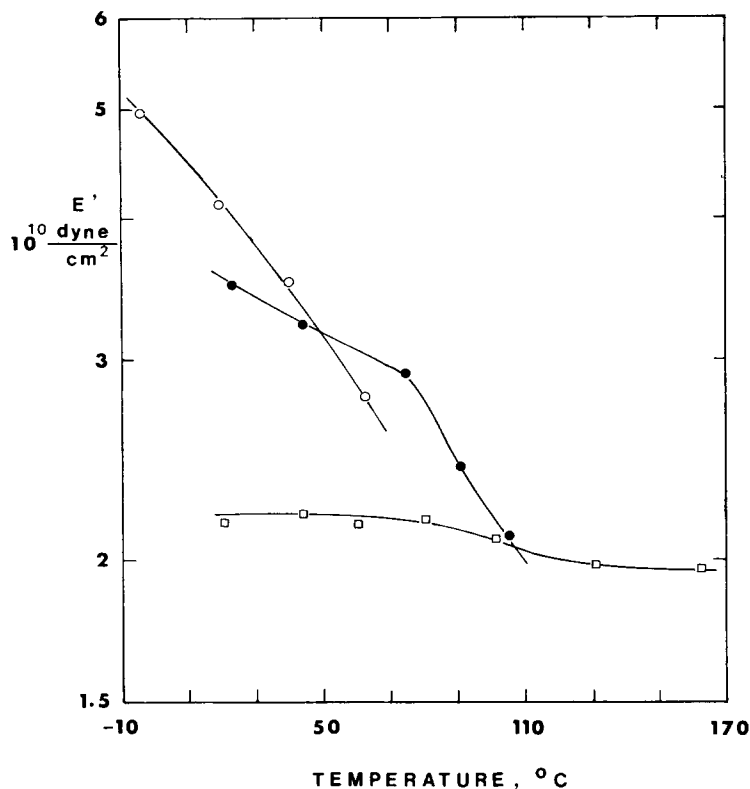


Fig. 2. Dynamic elastic modulus E' vs. temperature for polyester (O), Novolac epoxy resin (●), and polysulfone (□), at second-mode resonance (310–460 Hz).

of the vibration. Figure 1 also shows the effect of temperature on the dynamic resilience of the three polymers. At temperatures below 30°C, the resilience of the three polymers was quite high, between 80% and 90%, and did not differ very much. This is obviously due to the stiffness of polymers at low temperatures such that the energy stored in the successive cycles did not differ. As the temperature was raised, the polyester became more viscous than the epoxy resin, and so more heat was dissipated by internal friction so that considerably less energy was stored in the successive cycles, giving a low dynamic resilience. On the other hand, the dynamic resilience of polysulfone was relatively unchanged up to about 160°C. This again is due to the different glass transition temperatures of the polymers. It is also found that the relaxation times for the three polymers are quite different. At 45°C, the relaxation times for polyester, epoxy resin, and polysulfone were 2.93×10^{-3} , 1.24×10^{-2} , and 2.78×10^{-2} sec, respectively, at the second-mode resonance. This is due to the effect of viscosity. The dynamic tensile viscosities of the above polymers were 2.22×10^6 , 4.44×10^5 , and 1.74×10^5 poises, respectively, at 45°C.

Vibration Damping by Filled Polyesters

The damping characteristics of polymers could be modified by various methods such as by adding fillers, blending two or more polymers, preparing copolymers

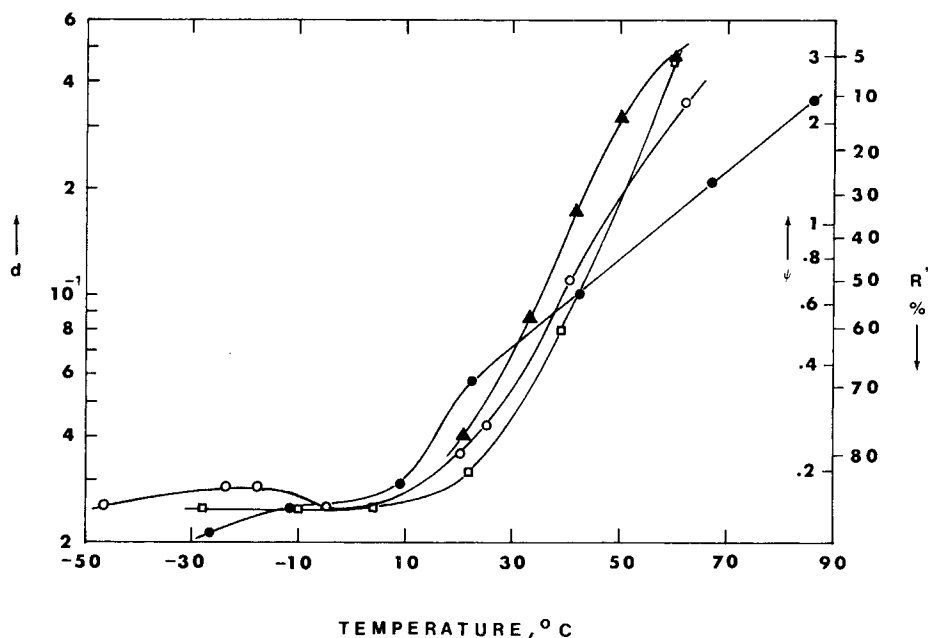


Fig. 3. Effect of lead on damping of substrate-borne sound by polyester resin at first-mode resonance (41–89 Hz): (O) polyester; (●) polyester filled with 20 phr lead powder; (□) polyester sandwiched with 20 phr lead foil; (▲) polyester filled with 20 phr lead alloy; d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

from monomers one of which makes a homopolymer with a high T_g and the other makes a homopolymer with a low T_g , and plasticizing a rigid polymer system having a high T_g . Figures 3 and 4 show the effect of lead powder on the damping of substrate-borne sound by polyester resin at the first- and second-mode resonances, respectively. It was found that at the first-mode resonance (41–89 Hz) the unmodified polyester gave better damping at temperatures lower than -5°C . This is explained by the ability of the segments of the polyester chains to move at such low temperatures. If such molecular movement dissipates energy, the acoustic energy will be damped. The motion will be restricted sterically in the presence of fillers such as lead powder. As the temperature was increased, the resins filled with lead powder or lead alloy gave better vibration damping than the unfilled resin. At high temperatures, the segmental motions are not hindered in the filled systems so that the controlling factor is the heavier mass of lead which absorbs more vibrational energy in the less rigid matrix which forms the viscous medium.

However, the lead foil-sandwiched polyester did not perform better than the unmodified resin. This suggests that in the temperature range of 5° to 51°C the lead foil stiffened the resin and, being unable to resonate, the foil reflected or transmitted the sound wave. The inclusion of lead foil does not seem to be a promising system for damping the natural resonances of structural materials at low temperatures. The results show, further, that at temperatures above 42°C , the polyester filled with lead powder was inferior to the base resin in damping at low resonance frequencies. This also indicates that the viscous behavior of the resin at higher temperatures plays the main role in damping or energy ab-

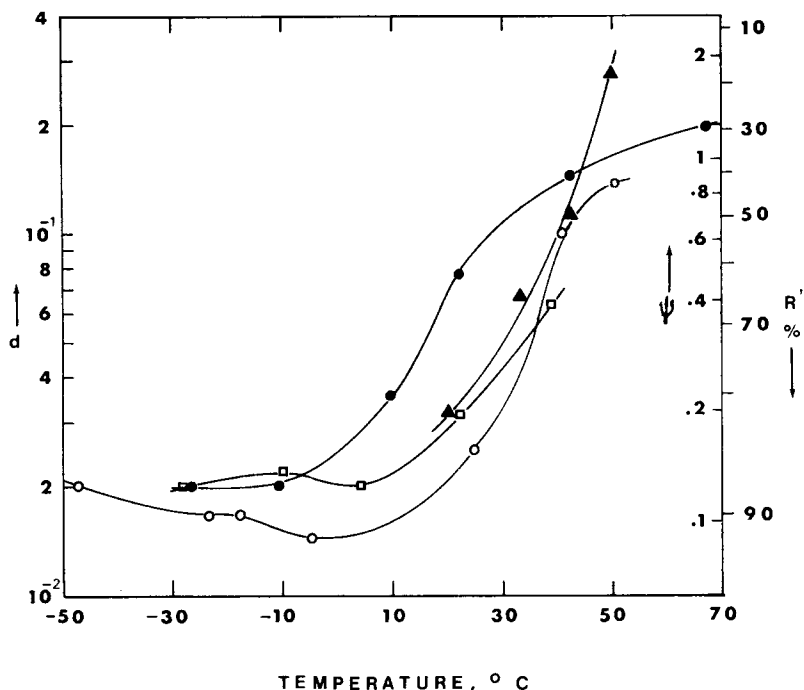


Fig. 4. Effect of lead on damping of substrate-borne sound by polyester resin at second-mode resonance (240–500 Hz): (O) polyester; (●) polyester with 20 phr lead powder; (□) polyester sandwiched with 20 phr lead foil; (▲) polyester with 20 phr lead alloy; d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

sorption. This can be illustrated by the lead alloy-filler polyester (Fig. 3). The lead alloy has a melting point of 47°C. Thus, at temperatures above 47°C, the alloy was in a molten state in the polyester matrix causing the whole system to be more viscous, and so high damping was obtained. The dynamic tensile viscosity of the lead alloy-filled polyester was 2.28×10^7 poises at 50°C, compared to 1.48×10^7 poises for the unmodified polyester.

When more acoustic energy is involved in the resonance of a substrate, this additional energy has also to be considered. For example, at the second-mode resonance (200–500 Hz) of the polyester and the lead composites (Fig. 4), the damping characteristics of the systems followed the same pattern for the first-mode resonance, except that at low temperatures, from -30°C to $+10^\circ\text{C}$, the unmodified polyester gave lower damping than the composites. This is due to the additional vibrational energy which favors the motion of the otherwise hindered macromolecular segments in the composites. Moreover, it was found that the damping of a polyester/lead composite was also greater than the base resin at temperatures above 42°C at higher resonance frequencies (240–500 Hz). The specific damping capacity of the polyester and its composites is shown in Figures 3 and 4. The results show that higher specific damping capacity was obtained for the composites. This means that more energy was dissipated by the composites than was absorbed by their ability to store the strain energy. It was found that at 50°C the specific damping capacity of the polyester/lead alloy composite at the second-mode resonance was 1.72, about two times larger than that of the unmodified polyester, again due to the effect of viscosity.

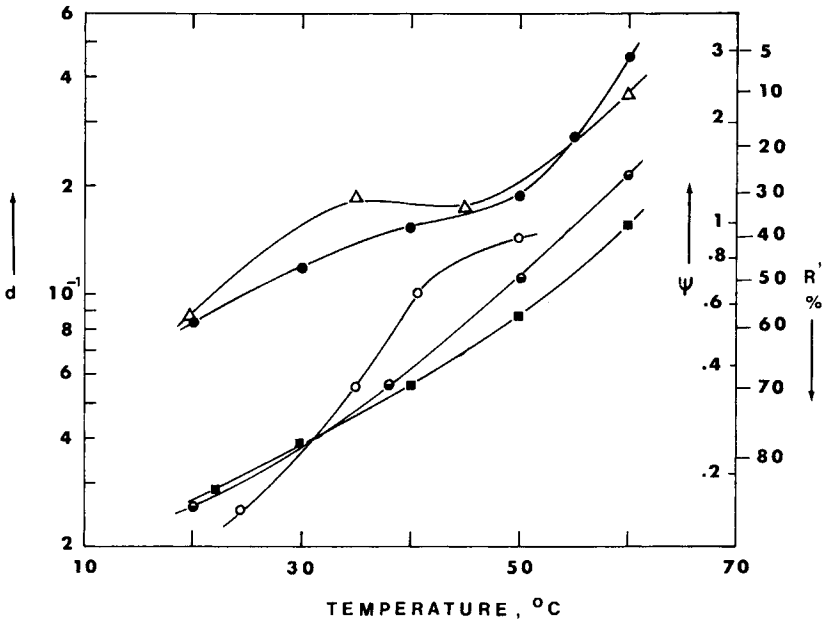


Fig. 5. Effect of polymer fillers on damping of substrate-borne sound by polyester at second-mode resonance (230–475 Hz): (O) polyester; (●) polyester/PVC-NBR (100/20); (Δ) polyester/PVC (100/20); (■) polyester/PMMA (100/20); (◐) polyester/SBR (100/20); d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

From the elastic modulus measurements, it was found that the resin matrix had the lowest value of E' at temperatures below 40°C and was consistent with the lowest damping observed. When lead alloy or lead powder was added to the polyester, stiffness of the system increased and so did the damping at temperatures below 40°C. At temperatures above 40°C, the values of E' for both composites decreased rapidly, and were smaller than those of the polyester for polyester/lead alloy composites above 40°C and for polyester/lead composites above 54°C. This again is due to the lowering of the glass transition temperature by lead and lead alloy because of their low bending stiffness. The glass transition temperature of the composites was found to be 41°C, and that of the matrix was 55°C. The rather low value of E' for the polyester/lead alloy composites at temperatures above 40°C is also attributed to the low melting alloy the presence of which imparts excellent dynamic resilience at temperatures near the glass transition temperature of the system, as shown in Figures 3 and 4.

Vibration Damping of Polyester Polyblends

Polymers can be used to modify the damping characteristics of other polymers. Figure 5 shows the effect of polymeric fillers on the damping of substrate-borne sound by polyester at the second-mode resonance. The results show that there are both favorable and unfavorable effects on the damping characteristics of the polyester. When the polyester resin was blended with either plasticized poly(vinyl chloride) or poly(vinyl chloride)/butadiene-acrylonitrile copolymer, the damping was greatly increased over the whole temperature range of 20°C to 60°C,

especially at lower temperatures where the damping was about five times better. On the other hand, fillers such as poly(methyl methacrylate) and styrene-butadiene copolymer did not improve the damping of the polyester except at higher temperatures, 60°C.

Thus, the damping efficiency of a polymer in terms of the loss factor is influenced by the frequency of vibration and the properties of the polymer fillers. If by the inclusion of a second polymer the glass transition temperature of the system is lowered, greater damping will be observed at lower temperatures, and it may cover a wider temperature range depending on the properties of the second polymer. Differential scanning calorimetry analysis showed that the T_g of polyester filled with plasticized poly(vinyl chloride) and of poly(vinyl chloride)/butadiene-acrylonitrile copolymer was lowered from 55°C to 34°C and 9°C, respectively, which explained the high damping observed for the two polyblends at lower temperatures. The wider damping range of the polyblends is obviously the result of the overlapping of damping peaks of individual polymer components. The glass transition temperature of plasticized poly(vinyl chloride) was 33°C, and those of poly(vinyl chloride)/butadiene-acrylonitrile copolymer were 28°C and -26°C, respectively. Thus, when they were used as fillers for a polyester resin, $T_g = 55^\circ\text{C}$, the damping peaks would overlap.

If, on the other hand, the polymer fillers have a higher T_g than the base resin, the overlapping of damping peaks will also occur, but at temperatures higher than the T_g of the unmodified system. Therefore, the damping efficiency of such polyblends will be lower than that of the original polymer at temperatures lower than its T_g . This is demonstrated by the polyester/poly(methyl methacrylate) polyblend. The glass transition temperature of poly(methyl methacrylate) was 95°C, and that of the polyblend was 69°C, which was 14°C higher than that of the polyester. Therefore, such a polyblend did not improve the damping efficiency at temperatures near the glass transition temperature of the unmodified resin.

Although the lowering and raising of the glass transition temperature of a polymer system has a great influence on vibration damping, especially for those situations which require specific service temperatures, damping characteristics of the additive polymers should also be considered and compared with those of the matrix system. A high damping polymer will, no doubt, improve the damping characteristics of a poor matrix, and a poor one or one with a lower loss factor than the matrix will definitely not improve the performance of the system. This is also illustrated by the polyester/poly(methyl methacrylate) and polyester/styrene-butadiene copolymer (with 70% styrene).

The specific damping capacities and dynamic resilience of the polyblends are also shown in Figure 5. The high damping capacities of the polyester/PVC and polyester/PVC-NBR blends again show the ability of the plasticized PVC and PVC-NBR to dissipate more energy. The resilience decreased rapidly with increasing temperature. The polyester/poly(vinyl chloride)/butadiene-acrylonitrile copolymer gave the best resilience characteristics with a dynamic resilience of 5.5% at 60°C at the second-mode resonance. This polyblend is, therefore, an excellent vibration-damping and low-resilience material for application where the service temperature range is 50–70°C. For higher service temperatures, polyester/PMMA and polyester/SBR blends could be used to achieve the same results.

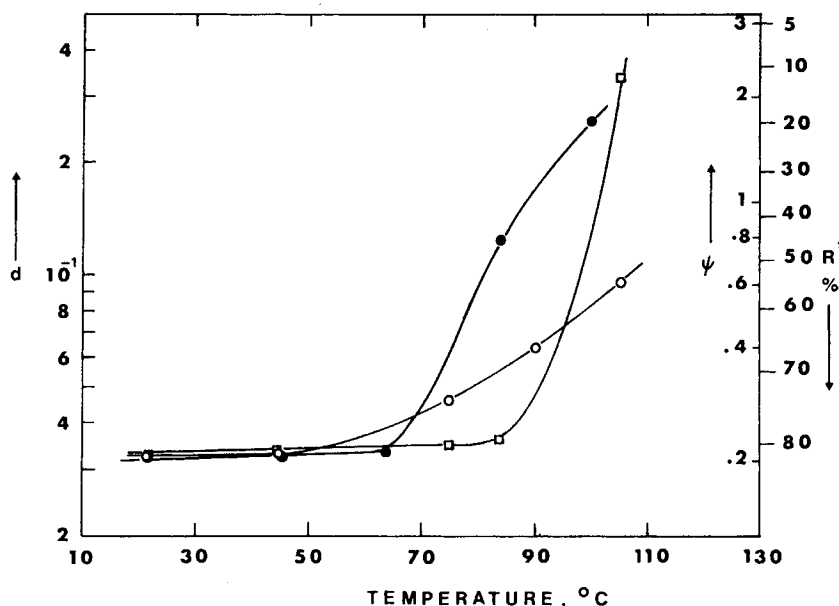


Fig. 6. Effect of polymer fillers on damping of substrate-borne sound by Novolac epoxy resin at second-mode resonance (260–400 Hz): (O) epoxy resin; (●) epoxy resin/hydroxyl-terminated polybutadiene (100/20); (□) epoxy resin/SBR (100/20); d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

Vibration Damping of Epoxy Polyblends

The concept of polyblending to achieve optimal damping and resilience characteristics of a material for certain service temperature ranges can also be applied to epoxy resin which often finds use in coatings. Figure 6 shows the damping characteristics of the epoxy resin and its polyblends with hydroxyl-terminated polybutadiene and styrene/butadiene (20/80) copolymer at the second-mode resonance. The damping was not changed significantly at temperatures below 65°C by the addition of rubbery materials to the epoxy resin. This is expected because the glass transition temperatures of the epoxy, epoxy/polybutadiene, and epoxy/SBR were 108°C, 83°C, and 100°C, respectively. Only when the temperature approaches the glass transition temperature will there be significant changes in damping. The damping factor of the polybutadiene blend at 70°C and that of the SBR blend at about 80°C increased rapidly. Thus, the damping efficiency of the epoxy resin can be increased greatly by the addition of rubbery materials for lower service temperatures. Both of the rubbery polyblends were excellent damping materials at temperatures around 100°C, where the epoxy resin was a poor performer by itself.

It was found that the addition of polybutadiene and styrene-butadiene copolymer lowered the stiffness of the epoxy resin considerably at the temperature range studied. Polybutadiene and styrene-butadiene copolymer are by themselves very elastic; but when blended with the epoxy resin, the polyblends became viscoelastic exhibiting low elastic or storage modulus and high loss modulus. The specific damping capacities of these materials are also shown in Figure 6. The results show that at 105°C the energy dissipated per cycle in the free vibration was about two times the maximum strain energy stored during the cycle at the

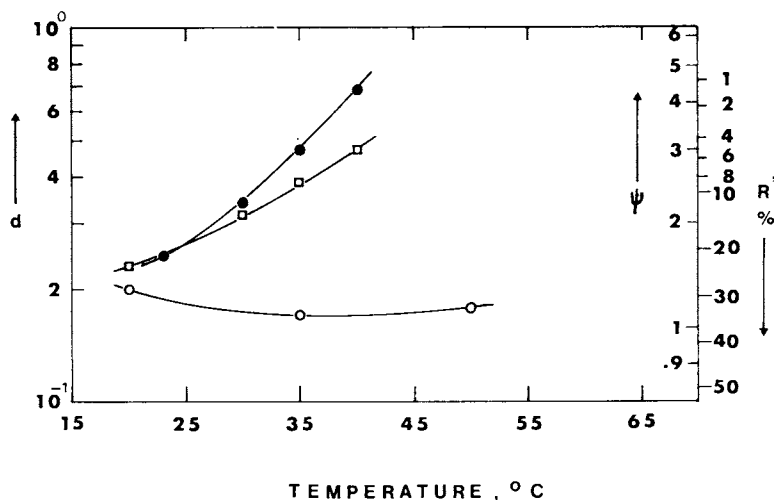


Fig. 7. Damping of substrate-borne sound by poly(vinyl chloride)/butadiene-acrylonitrile copolymer blends at second-mode resonance (76-165 Hz): (○) PVC-NBR; (●) PVC-NBR/lead (100/20); (□) PVC-NBR/PMMA (100/20); d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

second-mode resonance. This large amount of energy dissipation within the material gave rise to a low dynamic resilience of about 12% for the polyblends at 105°C. The results may be explained by the relaxation process of the macromolecules at temperatures near the glass transition temperature of the polymer. For example, at 105°C and the second-mode resonance, the relaxation times of epoxy/SBR and epoxy resin were 6.12×10^{-4} and 5.39×10^{-3} sec, respectively. The shorter relaxation time of the former indicates that the segmental molecular motions were less hindered and might respond to the sound waves giving rise to the viscous loss effect as shown by the dynamic tensile viscosity of 2.89×10^6 poises compared to 1.02×10^6 poises for the unmodified epoxy resin.

Vibration Damping of Poly(vinyl chloride)/Butadiene-Acrylonitrile Systems

In the previous discussion, it was suggested that any highly viscoelastic or elastic polymers or polyblends would impart excellent damping and dynamic resilience characteristics to a resin matrix which otherwise was a poor damping material at temperatures below its glass transition temperature. On the other hand, the matrix may be a highly viscoelastic material such as plasticized poly(vinyl chloride)/butadiene-acrylonitrile copolymer to which fillers such as lead powder and poly(methyl methacrylate) are added. Figure 7 shows the effect of temperature on the vibration damping (d) of such filled polymers. At the second-mode resonance (76-165 Hz), the poly(vinyl chloride)/butadiene-acrylonitrile copolymer itself is a good damping material, with a damping factor of about 0.2 for the temperature range investigated. When 20 phr of either lead powder or poly(methyl methacrylate) was dispersed into the matrix, the damping factor increased to 0.68 and 0.47 at 40°C, respectively.

The same damping pattern was observed for the systems at the third-mode resonance (160-500 Hz), except that the damping values for the composites did

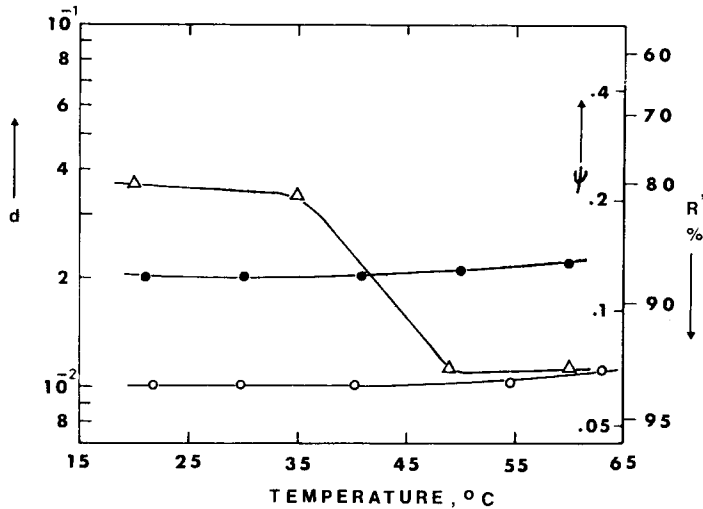


Fig. 8. Damping of substrate-borne sound by highly viscous-elastic polymers at second-mode resonance (300–450 Hz): (O) aluminum, substrates; (●) PVC-NBR applied to substrate; (Δ) Aquaplas F.70 applied to substrate; d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

not increase very much with increasing temperature. This shows that the effect of temperature on the vibration damping by highly viscoelastic materials is relatively small at higher resonance frequencies. The results also show that the specific damping capacities of the polymer systems are greater than unity, indicating that they are capable of dissipating large amounts of energy. Such systems are excellent vibration damping materials. The inclusion of the fillers such as lead and poly(methyl methacrylate) to the already excellent damping materials such as plasticized poly(vinyl chloride)/butadiene-acrylonitrile copolymer further improves the damping capacity of the polymer system by increasing the bending stiffness E' of the system. The increase in stiffness does not seem to be the result of an increase in density or mass by the addition of fillers. The density of the unmodified matrix was 1.182 g/cm³, and that of the poly(methyl methacrylate) filled blend was 1.183 g/cm³. More likely, it is related to the relaxation processes of the systems involving segmental motions of the macromolecules giving rise to the viscous versus elastic effect. It is suggested further than an optimization between the elastic and viscous components of the complex modulus has been achieved at temperatures below the glass transition temperature of the matrix.

Vibration Damping of an Aluminum Bar Coated with Polyblends

Vibration-damping materials can be used as coatings for all kinds of machinery, engines, equipment, pipes, and other structures which generate noise by vibration. Studies were carried out using the viscoelastic polyblends discussed previously to dampen the vibrations of aluminum at its resonance frequencies. Figure 8 shows the effect of the viscoelastic materials on the vibration damping of an aluminum bar at the second-mode resonance (300–500 Hz). The vibration-damping factor of the aluminum bar coated with poly(vinyl chloride)/

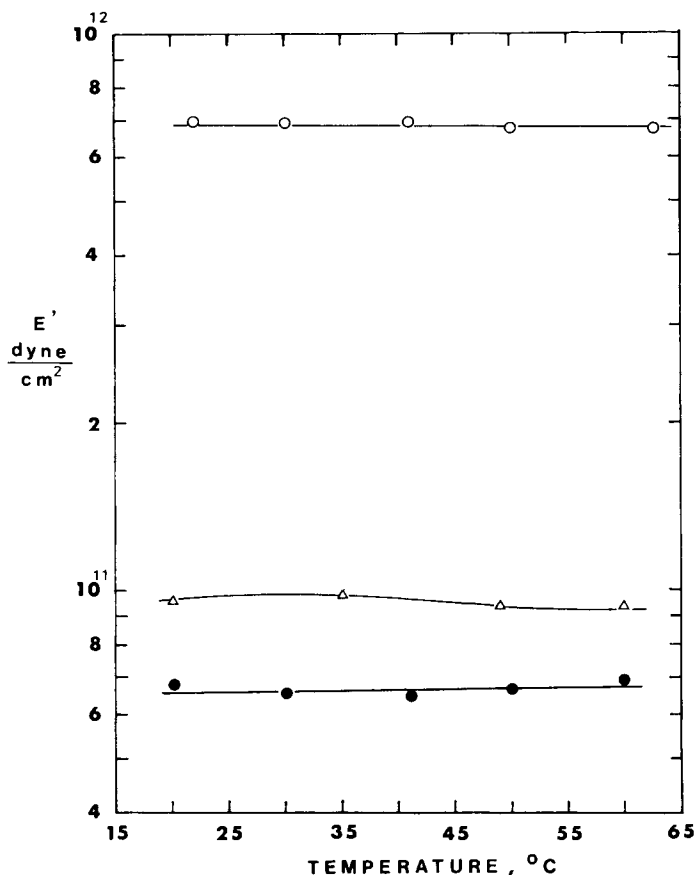


Fig. 9. Effect of polymer coatings on dynamic elastic modulus E' of aluminum bar at second-mode resonance (300–450 Hz): (O) aluminum bar; (●) aluminum bar coated with poly(vinyl chloride)/butadiene–acrylonitrile copolymer; (Δ) aluminum bar coated with Aquaplas F.70.

butadiene–acrylonitrile copolymer (PVC-NBR) was about two times larger than that of the untreated aluminum bar over the temperature range investigated. On the other hand, the commercial material Aquaplas F. 70 damped the vibrations excellently at temperatures below 35°C. Its damping efficiency decreased rapidly as the temperature was increased; and at temperatures higher than 48°C, it did not dampen the vibrations at all. The same damping characteristics were observed at the third-mode resonance (820–1300 Hz), except that much higher damping efficiencies were obtained.

The vibration damping factor of the aluminum bar coated with PVC-NBR was about 20 times larger than that of the uncoated one over the temperature range studied. The increase in damping of the aluminum bar by the viscoelastic polymers is obviously due to the lowering of the dynamic stiffness E' of the bar, as shown in Figure 9. The lowering of E' was about tenfold at all temperatures, and the values of E' were nearly unaffected by the temperature. In fact, aluminum was a good resonator at higher frequencies. It was found that the dynamic resilience of the aluminum bar was about 99% at the third-mode resonance (820–1300 Hz). The reduction of this unfavorable resilience is therefore desirable. The reduction by coating the aluminum bar with a thin layer of viscoelastic

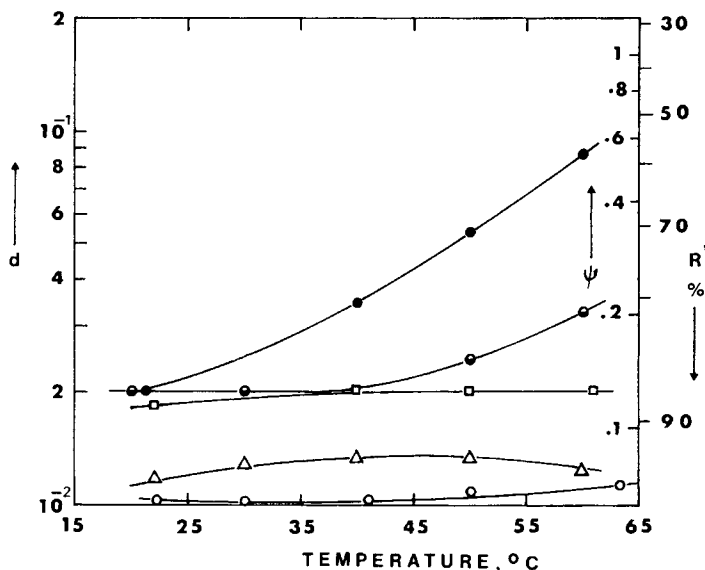


Fig. 10. Damping of substrate-borne sound by foamed polymers at second-mode resonance (390–450 Hz): (O) aluminum bar, substrate; (Δ) commercial open-cell polyurethane foam (Blachford) applied to substrate; (\square) closed-cell polyurethane/SBR foam with natural skin, applied to substrate; (\circ) closed-cell polyurethane/PVC-NBR foam with natural skin, applied to substrate; (\bullet) closed-cell polyurethane/SBR/(PVC-NBR) foam with natural skin, applied to substrate; d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

polymers was not satisfactory since only 20% to 40% reductions were achieved. Thus, other polymer systems were sought which would achieve nearly 100% reduction in dynamic resilience of the aluminum bar.

Vibration Damping of Foamed Polymers

Vibration Damping of Polyurethane-Based Foams

Polyurethane-based foams were evaluated for vibration damping and dynamic resilience when applied to a substrate such as an aluminum bar. Figure 10 shows vibration damping of an aluminum bar after treatment with a coating of foamed polymers at the second-mode resonance of the bar. The damping of the vibration of the aluminum bar was improved about two- to threefold by polyurethane/SBR and polyurethane/PVC-NBR foams, and about two- to tenfold by polyurethane/SBR/PVC-NBR foam from 20°C to 60°C. On the other hand, a commercial open-cell polyester urethane foam had only a minor effect on vibration damping. Similar results were obtained at the third-mode resonance (1100–1300 Hz), except that the improvement in damping was spectacular—the improvement was from tenfold to 200-fold at the temperature range investigated. The damping efficiency of the experimental products was also one to two orders of magnitude better than that of commercial product.

The experimental foams feel leathery or “dead” as a result of the inclusion of various viscous or elastic polymers such as poly(vinyl chloride)/butadiene-acrylonitrile copolymer, hydroxyl-terminated polybutadiene, or styrene-butadiene copolymer in the otherwise rigid polyurethane. Such foams dissipate the

vibrational energy of a substrate by internal energy absorption. This is shown by the dynamic resilience of the foam-coated aluminum panels. The open-cell commercial polyester urethane foam did not significantly reduce the dynamic resilience of the aluminum bar and was insensitive to temperature changes. On the other hand, the experimental foams, especially the polyurethane/SBR/PVC-NBR foam reduced the resilience of the aluminum. Greater reduction in dynamic resilience of aluminum by the foams was found at higher resonance frequencies of the aluminum. This can be attributed to the capacity of the viscous components of the foams to dissipate a greater amount of vibrational energy at these frequencies (1100–1300 Hz). The negligible reduction of dynamic resilience of the aluminum by a commercial foam is therefore due to its inability to dissipate energy, though it was elastic and could store strain energy. A reduction of dynamic resilience by about 85% was achieved at 40°C and at third-mode resonance by the polyurethane/SBR/PVC-NBR foam, and this reduction is obviously due to the viscous effect from the SBR and PVC-NBR present.

Vibration Damping of Polyurethane-Based Foams Coated with Polyblends

The vibration damping efficiency of the polyurethane-based foams could be increased further by coating with a thin layer of viscoelastic polyblends such as PVC-NBR. Figure 11 shows the effect of such coatings on the vibration damping of the polyurethane-based foams. At the second-mode resonance (350–450 Hz), the improvement in damping of the vibration of the aluminum bar was about four to seven times (compared with two to three times without coatings) by polyurethane/SBR and polyurethane/PVC-NBR foams, and about six to 40 times (compared with two to ten times without coatings) by polyurethane/SBR/PVC-NBR foam from 20° to 60°C. The damping efficiency of the foams is far superior to a commercial open-cell foam coated with a layer of viscoelastic material, Aquaplas F.70.100. The degree of damping increased from several-fold better at room temperature to some 20-fold better at 60°C in comparison with the commercial material.

The application of a coating of viscoelastic material to the foams resulted in the lowering of the dynamic stiffness E' of the treated panels. The degree of lowering, for example, was 39% to 40% from 20° to 60°C when a thin layer (about 0.10 cm) of plasticized poly(vinyl chloride)/butadiene-acrylonitrile copolymer (PVC-NBR) was applied to the polyurethane/SBR/PVC-NBR foam. The coating also greatly reduced the dynamic resilience R' of the panels. A reduction of dynamic resilience of the above panel from the original 58% to 9% at 60°C was achieved.

General

The acoustical performance of a polymer system is very dependent on the chemical composition and morphology of the system. The ability of the material to absorb and dissipate energy plays a very important part in the reduction of noise. Although physical characteristics such as density, porosity, surface texture, and shape and boundary layers between two phases are also important, the material factor is overriding. By properly selecting polymers, the acoustical performance of a system may be far superior to other systems with the best

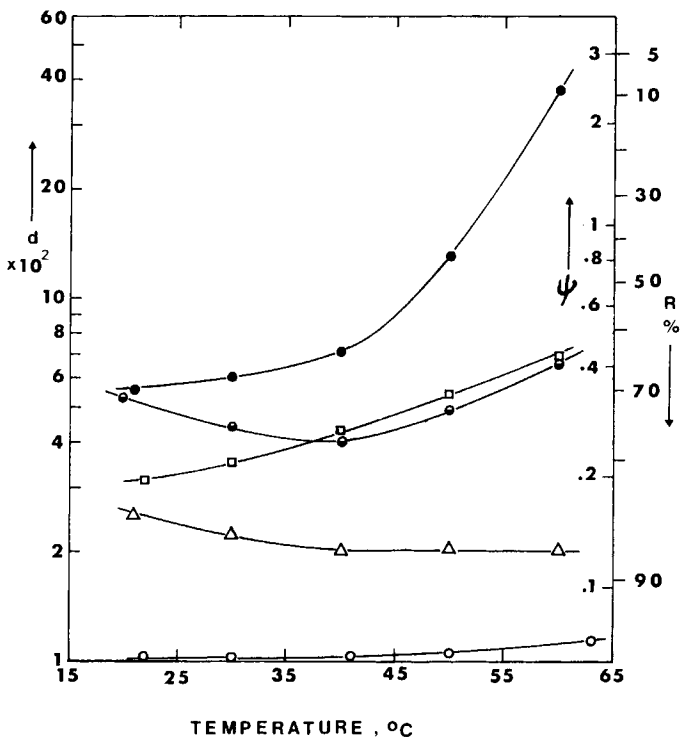


Fig. 11. Damping of substrate-borne sound by foamed polymers at second-mode resonance (350–450 Hz): (O) aluminum bar, substrate; (Δ) commercial Aquaplas F.70-100 foam, open-cell, applied to aluminum bar; (\square) closed-cell polyurethane/SBR foam with PVC-NBR skin, applied to aluminum bar; (\ominus) closed-cell polyurethane/PVC-NBR foam with PVC-NBR skin, applied to aluminum bar; (\circ) closed-cell polyurethane/SBR/(PVC-NBR) foam with PVC-NBR skin, applied to aluminum bar; d = damping factor; ψ = specific damping capacity; R' = dynamic resilience.

physical characteristics mentioned before. The acoustic energy attenuation by the elastic open-cell foams is mainly due to the interface friction between the air and the interconnecting cell walls. On the other hand, the viscoelastic closed-cell foams absorb the sound energy by the interface friction between the viscous continuous phase and elastic dispersed phase of the material in addition to the interface friction between the gas and the cell walls.

Vibration damping was dependent on temperature. Change in temperature would affect vibration damping factor as well as the resonant frequencies of a material. It was found that in all the polymer systems studied, an increase in temperature caused a lowering of the resonant frequencies. When log resonant frequency was plotted against reciprocal of absolute temperature, a straight line was obtained, and the slope is the temperature coefficient from which the resonance activation energy was calculated.

The activation energies at various mode ($n = 1, 2,$ and 3) resonances of the polymer systems are shown in Table I. The higher resonance activation energy of a polymer system indicates that the system is more sensitive to temperature changes, i.e., the rate of shifting of resonance frequencies to lower values as temperature increases is larger. It was found that resonance activation energies of polyblends and composites are generally larger than those of the original

TABLE I
Resonance Activation Energies of the Polymer Systems

Polymer system	Temperature range, °C	Resonance activation energy E_{fn} , kcal/mole		
		$n = 1$	$n = 2$	$n = 3$
Polyester (PES)	10–62	1.49	0.97	1.57
PES/lead (100/20)	20–85	1.89	2.79	1.45
PES/lead foil (100/20)	20–60	1.71	1.57	1.16
PES/lead alloy (100/20)	35–60	4.12	7.50	—
PES/PVC-NBR (100/20)	20–60	1.68	1.17	—
PES/PVC (100/20)	30–60	2.29	2.95	—
PES/PMMA (100/20)	20–60	1.28	1.14	0.79
PES/SBR (100/20)	30–60	2.34	1.75	—
Epoxy resin ECN1235	20–80	0.15	0.31	0.42
	80–105	2.12	1.37	1.28
ECN/SBR (100/20)	20–80	0.28	0.46	0.46
	80–105	1.11	2.39	1.90
ECN/PB _H T _S (100/20)	20–65	0.39	0.33	0.38
	65–100	1.39	4.12	—
Polysulfone	–35–165	0.20	0.20	0.16
PVC-NBR	20–55	—	2.95	2.45
PVC-NBR/PMMA (100/20)	20–40	—	3.20	3.13
PVC-NBR/lead (100/20)	20–50	—	7.16	4.76
Panels:				
Aluminum substrate	20–65	0.09	0.07	0.00
Aquaplas F.70-100 foam	20–60	0.15	0.16	0.35
Polyurethane/SBR foam with PVC-NBR skin	20–60	0.99	1.03	0.77
Polyurethane/SBR-PVC-NBR foam with PVC-NBR skin	20–60	0.32	0.78	0.45

polymers. For example, at the second-mode resonance, the resonance activation energy of polyester was 0.97 kcal/mole, compared to 2.79 kcal/mole, 7.50 kcal/mole, and 1.17 kcal/mole for the polyester modified with 20 phr of lead powder, lead alloy, and poly(vinyl chloride)/butadiene-acrylonitrile copolymer (PVC-NBR), respectively, at the temperature ranges indicated. The lead alloy had a melting point of 47°C, and therefore at the temperature range 35°C to 60°C, the alloy tended to flow at the lower temperature range and was molten at the upper range. Thus, when sound waves travel along the composite bar, they will be dampened by the viscous motion of the molten alloy. The velocity of sound at 50°C in the polyester/lead alloy was 1200 m/sec compared to 1700 m/sec in the unmodified polyester. This viscous attenuation of sound waves can also be achieved by using polymers with low glass transition temperatures, such as plasticized poly(vinyl chloride), butadiene-acrylonitrile copolymer, styrene-butadiene copolymer, and polybutadiene. For example, the velocity of sound at 50°C in polyester/PVC was only 1000 m/sec.

Acoustical properties of the polymer systems are related to the glass transition temperatures. The glass transition temperatures T_g of various polymer systems are listed in Table II. The polymer systems were so designed that a desired glass transition region was obtained for an optimal damping efficiency as maximal energy dissipation takes place near the glass transition region. Thus, in designing damping systems to solve noise problems, considerations should first be given

TABLE II
Glass Transition Temperature of Polymer Systems

Polymer system	Glass transition temperature T_g , °C ^a	
Polyester (PES)	55	
PES/lead (100/20)	41	
PES/lead alloy (100/20)	41	
PES/PVC (100/20)	34	
PES/PMMA (100/20)	69	
PES/SBR (100/20)	4	
PES/PVC-NBR (100/20)	9	
Epoxy resin ECN 1235	108	
ECN/SBR (100/20)	100	
ECN/PB _{HTS} (100/20)	83	
Polysulfone	188	
PVC plasticized	33	
PVC-NBR	-26	28
PMMA	95	
PVC-NBR/PMMA (100/20)	-13	83
PVC-NBR/lead (100/20)	-35	28
Aquaplas F.70	-4	
NBR	-35	
Polyurethane (PU)	67	
PU/(PVC-NBR)	4	
PU/SBR	37	
PU/PB _{HTS}	15	
PU/PVC	33	
PU/lead	44	
PU/lead alloy	25	
PU/fiber glass	86	
PU/(PVC-NBR)-SBR	34	

^aGlass transition temperatures were determined by using a du Pont 990 differential scanning calorimeter (DSC) at a heating rate of 10°C/min at atmospheric pressure and under nitrogen atmosphere.

to the selection of homopolymers with proper T_g value and range, then proceed by either polyblending the polymers, preparing copolymers, adding plasticizers, or adding fillers to achieve a broader T_g range for the expected use conditions.

The polyurethane-based foams described above possess many inherent advantages over commercial products. The foams are mixtures based on polyurethanes containing viscoelastic or elastic polymers, and are closed-cell with a natural protective skin. The inexpensive ingredients containing no lead or barytes may be mixed and then applied by spraying, painting, or dipping regardless of the shape of the surface. The whole operation can be rapidly and easily performed, even with large objects. The most important aspect, of course, is that the viscoelastic foams are excellent acoustical materials which can be used both as a sound absorber¹³ and for damping of structural vibrations at the same time. The products also retain the excellent thermal insulating properties of foams and the vapor or liquid barrier protection afforded by closed-cell, self skinning, hydrophobic polymeric materials.

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