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SOUND VELOCITY AND LOSS FACTOR OF POLYURETHANE COMPOSITES. PART I

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The paper reports development of elastic, unfoamed polyurethane compositions to be used as vibro-insulating materials. The examined compositions were prepared using poly(propylenoethers) of different molecular weights, toluylene diisocyanate and glass microspheres separated from fly-ashes. The effect of varied proportions of components on visco-elastic properties of the material, that is on sound velocity and loss factor was examined experimentally. The measurements were taken at room temperature within frequency range of 20 Hz to 1000 Hz. It was discovered that modification of the polyurethane binder content and alteration of the number of microspheres in a composition permit modification of properties of the material and especially its stiffness and internal damping.

1. Introduction

Production technology and methods of investigating the basic properties of syntactic foam were developed when searching for new thermoinsulating material to be employed in hyperbaric appliances operating at great depths under the water surface [5, 6, 7, 10]. Elasticity of the material was obtained through employment of soft unfoamed polyurethane as a binding agent, thermoinsulation and relatively low density being achieved by the introduction of spherical grains, empty or filled with neutral gas, as the filler of the microspheres. Such microbubbles are readily isolated while burning coal dust [3].

Apart from the initially demanded properties, the resulting material exhibits several other interesting features, such as, for example, insulating properties which have already been investigated [1, 2].

The task of the present paper is to determine experimentally the correlation between chemical composition of the polyurethane binder, the amount of the filter, and elasticity and damping capacity of the composite. Thus, we concentrated on sound velocity and loss factor. Both the latter quantities enable calculation of the components of Young's complex modulus, which is of fundamental significance for the proper choice of vibroinsulating materials.

2. Characteristics of the material

The object of our investigation was unfoamed polyurethane (PU) composition where micropheres obtained with a simple method from fly-ashes produced during burning coal dust were used as the filling agent. The PU binder is composed of poly(oxypropylene) trioles and diisocyanates.

The microspheres are built of glasslike substance and a considerable part of them take the form of spheres filled with gas (N_2 and CO_2). The shape and the size of the microspheres are shown in Fig. 1. Introduction of microspheres into the polyurethane composition induces changes in the PU lattice structure. It decreases mobility of the lattice fragments and increases rigidity of the polymer chain.

The investigation was carried out on four series of samples. In the first series, the ratio of the number of —OH functional groups to that of —NCO groups in the isocyanate was constant, amounting to 1:1.3, whereas the amount of microspheres varied from 10% to 60% depending on the main component of the PU composition chosen. One of the PU components was Rokopol M–12 i.e. poly(oxypropylene-ethylene) triole with the molecular weight of 4800, the other was TDI isocyanate, a mixture of 2,4- and 2,6-diisocyanatotolylene.

In the second series, properties of the binding agent were altered by choosing new proportions of the reacting isocyanate (NCO) and hydroxyl (OH) functional groups (—NCO:—OH) from 1.1:1 to 1.9:1, with the microsphere content of 30% remaining constant.

In the third series, the PU binder properties were again changed by substituting TDI with MDI isocyanate (4,4-diisocyanatodiphenylmethane), while the number of microspheres amount to 30% of the contents, and the functional group ratio (—NCO:—OH = 1.1:1) were held constant.

In the last series, the properties of the PU binder were changed once more by replacing Rokopol M–12 with Rokopol 111, characterized by molecular weight of 6000. The number of microspheres was constant (30%), and functional group ratios remained fixed (—NCO:—OH = 1.3:1 and 1.9:1). The second component of the PU binder was TDI isocyanate. Compositions with Rokopol 111 as the basic component were examined earlier and the results were reported in [1, 2].

3. Measurement method

In order to determine sound velocity and loss factor of the PU composites seen as a function of frequency, the vibration transfer function method was used. The idea of the measurement procedure is shown in Fig. 2. The theoretical model of this

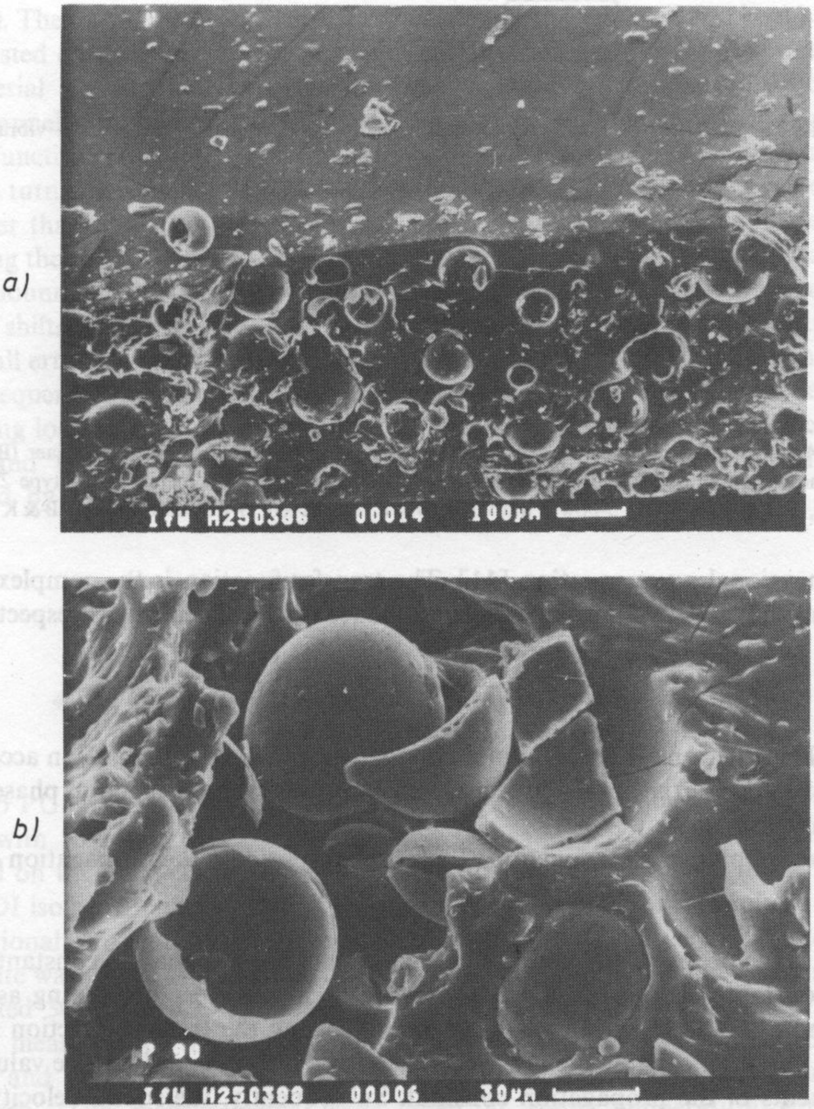


FIG. 1. Cross-section of syntactic polyurethane foam showing the shape and dimension of microspheres a–100-fold magnification, b–500-fold magnification

arrangement is, in the general case, a longitudinally vibrating rod with an end mass. For deriving the transfer function it is assumed that the cross-section of the rod is constant, the rod material is homogeneous and isotropic, the relation between stress and strain is linear, lateral motion is not prevented at the rod ends, and the width of the rod is much smaller than the mechanical wavelength [4, 8]. Under these assumptions, the longitudinal vibration of a rod is described by the well-known

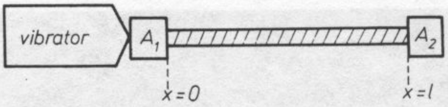


FIG. 2a. Rod-like specimen excited to longitudinal vibrations by means of a vibrator

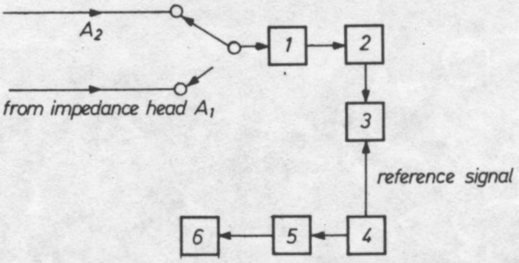


FIG. 2b. Arrangement for measuring the transfer function. 1-preamplifier, Brüel & Kjaer (B & K) type 2635; 2-measuring amplifier and filter, B & K type 2120; 3-digital phase meter, B & K type 2977; 4-sine generator, B & K type 1027; 5-power amplifier, B & K type 2706; 6-vibration exciter, B & K type 4809

one-dimensional wave equation [11]. The transfer function is the complex ratio of the vibration accelerations of the mass-loaded and excited ends, respectively:

$$T=\frac{A_2}{A_l}=|T|\cdot e^{i\varphi}=\left|\frac{A_2}{A_l}\right|e^{i\varphi} \tag{1}$$

where $|T|$ is the transfer function modulus, A_2 and A_l stand for vibration acceleration at the two ends of the specimen respectively, φ is the transfer function phase and i is the imaginary unit.

The complex transfer function, T, can be expressed by the propagation constant

$$T=[\operatorname{ch}\gamma l+(M/m)\gamma l\cdot\operatorname{sh}\gamma l]^{-1} \tag{2}$$

where γ is the propagation constant, $\gamma=\alpha+i\beta$, α is the attenuation constant, β is the phase constant, l is the rod length, M is the accelerometer, functioning as loading mass and m is the specimen mass. While measuring the transfer function modulus and the phase for each frequency, formula (2) served for establishing the values of the components of the propagation constant. Subsequently, the sound velocity, c, and the loss factor, η, were calculated from the well-known formulae

$$c=\frac{2\pi \mathrm{f}}{\beta},\qquad \eta=\frac{2d}{1-d^2} \tag{3, 4}$$

where f is the frequency and $d=\alpha/\beta$.

A block diagram of the measuring apparatus is presented in Figure 2b. Longitudinal vibrations were excited with an electrodynamic vibrator. A prism-shaped specimen of 1 cm^2 in cross-section and about 12 cm in length was bonded with a perfectly hardening adhesive to the impedance head A_1 (Brüel & Kjaer, type 8000) and the accelerometer A_2 (Brüel & Kjaer, type 4366) (see

Figure 2). The amplitude of vibration acceleration of the vibrator was kept constant and adjusted carefully not to exceed the dynamic strain limit of linear properties of the material investigated. In order to achieve the highest measuring accuracy, a one-channel technique was used for measuring the modulus and the phase of the transfer function. Due to the technique the error in measuring $|T|$ did not exceed 5% which, in turn, allowed us to estimate that the error in calculating sound velocity was also lower than 5%. The signal of an acoustic generator was used as reference for measuring the phase by the one-channel technique. The accuracy of the digital phase meter amounted to 0.1 deg. However, the error in the measured phase was larger due to phase shifts of the attenuators of the measuring amplifiers. It could be stated that the overall error in measuring the transfer function phase was not larger than 0.4 deg at all frequencies of investigation. Hence, we could estimate that the error in calculating loss factor did not exceed 10%. A detailed description of the measuring system and the method of identifying the values of the transfer function was published by Pritz in [8, 9].

4. Results and discussion

4.1. The effect of the Rokopol type on velocity and loss factor in PU compositions

Two PU compositions, one with Rokopol 111 as the basic component and the second with Rokopol M–12 were prepared to examine the effect of the type of Rokopol on the viscoelastic properties of the material under investigation. In both cases TDI isocyanate was added as the second component. The ratio of the number of functional groups —OH in macrotriole to that of the —NCO groups in isocyanate was raised to 1 : 1.3 and 1 : 1.9. Microspheres serving as the filling material constituted 30% of basic component. The modulus and the phase of the transfer function measured for the above compositions and the calculated values of sound velocity and loss factor have been shown in Figs. 3, 4 and 5, 6, for each type respectively. The measurements were taken at room temperature within the frequency range of 20 Hz–1000 Hz. Measurement of transfer function modulus for frequencies exceeding 1000 Hz was not possible because of significant damping of the signal in the investigated material. For the upper limit of the measurement range, the ratio of the length of the longitudinal wave to the width of the specimen was properly high which allowed for accepting insignificance of transverse vibrations when calculating sound velocity and loss factor.

As in Figs. 5 and 6, both sound velocity and loss factor greatly depend on the type of Rokopol. Substitution of Rokopol 111 with Rokopol M–12 results in an almost 2–fold increase in sound velocity at the frequency of 20 Hz, and a 1.5-fold increase at 1000 Hz. On the other hand we observed, marked suppression of the PU

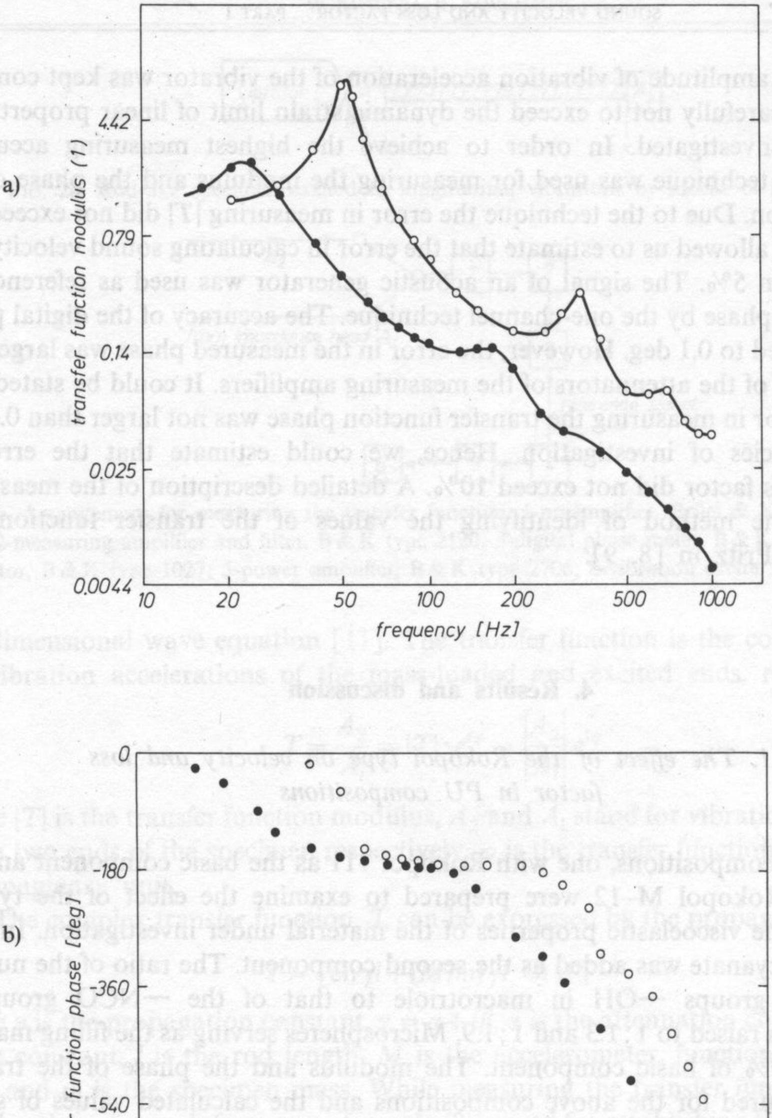


FIG. 3. Measured modulus (a) and phase (b) of the transfer function plotted against frequency for compositions with Rokopol M-12 —○—○— and Rokopol 111 —●—●— Molar ratio NCO/OH = 1.3

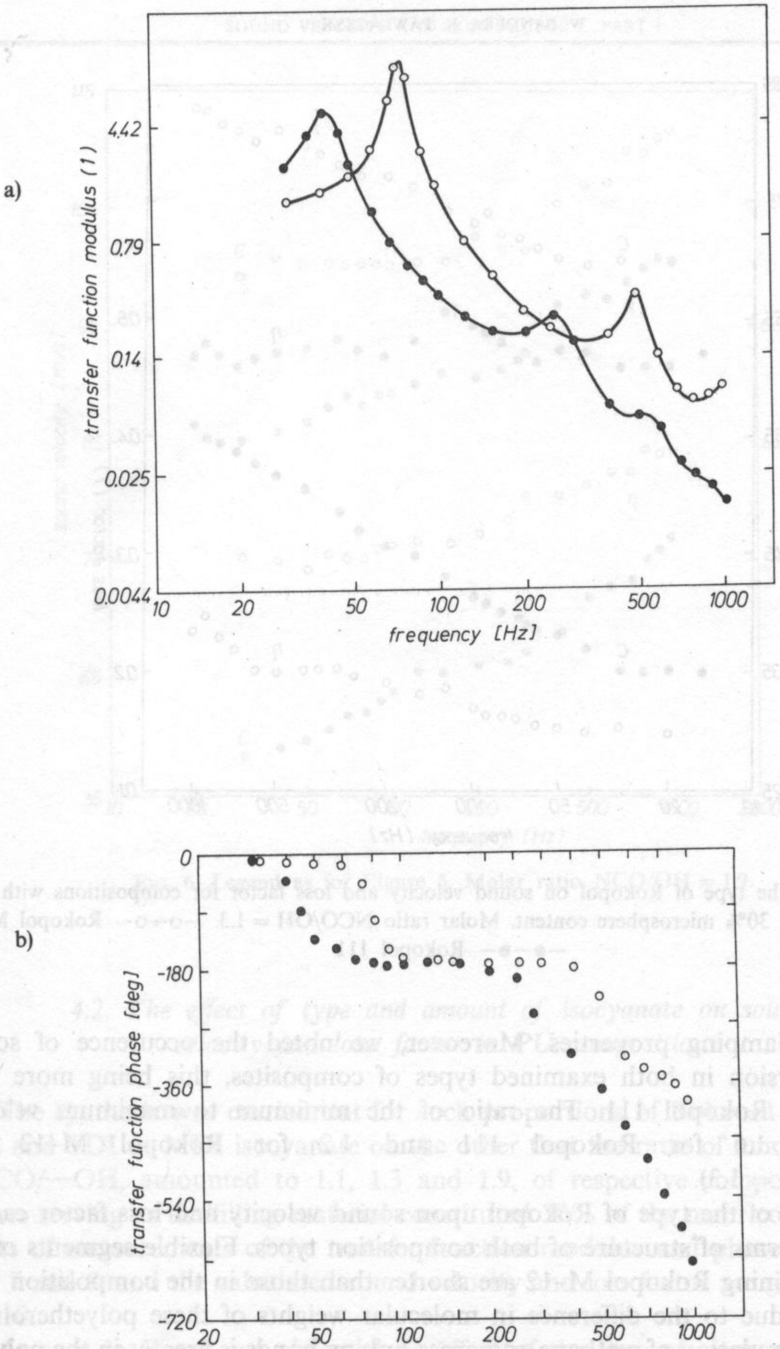


FIG. 4. Measured modulus (a) and phase (b) of the transfer function plotted against frequency for compositions with Rokopol M–12 —○—○— and Rokopol 111 —●—●— Molar ratio NCO/OH = 1.9

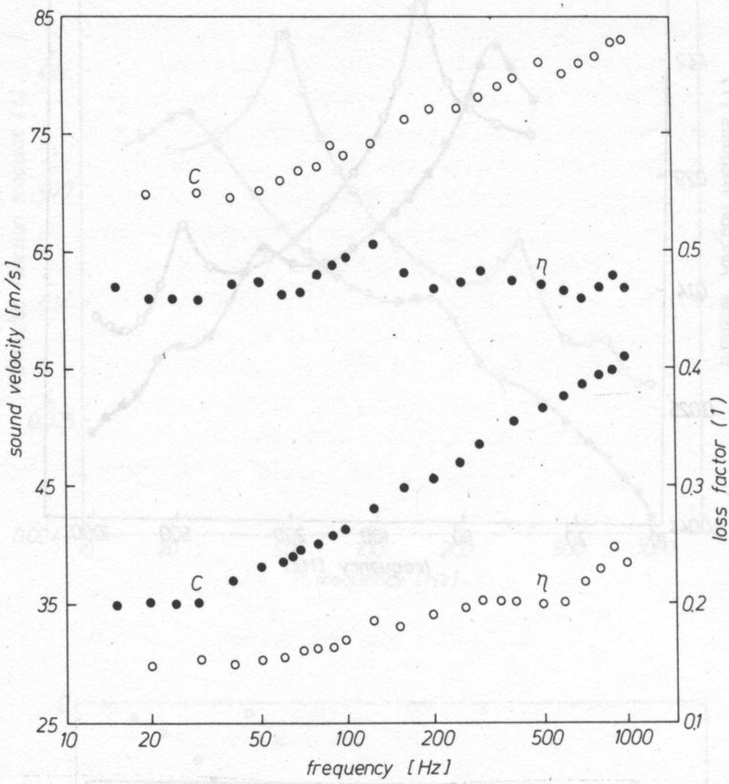


FIG. 5. Effect of the type of Rokopol on sound velocity and loss factor for compositions with TDI isocyanate, with a 30% microsphere content. Molar ratio NCO/OH = 1.3. —○—○— Rokopol M–12, —●—●— Rokopol 111

composition damping properties. Moreover, we noted the occurence of sound velocity dispersion in both examined types of composites, this being more pronounced with Rokopol 111. The ratio of the minimum to maximum velocity amounts to 1.6 for Rokopol 111 and 1.2 for Rokopol M–12 (for —NCO/—OH = 1.3).

The effect of the type of Rokopol upon sound velocity and loss factor can be explained in terms of structure of both composition types. Flexible segments of the material containing Rokopol M–12 are shorter than those in the composition with Rokopol 111 due to the difference in molecular weights of these polyetherols. In addition, accumulation of methane and cross-linking bonds is greater in the polymer containing Rokopol M–12, this being also the result of the polyetherol structure (shorter flexible segments). Materials containing Rokopol M–12 solidify faster and deaerate more readily compared to those with Rokopol 111, which is related to lower viscosity of Rokopol M–12, and in turn, affects damping properties of the composition.

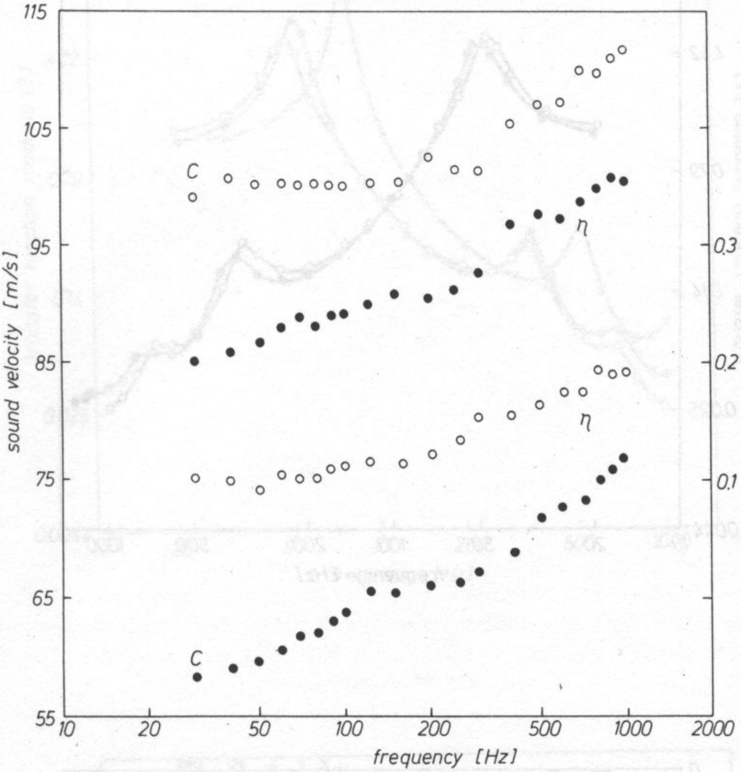


FIG. 6. Legend as for Figure 5. Molar ratio NCO/OH = 1.9

4.2. The effect of type and amount of isocyanate on sound velocity and loss factor in PU compositions

The synthesis was carried out for such proportions of Rokopol M–12 on one hand and TDI or MDI isocyanate on the other that the ratio of functional groups, —NCO/—OH, amounted to 1.1, 1.3 and 1.9, of respective components. Microspheres serving as the filling material constituted 30% of the main component. The results of measurements of the transfer function modulus and phase are shown in Figs. 7 and 8, and the calculated sound velocity and loss factor are given in Figs. 9 and 10.

As seen in Fig. 9, we observed no effect of the type of isocyanate on sound velocity within the frequency range investigated. The results obtained with TDI and MDI isocyanate are identical within experimental error. Nevertheless, with MDI isocyanate we noticed slight increase of the loss factor at frequencies up to 500 Hz.

Sound velocity is enhanced considerably upon the increase of the amount of isocyanate used in the synthesis (Fig. 10a), which is readily seen in the functional

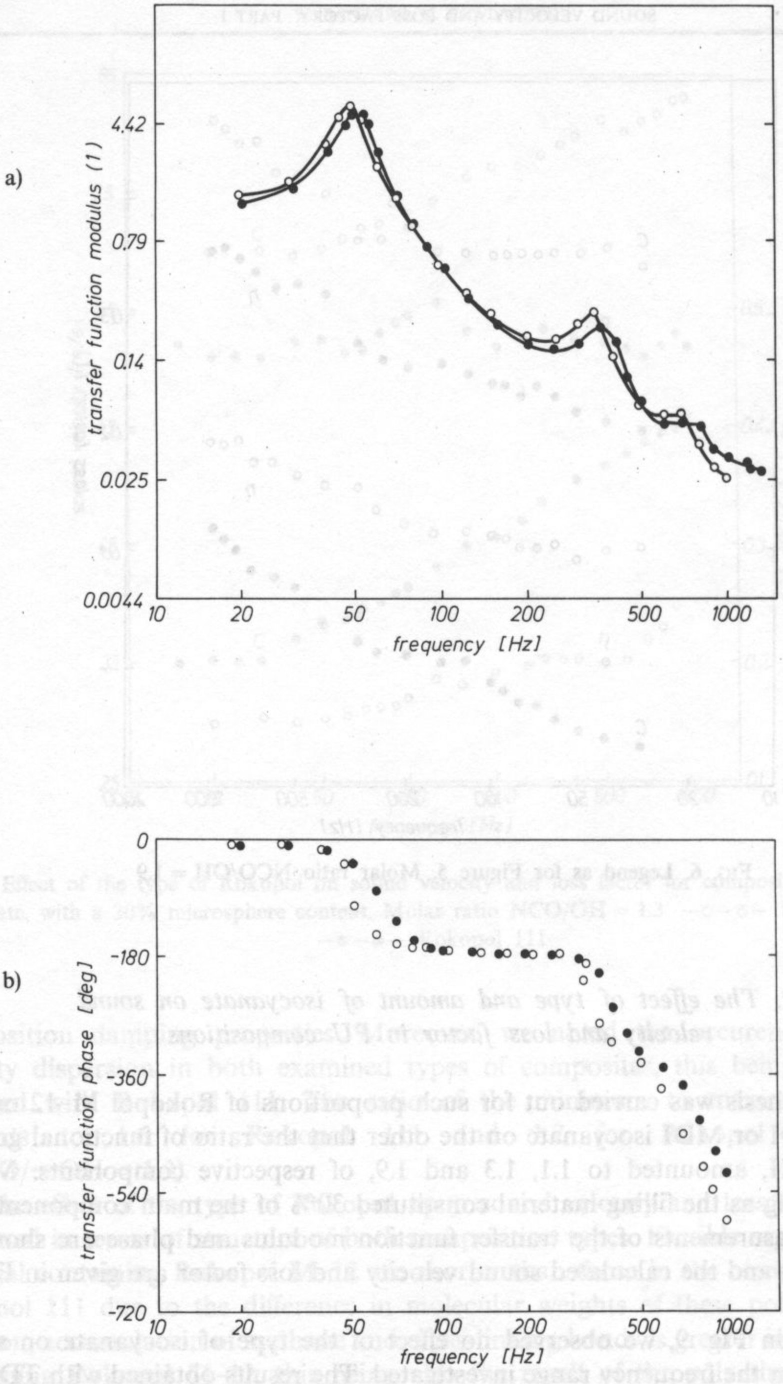


FIG. 7. Measured modulus (a) and phase (b) of the transfer function plotted against frequency for compositions with TDI isocyanate —○—○— and MDI isocyanate —●—●—. Molar ratio NCO/OH = 1.1

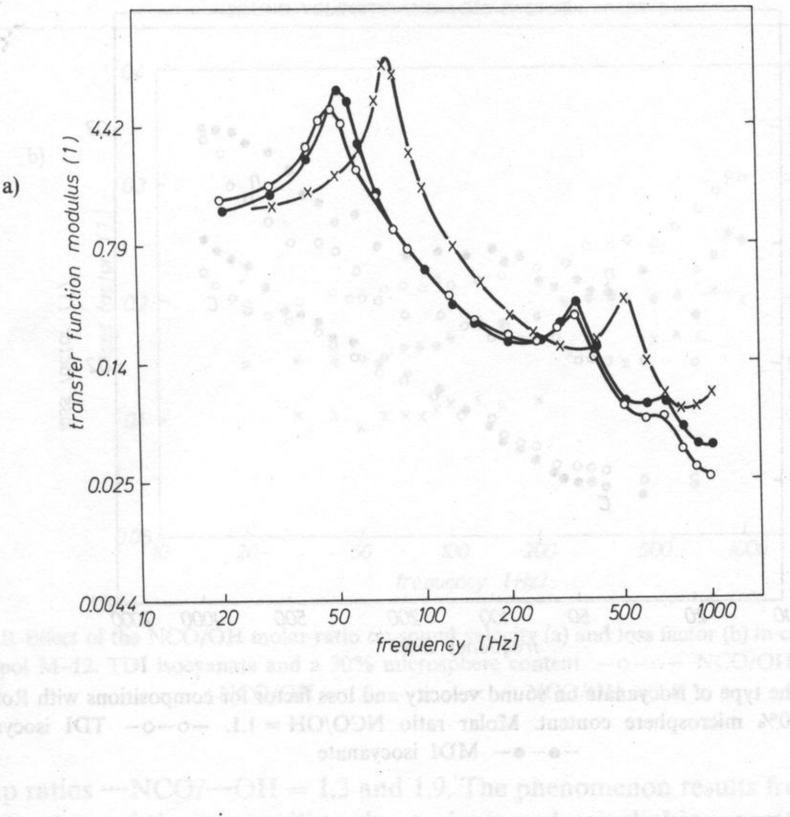


FIG. 8. Measured modulus (a) and phase (b) of the transfer function plotted against frequency for compositions with different ratio of NCO/OH. —○—○— NCO/OH = 1.1. —●—●— NCO/OH = 1.3. — × —×— NCO/OH = 1.9

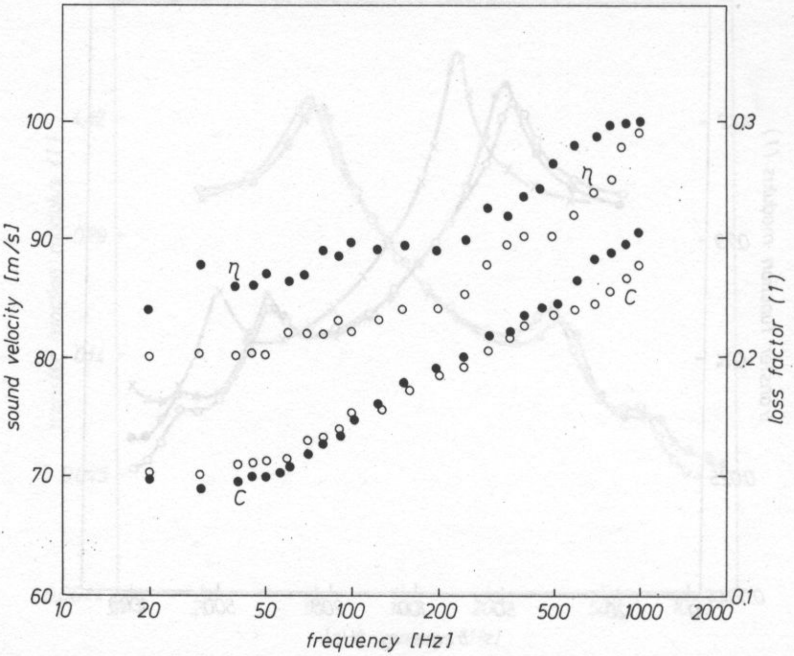
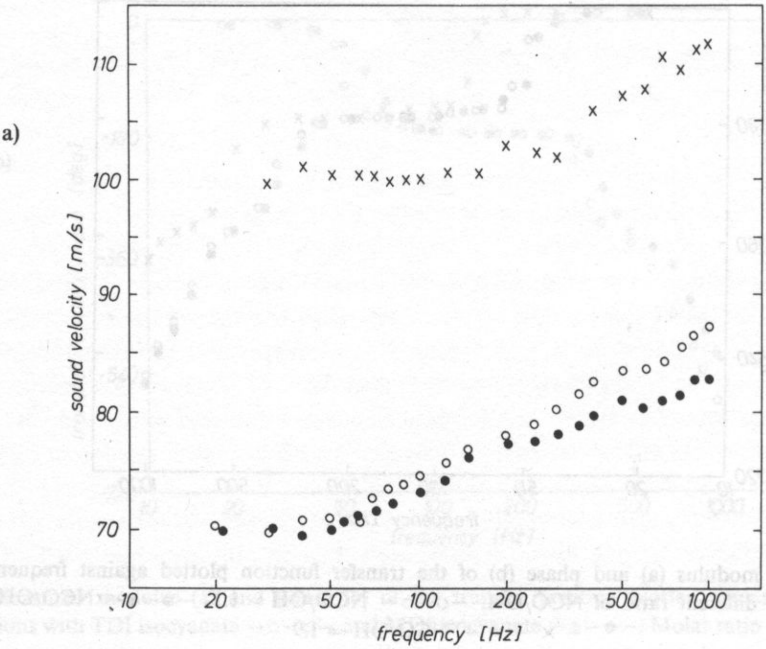


FIG. 9. Effect of the type of isocyanate on sound velocity and loss factor for compositions with Rokopol M–12, with a 30% microsphere content. Molar ratio NCO/OH = 1.1. –○–○– TDI isocyanate, –●–●– MDI isocyanate



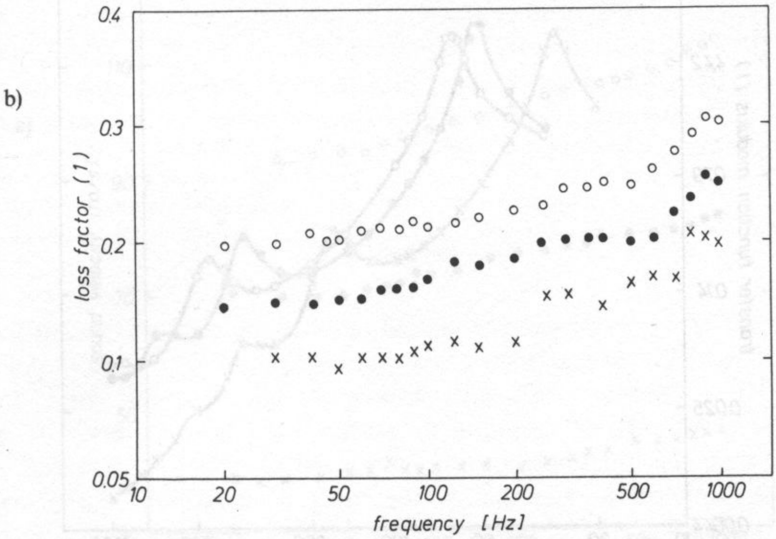


FIG. 10. Effect of the NCO/OH molar ratio on sound velocity (a) and loss factor (b) in compositions with Rokopol M–12. TDI isocyanate and a 30% microsphere content. –○–○– NCO/OH = 1.1, –●–●– NCO/OH = 1.3, – × – × – NCO/OH = 1.9

group ratios —NCO/—OH = 1.3 and 1.9. The phenomenon results from changes in the structure of the composition due to increased crosslinking, greater number of urethane bonds, and, hence, hydrogen bonds as well as increased number of rigid segments. An increased content of isocyanate in a PU composite results also in an almost two-fold drop in the loss factor (see —NCO/—OH = 1.1 and 1.9, Fig. 10b). The effect can be accounted for by increased rigidity of the composition.

4.3. The effect of the number of microspheres on the properties of PU composition

We prepared three PU compositions with different contents of microspheres (10%, 30% and 60%) in relation to the amount of basic polyurethane binder Rokopol M–12 in order to examine the effect which the number of microspheres might bear on sound velocity and loss factor.

The modulus and phase of the transfer function measured for the above compositions, as well as the calculated values of sound velocity and loss factor have been presented in Figs. 11 and 12, respectively.

As seen in Fig. 12a, sound velocity in the compositions investigated depended strongly on the amount of contained microspheres and enhanced when increasing their number. Simultaneously, we observed dispersion of sound, the dependence of the sound velocity on frequency being almost linear. The value of the loss factor was

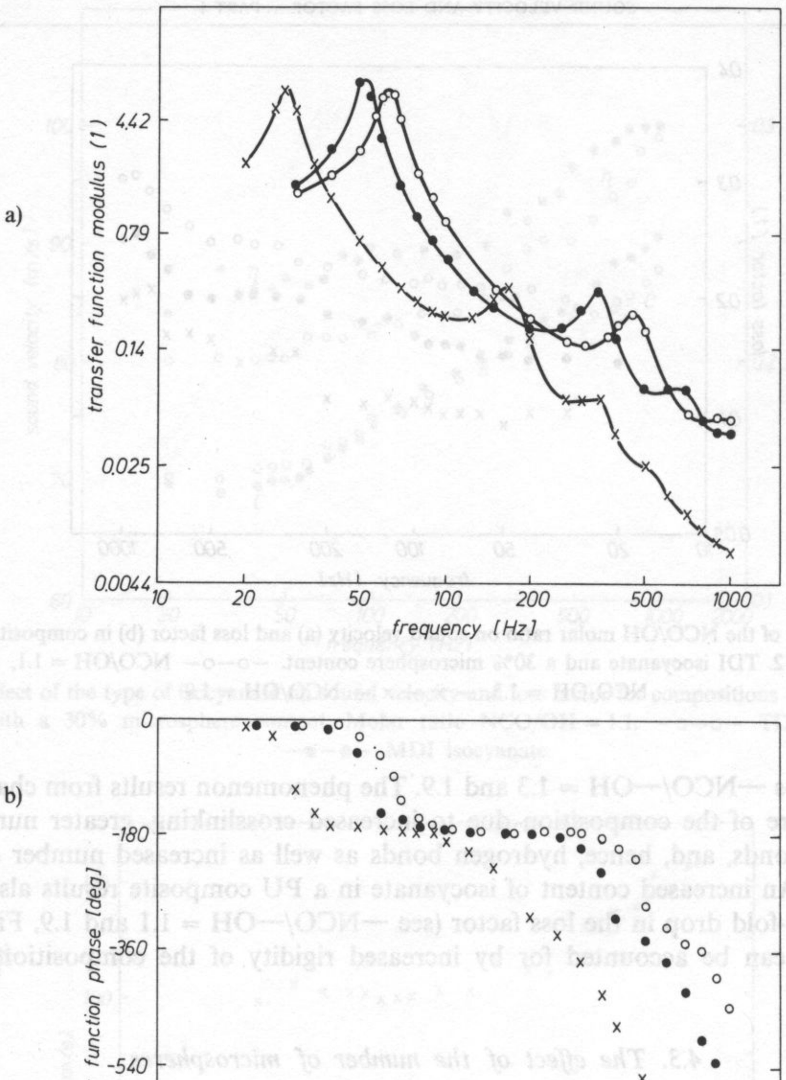


Fig. 11. Measured modulus (a) and phase (b) of the transfer function plotted against frequency for compositions with different contents of microspheres in relation to the basic PU binder. — × — × — 10%, — ● — ● — 30%, — ○ — ○ — 60%. Molar ratio NCO/OH = 1.3

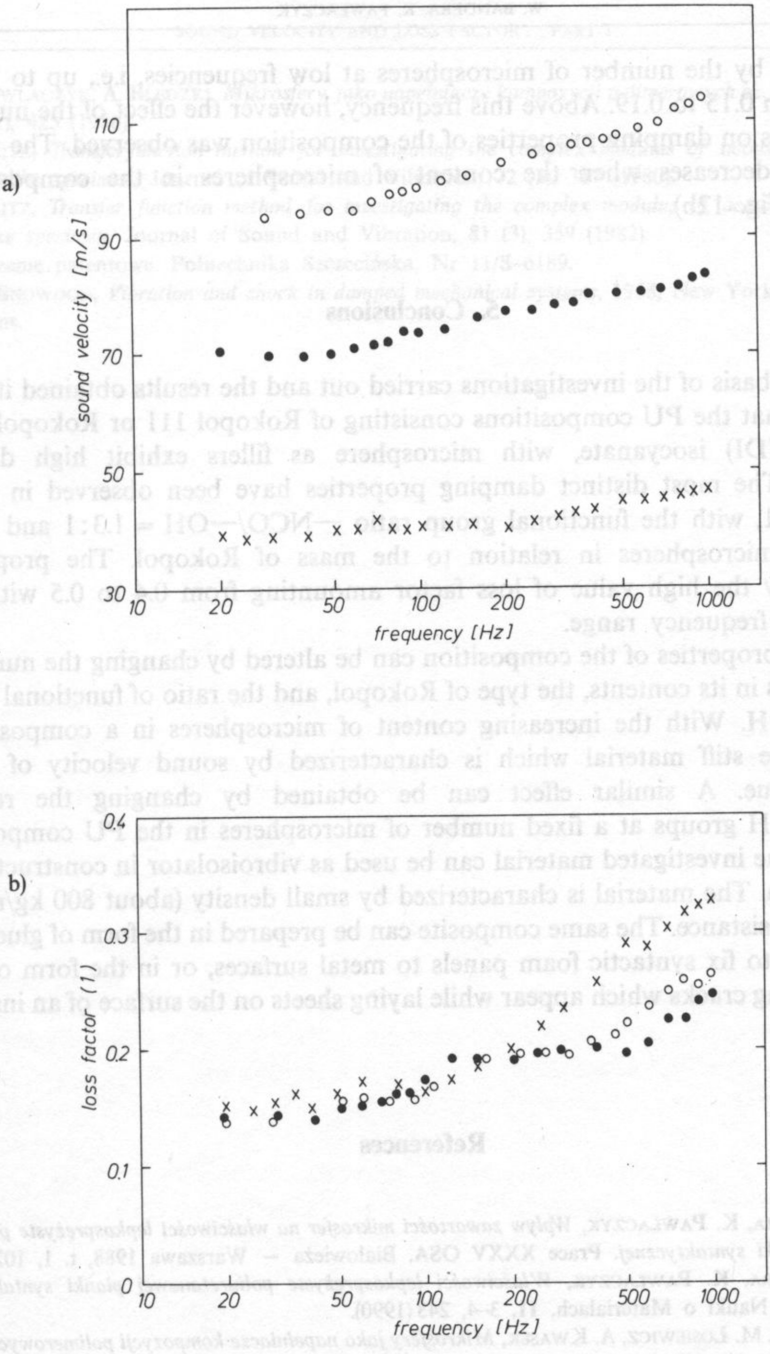


FIG. 12. Effect of microsphere contents on sound velocity (a) and loss factor (b) for compositions with Rokopol M–12 and TDI isocyanate. Molar ratio NCO/OH = 1.3. — × — × — 10%, — ● — ● — 30%, — ○ — ○ — 60% microsphere content

not affected by the number of microspheres at low frequencies, i.e., up to 200 Hz, varying from 0.15 to 0.19. Above this frequency, however the effect of the number of microspheres on damping properties of the composition was observed. The value of loss factor decreases when the content of microspheres in the composition is increased (Fig. 12b).

5. Conclusions

On the basis of the investigations carried out and the results obtained it can be concluded that the PU compositions consisting of Rokopol 111 or Rokopol M–12, TDI (or MDI) isocyanate, with microsphere as fillers exhibit high damping properties. The most distinct damping properties have been observed in case of Rokopol 111, with the functional group ratio —NCO/—OH = 1.3 : 1 and a 30% content of microspheres in relation to the mass of Rokopol. The property is evidenced by the high value of loss factor amounting from 0.4 to 0.5 within the investigated frequency range.

Elastic properties of the composition can be altered by changing the number of microspheres in its contents, the type of Rokopol, and the ratio of functional groups —NCO/—OH. With the increasing content of microspheres in a composite one obtains more stiff material which is characterized by sound velocity of almost doubled value. A similar effect can be obtained by changing the ratio of —NCO/—OH groups at a fixed number of microspheres in the PU composite. It seems that the investigated material can be used as vibroisolator in constructions of various types. The material is characterized by small density (about 800 kg/m^3 and high water resistance. The same composite can be prepared in the form of glue which can be used to fix syntactic foam panels to metal surfaces, or in the form of paste useful in filling cracks which appear while laying sheets on the surface of an insulated object.

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