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The measurements of density, velocity of ultrasonic waves at frequency of 2.5 MHz, and dynamic elastic modulus were made for a raw and HCl-demineralized bituminous coal (C^{daf} = 86.8%), subjected to action of selected solvents such as methanol, tetrahydrofuran, pyridine, and ethylenediamine. It was found that the measured values were different for samples after treatment with solvents. Ultrasonic velocities and elastic moduli were generally found to increase after solvent treatment in both demineralized and the raw coal samples. The dependence of elastic modulus on swelling exhibited the same nature as that for polymers.

Introduction

The accessibility of solvents to coal macromolecules is of importance for industrial processes such as coal liquefaction. Diffusion of the solvent in coal takes place through bulk material or pores.[1] Bulk diffusion effects the coal to swell. The coal swelling behavior has been investigated by many workers, using various standard experimental techniques.[2−11] Detection of a phase transition from a glassy state to a rubbery state during swelling was studied by means of NMRI, ^{1}H NMR, ^{2}H NMR, and ^{13}C NMR techniques,[2−6] with a polarizing microscope,[7] stress−strain analysis of solvent-swollen coals with microdilatometer,[8,9] and by differential scanning calorimetry.[10,11] For studies of coal swelling in the presence of solvents, various techniques nonfrequently used for coal, i.e., image analysis for evaluation of swelling of single coal particles heated with a CO_2 laser,[12] an optical microscope coupled with electronic image analysis and a Malvern laser diffraction particle sizer to measure swelling[13] and small angle neutron

scattering (SANS) to characterize soluble and insoluble fractions of coal[14] were also applied. It was found that the rates of solvent uptake and kinetics of swelling are strongly influenced by factors such as the nature of the coal, the size of the coal particles,[15,16] the nature of the solvent used,[17−21] the size and shape of the solvent molecules,[22,23] the accessibility of solvents to coal macromolecules,[1] solvent sorption and diffusion processes in coals,[24,25] temperature of heat-treatment,[20,26,27] the moisture content of the coal[27] and other features of its pretreatment.[27,28] Larsen et al.[29] and Nishioka et al.[30] stated that coal swelling provides the macromolecule with the opportunity to undergo conformational rearrangements and to adopt a lower free energy more highly associated structure. Hall et al.[31,32] applied Einstein specific heat model to elucidate changes in coal structure following solvent extraction. Nishioka[33] observed distinct irreversibility for two different ranks of coal which was consistent with the results of solvent

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extractability. Solvent swelling of macerals concentrates was investigated by Milligan et al.[34] Some of investigators[7,8,35-37] constructed various models for the swelling of coal.

In the presence of solvent, the coal macromolecules become more flexible, resulting in a change of elastic modulus of solvent-treated coal. Coals are complex, heterogeneous macromolecular solids. It is generally known[38] that structural and content changes as well as a change in the nature of the supermolecular organization of the macromolecules influence the effectiveness of intermolecular interaction. It is obvious that all these factors affect the magnitude and the nature of change in the dynamic modulus of elasticity and the velocity of sound. The latter two quantities give various pieces of information—first, information on the most important mechanical (deformation) properties of macromolecular substance, and second, an information on its chemical and physical structure, its composition, and state. It was stated for complex materials such as polymers[38] that there is a strict correlation between the chemical and physical structures as well as between the molecular mobility of complex macromolecular substance and the velocity of sound and the components of the complex moduli of elasticity.

Elastic properties of swollen coals were studied by Brenner[7] as well as by Cody et al.[8,9,39] Brenner estimated dynamic Young's modulus while the coal was in the swollen state; the magnitude of this modulus was shown to lie in the range of stiff rubber. Coal's elastic modulus and solidlike behavior might result either from a cross-linked network or from an extensive entanglement coupling. Similarly, Cody et al. found that mechanical behavior of coals had the characteristics of rubber-like materials. Coal was suggested[39] to be a highly entangled network with relatively stiff chains as opposed to one that is primarily connected by covalent cross-links.

The aim of this investigation was to obtain experimental results of density and ultrasonic velocity as well as dynamic elastic modulus for samples of a raw and HCl-demineralized bituminous coal subjected to action of selected solvents such as methanol (MeOH), tetrahydrofuran (THF), pyridine (PY), and ethylenediamine (EtDa) in order to determine whether and how the solvents alter the elastic properties of coal.

Experimental Section

Sample of the bituminous coal No.17 from Thorez mine (the Lower-Silesian Coal-Field) was used in the study. Results for selected parameters of elementary analysis and petrographic content in (wt %) of this sample[40] are the following: C^{daf} = 86.8, VM^{daf} = 20.6, ash = 8.0; V = 83.3, E = 1.9, I = 11.6, and mineral matter = 3.2 (clay = 3.2, pyrite and carbonates = 0). Density, velocity of ultrasonic waves, and elastic modulus were determined for this raw and demineralized sample before and after treatment with solvents. The demineralization procedure consisted in treatment with concentrated hydrochloric acid. Some portions of both raw and demineralized coal samples were flooded with four solvents, i.e., MeOH, THF, PY, and EtDa in ambient temperature and remained up for near 2 weeks to stabilize the coal level. Swelling ratios were determined. The swelling ratio was calculated as $Q = h/h_0$, where h is the height of the coal bed at time in which the swelling reached equilibrium and h_0 is the beginning height. Then samples were filtered and followed by vacuum-drying at the temperature of 105 °C for 18 h. Then they were divided into 2 parts. One part was used to determine the densities and the second part underwent ultrasonic measurements. The measurements of density were made using a helium pycnometer "Micromeritics" (USA). The velocities of ultrasonic waves of f = 2.5 MHz in coal particles were determined by suspension method.[41-43] Application of a method developed for suspensions of a dispersed phase of one material in a continuous second phase for coals was described in our previous papers.[40,44-46] Coal suspensions of the same concentration (3 wt %) were prepared in glycol using an ultrasonic disintegrator for about 15 min. The measurements of the ultrasonic velocities in pure glycol and in glycol suspensions of coal were performed in the temperature range of 15-40 °C with SW-08 apparatus (TPNZ, Poland) based on the "sing-around" pulse method. This ultrasonic technique used for investigations of liquid coal products has been described in our previous papers.[47,48] The ultrasonic velocities in glycol and suspensions at t = 20 °C were calculated from the experimental dependencies of velocity on temperature. The ultrasonic wave velocities in coal particles v were calculated according to the following equation:[40,42]

$$v_s = \frac{v_1}{\left\{\left[1 + q\left(\frac{\rho}{\rho_1} - 1\right)\right]\cdot\left[1 - q\left(1 - \frac{\rho_1 v_1^2}{\rho v^2}\right)\right]\right\}^{1/2}} \quad (1)$$

where v_s is the velocity of ultrasonic wave propagated in suspension, v_1 is the velocity of ultrasonic wave in pure liquid, ρ_1 and ρ are the densities of the pure liquid (subscript l) and of particles of suspended matter, respectively, and q is the volumetric concentration of particles of suspended matter.

Detailed discussion about the applicability of eq 1 was presented in ref 42. Generally, this equation is valid for the condition $d \ll \lambda$ (where d = particle diameter, λ = wavelength) and for small concentrations of spherical particles. The above requirements for coal samples were fulfilled for the following parameters: frequency of ultrasonic wave equal to 2.5 MHz, particle diameters <10 μm, liquid is ethylene glycol, volume concentration of coal particles is 2.5%. The dynamic modulus of elasticity E' was determined from the expression $E' = \rho v^2$, where v is the ultrasonic velocity and ρ is the density.[38]

All samples were ground in an agate ball mill to obtain the size of particles of about 10 μm to fulfill the requirements of suspension method. All measurements, i.e., those of density, velocity, and swelling ratio, as well as demineralization procedure were made using this granulation. Densities and swelling ratios for raw and demineralized sample No. 17 subjected to action of MeOH, THF, PY, and EtDa are presented in Table 1.

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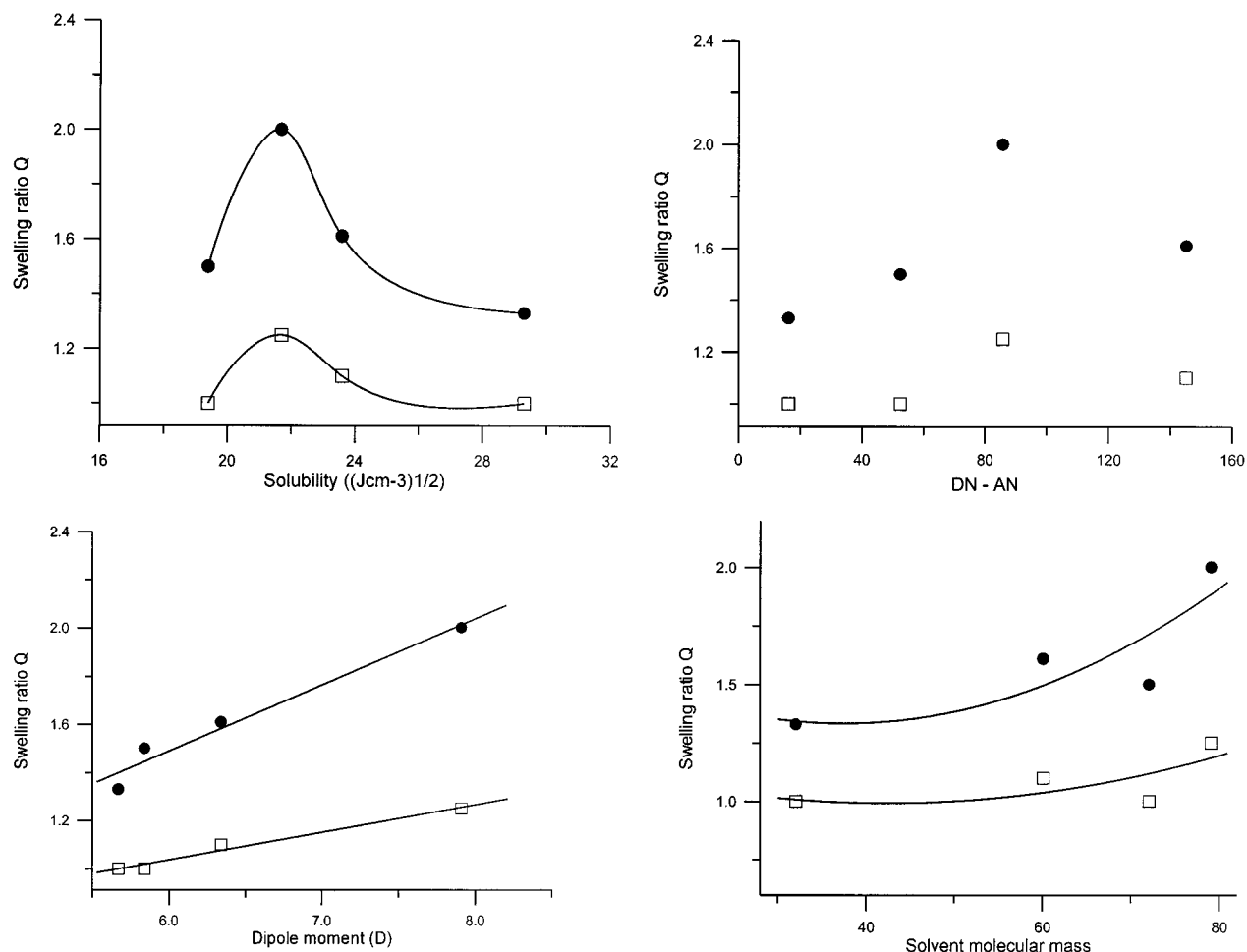(35) Painter, P.; Shenoy, S. *Energy Fuels* **1995**, *9*, 364-371.

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Figure 1. Correlation of the swelling ratio Q of coal No. 17 with the following solvent parameters: solubility parameter δ (a), DN-AN (scaled) (b), molecular dipole moment μ (c), and molecular mass m_{sv} (d); (●) raw coal, (□) demineralized coal. The values of solvent parameters are put on the X axis in order: THF, PY, EtDa, MeOH for (a); MeOH, THF, PY, EtDa for (b); MeOH, THF, EtDa, PY for (c); MeOH, EtDa, THF, PY for (d). Solid lines for (c) and (d) denote the fitting of the experimental data with correlation coefficients r equal to 0.96 and 0.98 (c); 0.70 and 0.47 (d) for the raw and the demineralized samples, respectively.

Table 1. Densities (g/cm³) and Swelling Ratios for the Raw and the Demineralized Sample No. 17 Quoted from Ref 44

	raw coal		demineralized coal	
solvent	density	swelling ratio	density	swelling ratio
no solvent	1.357	-	1.353	-
MeOH	1.403	1.33	1.355	1.00
THF	1.394	1.50	1.392	1.00
PY	1.387	2.00	1.341	1.25
EtDa	1.430	1.61	1.377	1.10

Results and Discussion

Bituminous coal No. 17 was characterized with carbon content of about 87 wt %. According to ref 49, for coals with the above carbon content there is a maximum of average molecular weight between two neighboring cross-links. It means that such coal is low cross-linked. This coal was subjected to four solvents from various solvent classes between I and V (Dryden's classification of solvents[50]), i.e., MeOH, THF, PY, and EtDa. The mutual relationships between swelling ratio, elastic modulus, and a degree of cross-linking will be discussed below.

Table 2. Parameters Characterizing the Solvents Used in the Study: Solubility Parameter δ,[51] the Excess Donicity DN-AN (scaled),[50,52] Molecular Dipole Moment μ[51] Extraction Yield in Ambient Temperature for Coal with Carbon Content 85%[53] (wt %), and Molecular Mass (m_{sv})

solvent	δ [Jcm^{-3}]$^{1/2}$	DN-AN (scaled)	μ [D]	extraction yield C = 85%	m_{sv}
MeOH	29.3	16.2	5.67	1.1	32.04
THF	19.4	52.5	5.84	3.5	72.10
PY	21.7	85.8	7.91	13.8	79.10
EtDa	23.6	145.1	6.34	7.2	60.10

Swelling Ratio Q. The studies of the dependencies of the swelling ratio on solvent parameters such as the δ parameter of Hildebrand (or solubility parameter), the excess donicity DN-AN (DN is donor number and AN is acceptor number), molecular dipole moment μ, and molecular mass of solvent m_{sv} were performed. Figure 1a−d shows the dependence of the swelling ratio Q versus the above parameters for raw and demineralized coal No. 17. Table 2 presents the parameters characterizing the solvents (quoted from refs 50 to 53), used for

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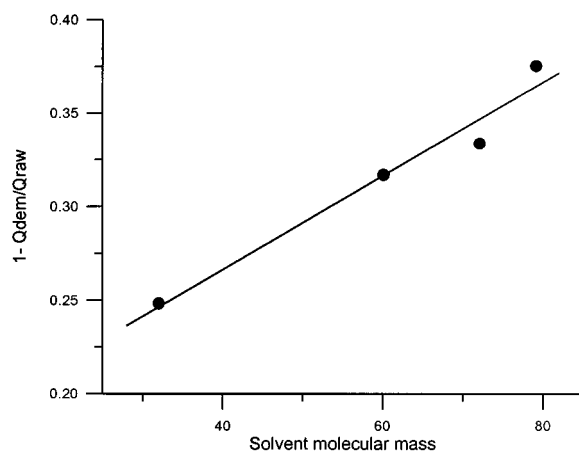(50) van Krevelen, D. W. In *COAL Typology-Physics-Chemistry-Constitution*; Elsevier: Amsterdam, 1993; p 570.

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Figure 2. Correlation of the reduction of swelling ratio $(1 - Q_{dem})/Q_{raw}$ with the solvent molecular mass m_{sv}; correlation coefficient $r = 0.96$.

preparation of the above figures. It is clear that shapes of the plots are the same as those published for other coals,[50] but in the case of δ and DN-AN, they have different places of maxima. Maximum of swelling for coal No. 17 (C $\cong$ 87 wt %) occurs at $\delta \cong 22$ J$^{1/2}$ cm$^{-3/2}$ and DN-AN $\cong$ 86 (PY). It is obvious, since our sample was characterized with different carbon content. It was found that molecular dipole moment μ and molecular mass of solvent m_{sv} give the simple proportional dependence: the greater μ or m_{sv}, the greater is swelling ratio. Shapes of the plots are the same for both raw and demineralized coal samples. The same courses of Q dependence indicate the same mechanism during swelling for both raw and demineralized samples. The degree of solvent swelling that takes place is different for raw and demineralized coal. It can be seen from Table 1 that swelling ratios for HCl-demineralized sample are reduced in comparison with those observed for raw coal. It was reported in ref 34 that swelling ratios and pyridine extraction yields were higher for demineralized coals as compared to untreated coals for low rank (about 69% up to about 84% carbon content). This discrepancy between those and our results can be explained by different carbon content in our samples and using only the first step of demineralization. HCl-demineralization of coal samples considerably decreases swelling in the presence of PY and EtDa and completely reduces for MeOH and THF. These results are consistent with our previous studies.[40] Differences between degrees of swelling in the presence of the studied solvents are smaller for demineralized sample in comparison with the raw sample. Solvents affect more the raw than the demineralized coal. The reduction of the swelling degree defined as "$(1 - Q_{dem})/Q_{raw}$" depends, like the swelling ratio Q, on the same solvent parameters, i.e., δ, DN-AN, μ, and m_{sv} in a similar, but not the same way. Figure 2 shows the plot of $(1 - Q_{dem})/Q_{raw}$ vs solvent molecular mass. This dependence is linear contrary to the plot of Q vs m_{sv} (Figure 1d). It was found that the greatest decrease of swelling occurred for PY, then for THF, EtDa, and MeOH. It is supposed that the reduction of swelling ratio indicates probably the higher cross-linking of the demineralized sample. It is known for natural rubber that the greater degree of cross-linking, the lower equilibrium swelling ratio.[54] Milligan et al.[34] suggested that acid washing removes the interacting cations (Ca^{2+},

Na$^+$, etc.), which may then allow the functional groups such as −COOH and −OH to form coal−coal bonding upon drying, effectively increasing the noncovalent cross-link density. Larsen et al.[55] found that the demineralization significantly affects the dilatometric properties of coals. Residual acid in the coal may induce polymerization on heating that results in a loss of plastic properties and a decrease in dilation.

Density of Samples after Solvent Treatment. Table 1 presents the densities of solvent-treated raw and HCl-demineralized samples. Coal No. 17 did not contain carbonates, which would be washed out in HCl demineralization procedure. This sample ought to exhibit the smallest changes of measured values. In fact, the density remains almost the same after acid treatment. As it is shown in Table 1 only the density of demineralized sample subjected to methanol is the same (within the experimental error) as that of the initial sample. It seems obvious, because methanol does not cause both swelling and extraction of demineralized coal. Other values are higher than densities of initial samples except that of ρ for demineralized coal after treatment with pyridine. Coal flooded with various solvents, even in room temperature experiments, is extracted with different yields that results in a decrease of mass in comparison with the initial sample. Simultaneously, the vacation of a part of pores in macromolecular phase by molecular phase changes a sample volume. If densities of both phases were equal, extraction would not alter coal density. Probably these densities are different, and therefore the coal density is not the same after treatment with a solvent. It is not the only reason of densities changes. Samples were filtered and dried before measurements of ρ and v, that led to removal of swelling. However, coal did not return to its initial state. Considerable differences of densities cannot be explained by the presence of the remaining solvent. They can be accounted for modifications of structure of samples after solvent action caused by removal of a part of molecular phase and, what more, of looseness and even rupture of bonds. After drying, samples approach a new state with different density. Deviations from the density of initial samples depend on the type of solvent. Densities of samples produced from demineralized coal with solvents treatment are smaller than those for samples from undemineralized coal.

Elastic Properties of Solvent-Treated Coal. Stiffness of material expressed by stiffness (or elasticity) tensors represents resistance to deformation, and it is a much simpler property than strength and toughness, which relate to failure. The most important reason is that it is much easier to relate stiffness to molecular structure than it is to relate the other more complicated mechanical properties. For that reason, stiffness is the most informative single mechanical measurement one can make on a material. The velocity of sound propagation in a material is simply related to the stiffness (or elasticity) constants and density. It is a very convenient method in practice and gives simple and unambiguous results, e.g., in the case of oriented glassy polymers.[56]

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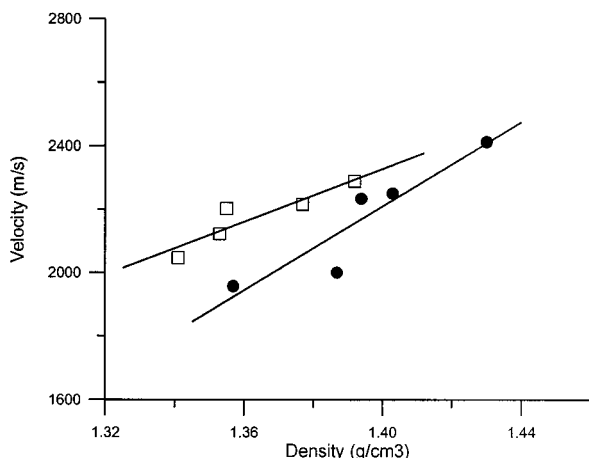
Figure 3. The plot of the ultrasonic velocity vs density for solvent-treated samples: raw (●) and previously HCl-demineralized (□); correlation coefficients *r* are 0.86 and 0.84, respectively.

Figure 3 shows the plot of the ultrasonic velocity versus density of the raw and demineralized samples after solvent-treatment and drying. It is known that the velocity of ultrasonic wave propagation in denser materials is generally greater. It was also observed for the studied coal samples. It can be seen from Figure 3 that for the same density, the velocity in solvent-treated demineralized sample is greater than that in solvent-treated raw sample. It means that HCl-demineralized material is stiffer, and probably has greater number of cross-links, even after solvents treatment.

It was found that elastic dynamic modulus for the initial (before solvent action) demineralized sample E'_{dem} = 6.10 GPa is higher than modulus for the initial raw sample E'_{raw} = 5.19 GPa, what gives evidence that HCl-treatment increases stiffness of coal. For the raw coal elastic moduli of samples after solvents treatment are higher than those found for the initial sample for all solvents, while for the demineralized coal it is true for MeOH, THF, and EtDa. The elastic dynamic modulus of the raw and the demineralized coal samples subjected to solvents in relation to initial modulus versus the solvents parameters was plotted in Figure 4a–d. It was found that the above dependencies are similar to those plots of swelling ratio *Q* vs solvents parameters, but they are reversed and more scattered. We can conclude that the greater swelling, the lower the elastic modulus of the dried sample. The elastic modulus data for the demineralized samples are less scattered than those for the raw samples. This suggests that demineralized material is better ordered than a raw sample.

Treloar[54] showed the relation between the equilibrium swelling and the degree of cross-linking for polymers, e.g., for butyl rubbers with various degrees of cross-linking. For a given polymer subjected to varying amounts of cross-linking there is a relationship between the equilibrium degree of swelling (in a given liquid) and the modulus. The greater swelling (the greater number of disrupted cross-linkages), the lower stiffness, the lower elastic modulus. Figure 5 shows the plot of elastic modulus versus swelling ratio *Q* for the coal

No.17. Curves shown in this figure are similar in shape to the relations between elastic constant and $1/v_2$ for equilibrium swelling in a series differently cross-linked butyl rubbers.[54] For an isotropic expansion of the network, the value of $1/v_2$ is the volume swevlling ratio.[54] It can be seen from the Figure 5 that pyridine disrupts the greatest number of cross-links that results in the lowest elastic modulus. Thus, the swelling of both raw and demineralized coal samples proceeds similarly to swelling in polymers. It means that samples obtained with solvent treatment from the initial (raw as well as demineralized) coal exhibit various degrees of cross-linking. As shown in Figure 5 differences between the raw and the demineralized samples are clear. Milligan et al.[34] suggested that the demineralization process may modify the interactions within the coal structure; thus swelling ratios obtained on demineralized samples should be viewed in this context. The above statement applies also to other parameters, e.g., elastic moduli.

The Dependence of *E* on the Degree of Cross-Linking. For a continuous spectrum of relaxation times $H(\tau)$, the relationship between the elastic properties of net polymers and the cross-linkage factor can be written in the following form:[38,57]

$$E' = E_0 + \int_0^\infty [H(\tau)\omega^2 \, \tau^2/(1 + \omega^2 \, \tau^2)] \, d\tau \qquad (2)$$

where E_0 is the equilibrium modulus, ω is the frequency of the periodic action on the polymer, and τ is the relaxation time. It was supposed[38,57] that the density of the relaxation spectrum $H(\tau)$ is expressed by the following relation:

$$H(\tau) = \varphi H_1(\tau) + (1 - \varphi) \, H_2(\tau) \qquad (3)$$

where $H_1(\tau)$ is the density of the relaxation spectrum in a polymer with a maximum possible degree of cross-linking; $H_2(\tau)$ is the density of the relaxation spectrum in a polymer of the same chemical structure but with no chemical cross-links; $\varphi = \phi/\phi_m$ (ϕ_m is the maximum possible value of ϕ; ϕ is the degree of cross-linking). Formulas 2 and 3 allow us to explain, at least qualitatively, the dependence of E' on the degree of cross-linking at any temperature and frequency studied. Analogous expressions can also be obtained for the sound velocity.

In the region of the rubbery state ($\omega\tau \ll 1$),

$$E \approx E_0 = 3\phi RT = 3\rho RT/M_c \qquad (4)$$

and

$$\phi = \rho/M_c \qquad (4a)$$

where R is the universal gas constant, T is the temperature, ρ is the density, and M_c is the molecular weight of a section of a polymer chain between two cross-links for cross-linked polymers or between two adjacent entanglements for linear amorphous polymers. In this case, on the basis of acoustic measurements one can estimate the network density. In the plateau region the dynamic modulus and the sound velocity will increase

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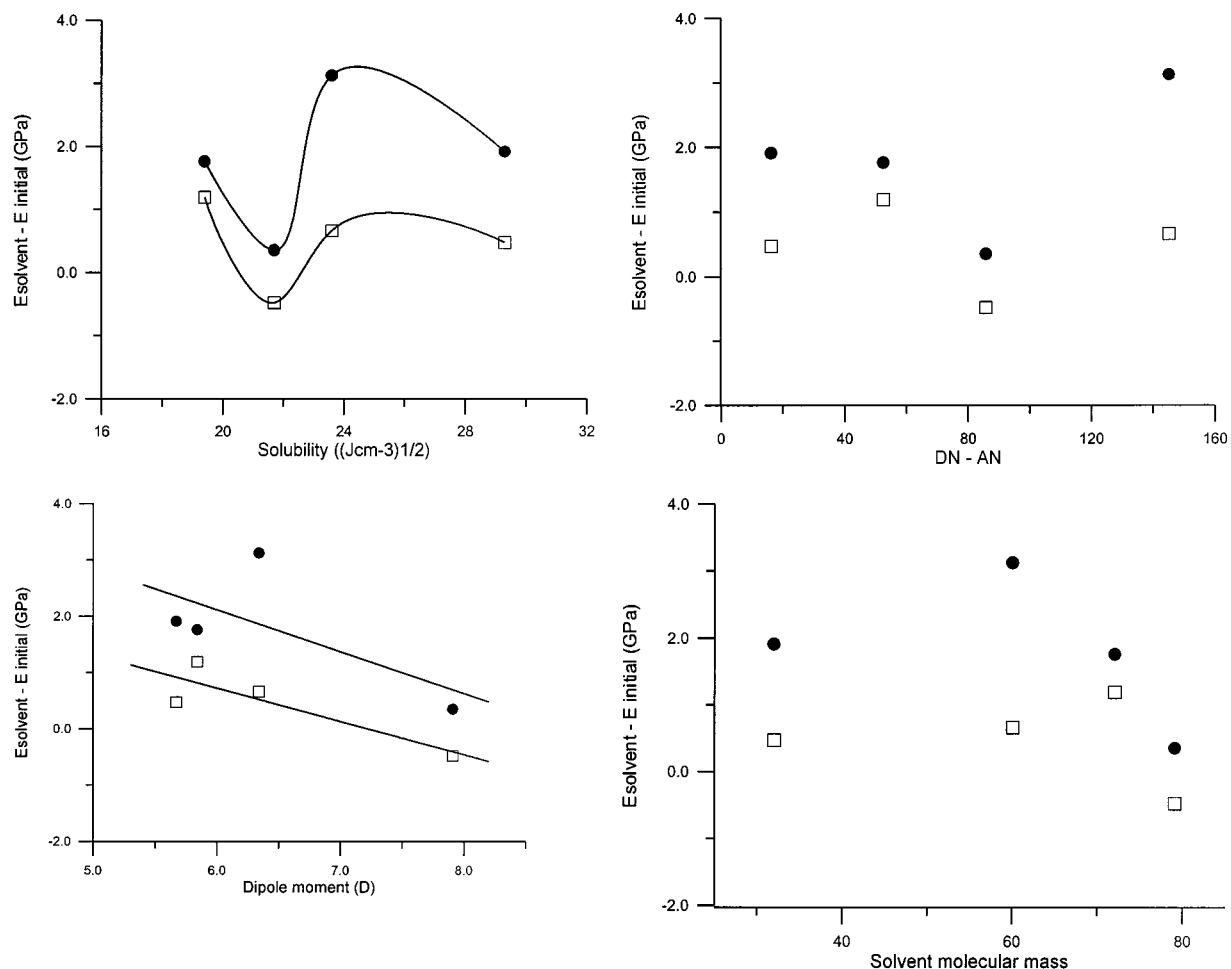
Figure 4. Correlation of the relative elastic dynamic modulus $E_{solvent} - E_{initial}$ of coal No. 17 with the following solvent parameters: solubility parameter δ (a), DN-AN (scaled) (b), molecular dipole moment μ (c), and molecular mass m_{sv} (d); (●) raw coal, (□) demineralized coal. The values of solvent parameters are put on the X axis in order: THF, PY, EtDa, MeOH for (a); MeOH, THF, PY, EtDa for (b); MeOH, THF, EtDa, PY for (c); MeOH, EtDa, THF, PY for (d). Solid lines for (c) denote the fitting of the experimental data with correlation coefficients r equal to 0.45 and 0.75 for the raw and the demineralized samples, respectively.
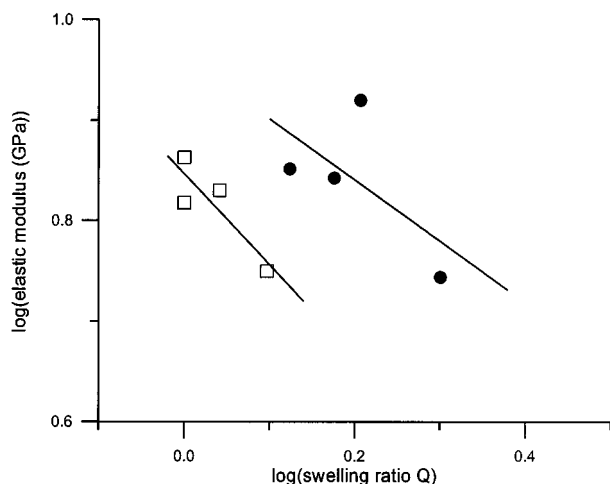
Figure 5. Relation between equilibrium swelling Q and elastic modulus for raw (●) and demineralized (□) coal samples treated by means of various solvents. The values of swelling ratio Q are put on the X axis in order: MeOH, THF, EtDa, PY for both samples. Solid lines denote the fitting of the experimental data with correlation coefficients r equal to 0.42 and 0.78 for the raw and the demineralized samples, respectively.

with increasing degree of cross-linking. Such a dependence of the modulus of elasticity on the cross-linkage

factor is encountered the most frequently and is considered to be normal.

In the glassy state, where $E' \approx 10^2$ to 10^3 MPa, it is evident that the quantity E_0 in eq 2 can be neglected, and the major contribution to E' will be introduced by the integral consisting of two components according to eq 3. Relationships between the above components give normal and anomalous dependencies of E' on ϕ. Thus, the normal dependence of E' on ϕ for which E' is proportional to ϕ can be observed not only in the region of the rubbery plateau. In this case, however, the dependence of E' on ϕ in not unique. Formulas 2 and 3 allow us to account for the "anomalous" dependence of the dynamic modulus on the degree of cross-linking, i.e., the modulus will decrease with increasing network density. The anomalous dependence of E' on ϕ has been detected in cured epoxide resins and in copolymers of unsaturated polyesters and styrene.[38]

The dynamic elastic moduli determined at the room temperature for the studied samples using the velocities of ultrasonic waves with the frequency of 2.5 MHz were contained within the range of 1−10 GPa. For polymers, it is the region of the glassy state. The physical properties of polymer in the glassy state differ very significantly from those in the rubbery state. In the glassy

state, with the molecular mobility remaining unchanged (the segmental motion is frozen) the sound velocity depends linearly on the temperature and the temperature coefficient of sound velocity is relatively small. In the glassy state the intermolecular interaction is considerably greater than in the rubbery state, where the dynamic elastic moduli of the same polymers range from 0.1 to 1 MPa.[38,57,58]

It was earlier reported that elastic dynamic moduli were

$$E'_{raw} = 5.19 \text{ GPa}$$

and

$$E'_{dem} = 6.10 \text{ GPa}$$

for the raw and the demineralized coal samples before solvent action, respectively. It means that $E'_{dem} > E'_{raw}$. If the dependence of E' on cross-linking is normal (the greater cross-linking, the higher modulus) for coal, the greater value of E' for the demineralized coal would suggest that it is more cross-linked than the raw one. Figures 1a–d show that for the demineralized coal, i.e., more cross-linked coal, there is a reduction of swelling. It is consistent with our previously reported results.[40]

Conclusions

Since the changes in the nature of the super-molecular structure of macromolecules and the composition of the components in compounded macromolecular materials lead to a change in the effectiveness of intermolecular interaction, it is clear that all these factors have a very appreciable effect on the magnitude and nature of the dynamic elastic modulus and sound velocity. Thus, the dynamic elastic modulus and sound velocity enable us to obtain information of two kinds: first, information concerning the most important mechanical (deformation) properties of the material and, second, information about the constitution, structure, and state of the material. It was found for solvent-treated coal that

1. Swollen samples do not return to the initial state after filtering and drying. Changes of density, ultrasonic velocity, and elastic modulus confirm that.

2. Ultrasonic velocities and elastic moduli after solvent treatment are generally greater in samples obtained from demineralized coal than those obtained from raw coal. It suggests that demineralized coal exhibits higher stiffness and conserves its value also after solvent treatment.

3. The dependence of elastic modulus on the swelling ratio exhibits the same nature as that found for polymers.

4. Demineralized coal seems to be more cross-linked than undemineralized coal.

It was stated in ref 55 that the solvent-swelling technique and the molecular weight determinations usually applied for coals are not extraordinarily sensitive probes capable of detecting small structural alternations. Thus, the ultrasounds may be useful for studying coals under various chemicals treatment, e.g., demineralization procedure, solvent swelling, etc.

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