Dielectric relaxation study of poly(styrene-*co*-4-vinylbenzoic acid)/poly(ethyl methacrylate-*co*-4-vinylpyridine) blends

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Summary

The α-relaxations, located in the neighborhood of glass-transition region (Tg), of a styrene-*co*-4-vinylbenzoic acid (PSVBA) random copolymer blended in several weight proportions with an ethyl methacrylate-*co*-4-vinylpyridine (PEMAVP) random copolymer have been investigated by dielectric spectroscopy in the temperature and frequency ranging from 25 to 180 °C and 0.1 to 100 kHz, respectively. The analysis of the obtained results shows that the dielectric spectra of the miscible blends, essentially dominated by the response of PEMAVP, are composition dependent becoming broader with its content. These observations are correlated with segmental dynamic heterogeneities and blend concentration fluctuations.

Introduction.

Polymer miscibility has become in the past years an important field of investigation because blending of available polymers is an inexpensive route to develop new materials with controllable properties. The required performance of such materials is closely related to the homogeneity of the blend. Unfortunately, most of the polymeric blends are immiscible. Among several innovative methods, the introduction of antagonist functional groups capable of developing intermolecular specific interactions was found (1-4) sufficient to induce miscibility of initially immiscible polymer systems. Hence immiscible polymers like polystyrene and polymethacrylate can be compatibilized by introducing within each polymer substituents that can develop hydrogen bonds (5, 6).

It is well established that miscible amorphous polymer mixtures are characterized by a single glass transition temperature (Tg) which generally appears in a region limited by the Tg's of the pure components (7,8). In most of the cases, the breadth of the glass transition region of the blend is larger than that of its constituents. This broadening is well revealed by techniques which are sensitive to short-range structure such as

NMR (9), dynamic spectroscopy, dielectric spectroscopy (10-13) and nonradiative energy transfer (14), and has been attributed by several authors (15-17) to residual morphological heterogeneities observed even in the macroscopically homogeneous systems. These structural heterogeneities have been related to local composition variation in the mixture, inherent to the blending which in turn modify the chain mobility. In this contribution, we report a dielectric spectroscopy study of the α-relaxation on the binary polymer blends, poly (styrene-*co*-4-vinylbenzoic acid) / poly (ethyl methacrylate-*co*-4-vinylpyridine).

Experimental

Poly (styrene-*co*-4-vinylbenzoic acid) (PSVBA) containing 7.4 mol % in acidic moieties and poly (ethyl methacrylate-*co*-4-vinylpyridine) (PEMAVP) containing 12.5 mol % of aromatic units, were synthesized by free radical solution copolymerization, at 60 °C in methyl ethyl ketone (Merck), using AIBN (0.1 weight %) as initiator. The copolymers were isolated and purified by precipitation in petroleum ether (Merck). Molecular weights were determined by GPC; $Mn_{PEMAVP} = 10^5$, $Mn_{PSVBA} = 1.35.10^5$. The mixtures were prepared by coprecipitation from 10 % (w/v) THF (Aldrich) solutions into a 10-fold volume excess of hexane (Aldrich). All materials were dried in a vacuum oven for 72 hrs at 70 °C.

Dielectric measurements were accomplished with a General radio model 1693 precision capacitance system, on samples of 0.3 gr. of dry material powder, compression molded at Tg + 50°C under 1.5 metric tons of pressure into disks of 20 mm diameter and 0.6 mm thickness. The polymer sample was placed between two parallel electrodes of 2-cm diameter, the distance of which can be varied by a Mitutoyo micrometer screw. The temperature was monitored through a thermocouple mounted next to the sample. Measurements were performed over a frequency range 0.1 to 100 kHz and a temperature domain 25 to 180°C in steps of approximately 3°C, 15 min. period was allowed for thermal equilibration.

Results and Discussion.

Dielectric spectroscopy of PEMAVP.

Figure 1 shows the temperature dependence of the dielectric tan δ (tan δ = ε'' / ε') of PEMAVP. The behavior of the copolymer PEMAVP in the neighborhood of the Tg is similar to that observed for PEMA (18). The obtained spectra exhibit a single relaxation peak at each frequency. It can be noticed that an increase in frequency shifts the maximum of the loss factor to higher temperature and expands the breadth of the curve.
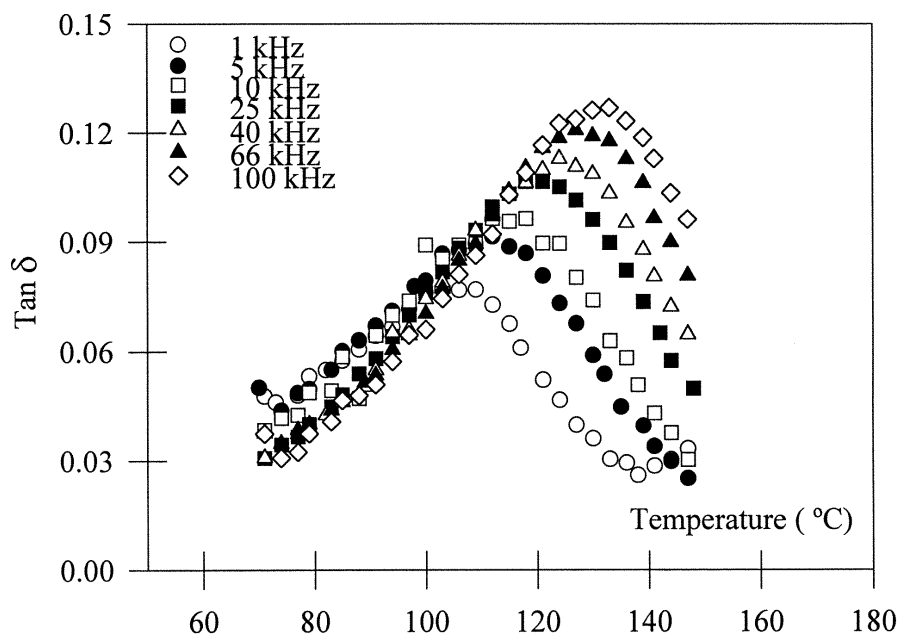
Figure 1: Temperature dependance of dielectric Tan δ of PEMAVP at
selected frequencies.

The isothermal tan δ curves obtained for PEMAVP are shown in Fig.2. It can be seen that the maximum of tan δ shifts to higher frequencies and its height increases with increasing temperature, reflecting a higher mobility of the relaxing dipoles. Table 1 resumes the characteristic dielectric parameters as determined from Havriliak - Negami (19) empirical equation:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega) = \varepsilon_u + [(\varepsilon_r - \varepsilon_u)\,/\,(1 + (i\omega\tau)^\alpha)^\gamma]$$

α and γ are dimensionless shape parameters, $(0 < (\alpha,\gamma) \leq 1)$; the Debye behavior is given by $\alpha = \gamma = 1$, ε_r and ε_u are the relaxed and unrelaxed values of the dielectric constant which represents the real part of the complex dielectric function $\varepsilon^*(\omega)$. The dielectric loss $\varepsilon''(\omega)$ represents the imaginary part of HN function, τ is the relaxation time and the quantity $\varepsilon_r - \varepsilon_u = \Delta\varepsilon$ represents the dielectric relaxation strength. From these results, it comes out that the dielectric strength $\Delta\varepsilon$ increases with temperature while the relaxation time decreases with increasing temperature. The values of the ß parameter of Kohlrausch - Williams - Watts (21) equation:

$\phi(t) = \phi(0)\,\exp - (t\,/\,\tau)^\beta$, $(0 < ß \leq 1)$ shows clearly that the shape of the dielectric dispersion remains constant with temperature. This result is confirmed by the normalized loss curve, Fig.3, which shows that the shape of the peak is unchanged.
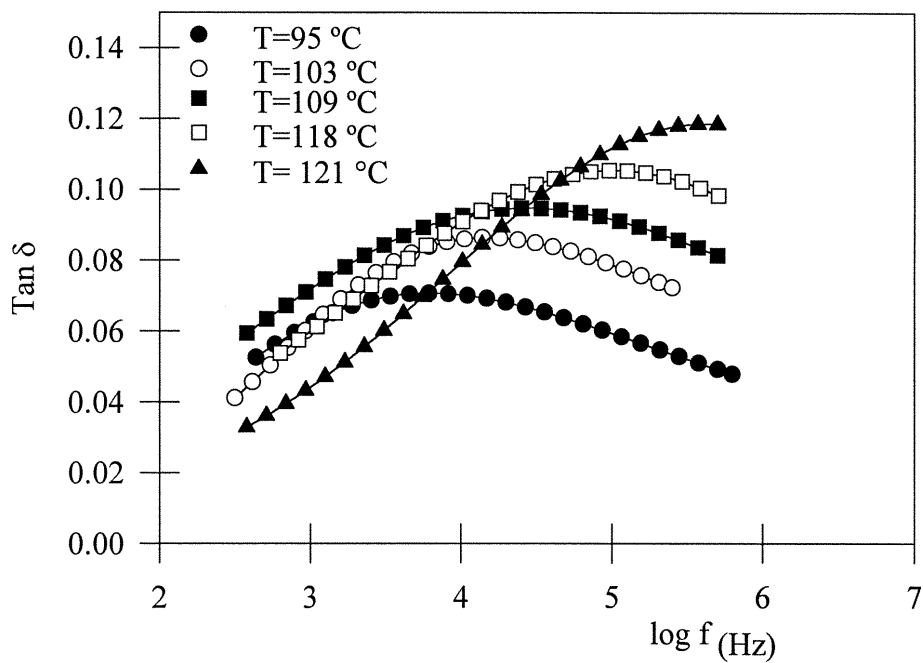
Figure 2: Isothermal dielectric tan δ of PEMAVP at different temperatures, fitted by Havriliak - Negami equation (lines).
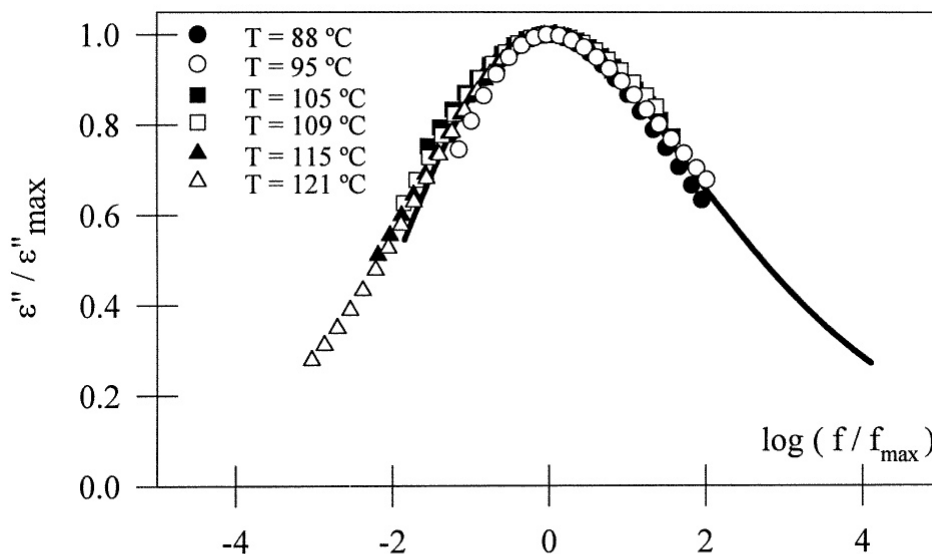

Figure 3 . Reduced dielectric loss ($\varepsilon''/\varepsilon''$max) mastercurve associated with the glass transition for PEMAVP along with the best fit curve (line) calculated by KWW equation ($\beta = 0.24$; $\tau = 6\ 10^{-4}$s).

Table 1. Dielectric characteristic parameters for PEMAVP / PSVBA systems.

PSVBA(wt%)	T (°C)	1-α_{HN}	γ_{HN}	$\Delta\varepsilon_{HN}$	$\tau_{KWW}(s)$	β_{KWW}[a]
0	88	0.59	0.53	1.05	1.3^e-4	0.23
	95	0.61	0.58	1.74	1.0^e-4	0.24
	103	0.59	0.59	1.80	4.1^e-5	0.24
	109	0.66	0.63	2.49	2.4^e-5	0.25
	115	0.65	0.65	2.60	5.8^e-6	0.27
	121	0.65	0.80	2.73	1.5^e-6	0.27
33	102	0.61	0.32	1.29	3.0^e-5	0.17
	110	0.67	0.46	1.64	2.0^e-5	0.19
	118	0.69	0.72	1.81	1.8^e-5	0.20
	130	0.78	1.00	2.86	2.5^e-6	0.22
50	98	0.48	0.26	0.51	5.8^e-4	0.28
	107	0.50	0.35	0.73	3.5^e-4	0.29
	113	0.60	0.51	0.84	3.3^e-4	0.30
	116	0.60	0.56	0.83	2.7^e-4	0.32
	119	0.35	0.78	0.84	2.0^e-4	0.35
	130	0.35	0.76	0.92	4.5^e-5	0.46
66	122	0.48	1.00	0.21	1.0^e-4	0.42
	130	0.40	1.00	0.41	1.5e-4	0.52
	141	0.28	1.00	0.42	4.4^e-5	0.60
	150	0.25	0.96	0.46	3.6^e-5	0.61
100	125	0.55	1.00	0.21	1.7^e-4	0.35
	130	0.64	1.00	0.27	1.1^e-4	0.27
	138	0.69	1.00	0.32	3.0^e-5	0.27

(a) The β_{KWW} values were determined from the best fits of the dielectric loss spectra.

Dielectric spectroscopy of PSVBA/PEMAVP blends.

Polymer-polymer miscibility can be easily ascertained by a simple comparison of the temperature dielectric loss curve of the pure components and polymer blends. Miscible
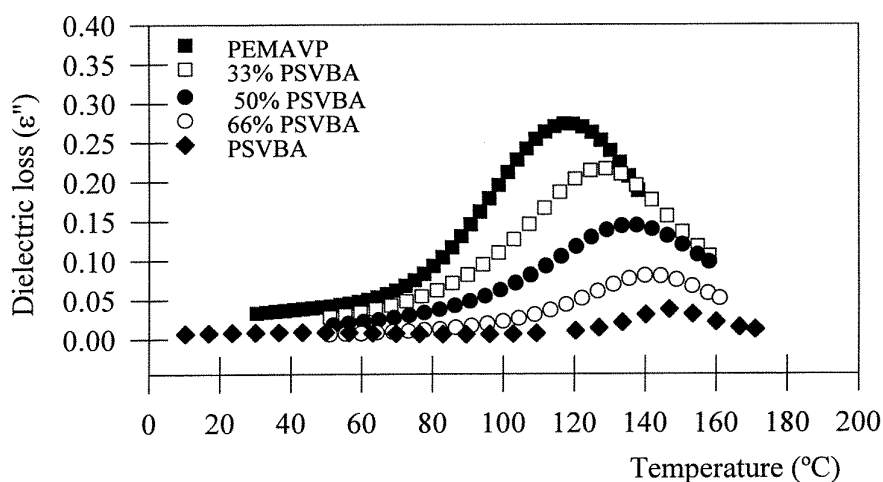

Figure 4: Temperature dependence of dielectric loss curves of PEMAVP/PSVBA mixtures at 10 kHz.

binary systems are characterized by single composition dependent relaxation process. The temperature dependence of tan δ at 10 kHz of PSVBA/PEMAVP mixtures at different compositions is displayed in Fig. 4.

It is apparent that the dielectric loss of PSVBA is strongly modified by blending with PEMAVP. In each case, a single well-defined maximum associated with the segmental α-relaxation is observed. Furthermore the location of the peak shifts to lower temperature while it's maximum as well as the area under the loss curve increases significantly with increasing PEMAVP weight fraction.

Figure 5 depicts the variation of the dielectric Tg's with the composition of PSVBA at selected frequencies of 1, 10 and 100 kHz. Positive deviations from weighted arithmetic mean linearity are observed. By analogy with the Kwei approach (20), these deviations are attributed to strong intermolecular interactions that can take place between acid residues of PSVBA and either the basic or ester groups of PEMAVP.
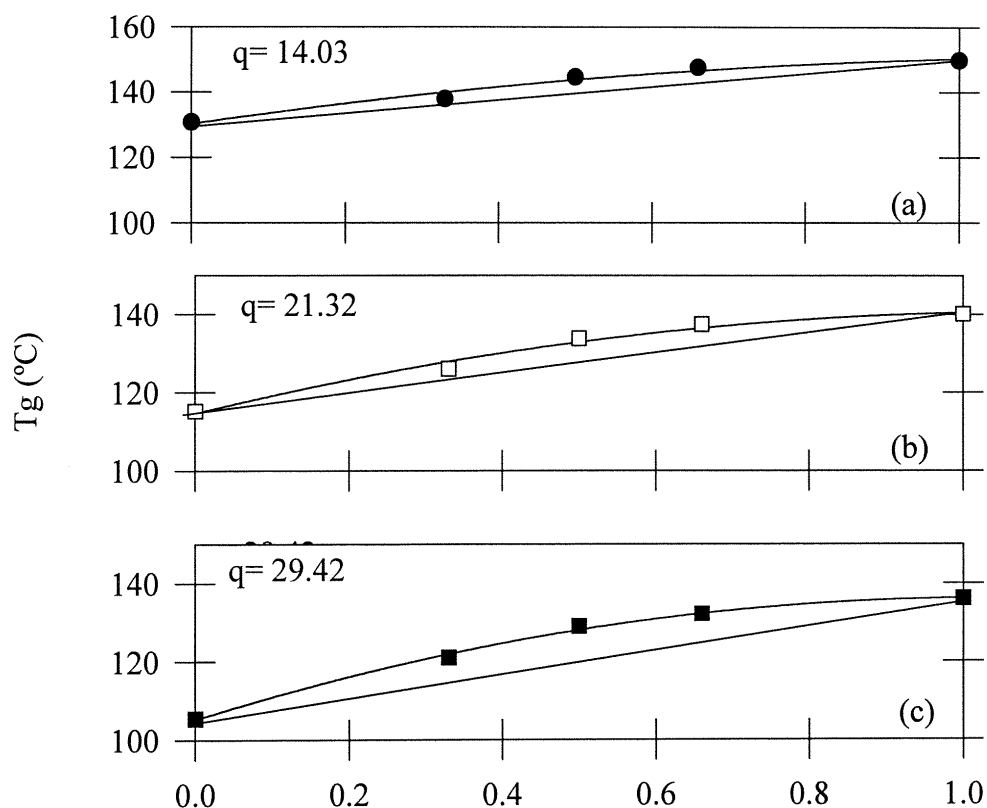

Figure 5. Dielectric Tg-composition curves at 100 kHz (a), 10 kHz (b), and 1 kHz (c) as fitted by the Kwei equation: $Tg_{blend} = [(w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2)] + q w_1 w_2$, where w_i, T_{g_i} are the weight fraction and glass transition temperature of the ith constituent and k and q adjustable parameters.
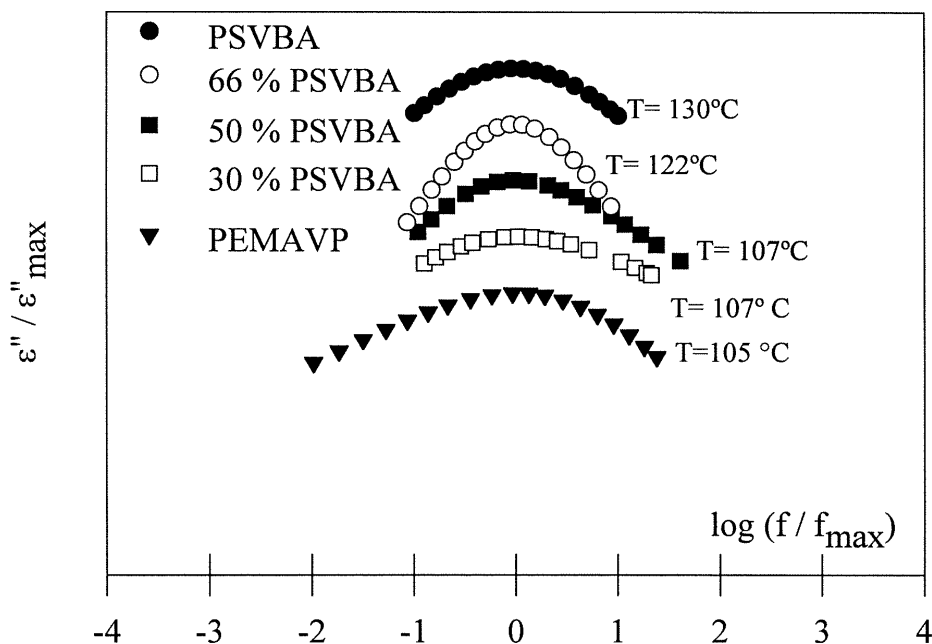
Figure 6: Normalized dielectric loss curves for PEMAVP/PSVBA mixtures. The curves have been shifted vertically to facilitate comparison of the shapes.

One should also notice the decrease of q-parameter values when the frequency increases. Hydrogen bonds are regarded as dynamic crosslinks and produce thereby intermolecular constraints on segmental motions, which can be broken out when highly solicited.

Figure 6 illustrates the normalized curves of tan δ for 33, 50 and 66 % weight of PSVBA in PEMAVP/PSVBA mixtures. These curves become increasingly broader with increasing PEMAVP content. This broadening is attributed to the fluctuation about the average value of the local composition, and to heterogeneity in segmental dynamics in the mixture. This heterogeneity is induced by the fact that even in a miscible blend, the chain segments are not equivalently perturbed by the surrounding segments. Such phenomenon is also magnified by the presence of hydrogen bonds which produce an intermolecular constraints on segmental motions as reflected through an asymmetry of the dielectric blends spectra.

Although several authors have reported (18,22) that in general β_{KWW} parameters of blends are intermediate between those of the pure constituents; the behavior of PEMAVP / PSVBA blends, Table1, do not follow such a trend. This might be due to the complexity introduced by the formation of strong hydrogen bonds in the mixtures.

Conclusion

The α-relaxation processes in PEMAVP/PSVBA blends have been investigated. It is found that the dielectric segmental mode of the studied blends becomes broader with increasing amount of PEMAVP content. This behavior is due to (i) intermolecular

correlations introduced by hydrogen bonds and (ii) heterogeneous domains, which occur in miscible blends.

References

1. Ueda H, Karasz FE (1992) Polymer J 24: 6664.
2. Li H, Prud'homme RE (1993) J Polym Sci Polym Phys Ed 31: 719.
3. Luo X, Goh SH, Lee SY (1997) Macromolecules 30: 4934.
4. Schneider HA (1998) Polym. Bull. 40: 321.
5. Coleman MM, Graf JF Painter PC (1991), Specific Interaction and the Miscibility of Polymer Blends, Technomic Publishing Co Lancaster.
6. Li D, Brisson J (1998) Polymer 39: 801.
7. Stoeting J, Karasz FE, MacKnight WJ (1970) Polym Eng Sci 10: 133.
8. Rostami S (1992), In Multicomponents Polymer Systems, Miles IS and Rostami S (eds) Longman Scientific and Technical New York. Chap. 3.
9. Chung GC, Korfield JA, Smith SD (1994) Macromolecules 27: 964.
10. Garwe FE, Schönhals A, Lockwenz H, Beiner M, Scröter K, Donth E (1996) Macromolecules 29: 247.
11. Dionisio MS, M-Ramos JJ (1994) Polymer 35: 1704.
12. Ngai KL Roland CM, O'Reilly SM, Sedita JS (1992) Macromolecules 25: 3906.
13. Lei D, Runt J, Safari A, Newnham RE (1987) Macromolecules 20: 1797.
14. Amrani F, Hung JM, Morawetz H (1980) Macromolecules 13: 649.
15. Spall S, Goodwin AA, Zipper MD, Simon GP (1996) J Polym Sci Polym Phys Ed 34: 2419.
16. Katana G, Fischer EW, Hack T, Abetz V, Kremer F (1995) Macromolecules 28: 2714.
17. Roland CM, Ngai KL (1992) Macromolecules 25: 363.
18. Dionisio MS, M-Ramos JJ, Fernandes AC, (1966) J Appl Polym Sci 60: 903.
19. Havriliak S, Negami S (1966) J Polym Sci Part C14 : 99.
20. Kwei T K (1984) J Polym Sci Polym Lett Ed 22 : 307.
21. (a) Kohlrausch R, (1847) Pogg Ann Phys 12: 393.
    (b) Williams G, Watts DC (1970) Trans Faraday Soc 66: 80.
22. Alegria A, Telleria I, Colmenero J (1994) J Non-Cryst Solids 172-174: 961.