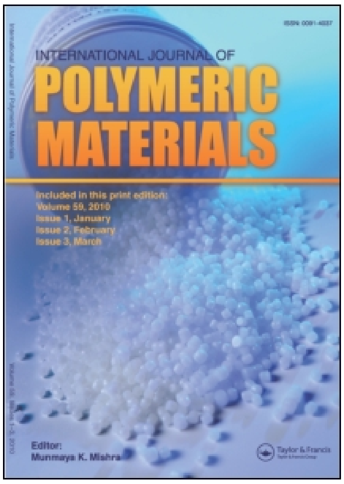

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Study of Dielectric Relaxation of Chlorinated Polyvinyl Chloride (CPVC)–Poly(Ethylene Succinate) (PES) Blend

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Thermally stimulated depolarization current (TSDC) technique was used to study the dielectric relaxations of chlorinated polyvinyl chloride (CPVC) blended with poly (ethylene succinate) (PES) over the temperature range 300–400 K, covering α and ρ regions. α-relaxation was suggested to be due to cooperative motion of both C—Cl and —COO groups of the blend, while ρ-relaxation is of space-charge nature. Thermal peak cleaning was used to deconvolute the global TSDC spectra, giving apparent activation energies (E_a) over the temperature range 360–400 K. Maximum value of E_a was found at T_g. Thermal peak cleaning data were fitted using Frohlich method.

Keywords: Chlorinated PVC; polyethylene succinate; blends; dielectric relaxations; activation energies

INTRODUCTION

It is well known that several polyesters are miscible with PVC [1–3]. Miscibility is however not found if the CH_2/COO ratio of the polyester is smaller than four [4, 5], since a high degree of chain mobility is required in order to have miscibility. It is also know that [5] a high degree of chain concentration is necessary for obtaining miscible polyester/chlorinated polymer blends. For example, polycaprolatone (PCL) is miscible with PVC [1], and with chlorinated polyethylenes (CPE) containing 48, 42 and 36 wt% Cl [6], but it is not miscible with polyethylene [7] and a CPE containing 25 wt% Cl [6]. Similarly, poly(valerolactone) (PVL) and pol (α-methyl-α-propyl-β-propolactone) (PMPPL) are miscible with PVC [2, 3] but they are not miscible with any of the CPE mentioned above [6]. It is then expected that several polyesters, including PCL, PVL and PMPPL, will be miscible with chlorinated polymers having a Cl concentration higher than that of PVC. Then chlorinated polyvinyl chloride (CPVC) is expected to be miscible with polyester more than PVC.

The first thermally stimulated depolarization (TSD) experiment was performed in 1964 in the study of point defects in alkali halides, and the theoretical basis of the method was developed in 1966 [7]. The TSD technique has been applied to the study of transitions in polymers since 1971 [8]. Generally, TSD is a technique which has contributed significantly to the current understanding of the charge-stored and charge-decay processes in electrets [9, 10]. The principal concern of the technique is to study the charge decay by heating the sample at a constant rate. In general it is highly desirable to observe if TSD and complementary techniques, such as DC step-response [11], AC response, differential thermal analysis (DTA), and other methods, are consistent with each other. The TSD method (sometimes referred to as thermally stimulated dielectric relaxation) is highly sensitive and gives reproducible results in terms of polymer transitions, as is indicated by several articles [9, 10, 12]. The low equivalent frequency of TSDC ($10^{-4}-10^{-2}$ Hz) leads to enhanced resolution of the different relaxation processes, allowing direct comparison with DSC in terms of viscoelastic relaxations such as the glass transition (or α-relaxation). Other more complicated transitions due to injected space-charges, charge trapping at crystal interfaces, and crystal growth have been detected by this technique [12]. One disadvantage of ac dielectric techniques is that the relatively high probe frequencies ($1-10^{12}$ Hz) cause the various transitions due to molecular motions to merge at higher frequencies [13]. Other complications occur when dealing with crystallizable polymers because the α-relaxation shifts to higher temperatures with increasing frequency. Because of this, when one attempts to study the relaxation in amorphous polymers using ac dielectric properties at frequencies above a few Hz, the sample crystallizes during the measurement. Due to its low equivalent frequency, TSDC is quite useful for the study of the α-relaxation in amorphous polymers.

The aim of the present work was to study the mechanisms of relaxations in CPVC-PES blend using the TSDC technique.

EXPERIMENTAL

The two polymers used in the present work are chlorinated polyvinyl chloride, obtained from B. F. Goodrich Chemical Division with $M_w = 119{,}000$, $T_g = 352\,\mathrm{K}$ and it contains 67.2 wt% chlorine and poly(ethyl succinate), obtained from Aldrich Chemical Co. with $M_w = 22{,}000$ and $T_g = 225\,\mathrm{K}$. Blend of the two polymers was prepared by slowly casting films from tetrahydrofuran (THF, Aldrich) solutions. The resulting films were dried until it reaches constant weight. Film thickness was 0.05 mm. Gold was evaporated on both sides of the film as a metal electrode.

The glass transition temperature of the blend was calculated using the Gordon-Taylor equation [14]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + w_2} \qquad (1)$$

where T_g is the glass-transition temperature of the blend, T_{g1} and T_{g2} are those of components 1 and 2, w_1 and w_2 the corresponding weight fractions and k an adjusting parameter. The parameter k is semi-quantitatively related to the strength of the interaction between the two polymers. The value of k for CPVC was 1.0 [15]. The calculated value of T_g for the blend is 340 K.

To analyze the relaxation peaks obtained in the TSDC spectra two different methods of the sample polarization were used.

The First Method

In order to obtain the global TSDC spectra of a given peak the sample was polarized using a static electric field $(E_p) = 20\,\mathrm{kV/cm}$ at a polarizing temperature $(T_p) = 390\,\mathrm{K}$, well above the current peak during a certain time of polarization $(t_p) = 30\,\mathrm{min}$ and then quenching the sample to freezing temperature (T_0) in the presence of the field. The freezing temperature is well below the temperature region where the peak appears, and the cooling to T_0 freezes the dipolar orientations. With the field turned off and the sample short-circuited, the depolarization current due to dipolar orientation was measured as the temperature was increased at a constant rate (1 K/min) from T_0 to a final temperature $T_f > T_p$. This method of polarization is termed TSDC global experiment.

The Second Method

To analyze the components of a complex relaxation process one may apply the polarizing field during the following thermal cycle: 5 min at T_p and sudden cooling to $T_p - 5\,\mathrm{K}$. T_p is in the temperature range at which the peak appears. The field is then removed, the sample remains isothermal for 2 min and is then quenched to a temperature T_0 well below the glass transition temperature. The depolarization current was then measured as the temperature was increased at a constant rate (1 K/min) from T_0 to a temperature T_f well above the peak maximum ($T_f \sim T_p + 30\,\mathrm{K}$). Different experiments with T_p varying in the peak's temperature range allow activation of fractions or segments of the global TSDC spectrum of the peak (narrow relaxation distribution). This technique of the sample polarization is called thermal cleaning or thermal windowing, and enables the global peak to be separated into the individual relaxation modes.

RESULTS AND DISCUSSION

Global TSDC spectra for CPVC–PES blend was shown in Figure 1 as a function of temperature. It is observed that the spectrum contains two peaks, one originates at the glass transition temperature, as calculated from Eq. (1), which called α-relaxation peak. The other peak lies at slightly higher temperature which called ρ-relaxation peak.

The α-relaxation observed at 340 K may be due the [16] the release of the frozen-in dipoles (C—Cl dipoles of CPVC and —COO dipoles of PES) by their cooperative motion with adjoining segments of the main chains, which at these temperatures start to rearrange their confirmations. The C—Cl groups form permanent dipoles which can rotate singly or together with the main chain segments which may

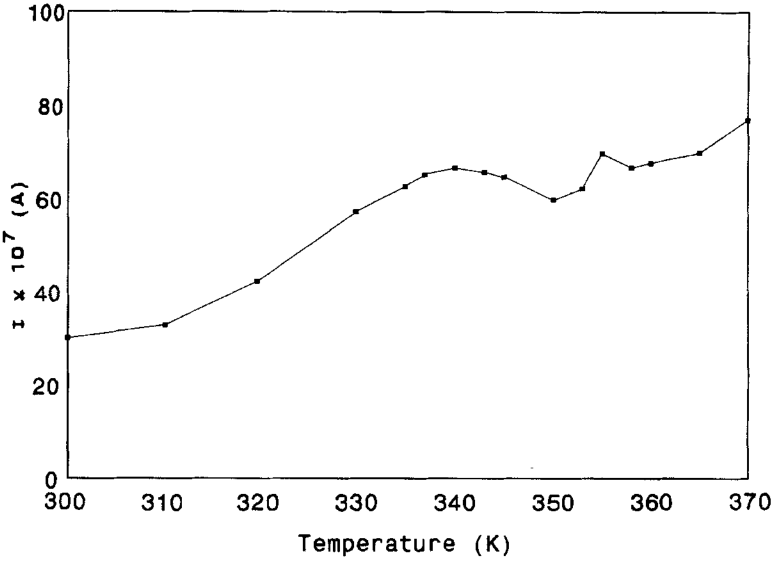

FIGURE 1 Global TSDC spectrum for CPVC-PES blend.

contain all together at least 10,000 monomer links, require more energy, hence it occurs well above room temperature when the sample is soften and become rubbery. The local motions of the polar —COO groups by rotation around their C—C links with the main chains, occur at slightly higher temperatures. This is the reason of the lowering of T_g of the blend than that of pure CPVC [17].

In order to calculate the relative number of dipoles taking part in the polarization phenomena one may use [18, 19]

$$N = \frac{3kQT_m}{Ap^2E_p} \tag{2}$$

where N is the number of dipoles per unit volume, Q the released charges, k Boltzmann constant, A the electrode area, E_p the polarizing field and p is the dipole moment. One may suggests that the product $A\,E_p p^2$ has a constant value and also $Q \sim I_m$ then

$$N = I_m T_m \tag{3}$$

The approximation (3) was similarly derived by Kovarskii *et al.* [20]. The obtained values of N is 2.2×10^{11}. The maximum height of α-relaxation peak as well as the maximum value of the relative number of dipoles, which are involved in the α-relaxation, are observed. This phenomenon was attributed to a decrease in the conductivity, which cause a decrease of the trapped charges and an increase of the fluent compensation charge which is released at T_g [21].

The ρ-relaxation occurs at temperature higher than T_g (355 K). Although the exact nature of the relaxation seems to vary depending on the polymer. For semi crystalline polymers, chain trapping of interfaces or Maxwell–Wagner polarization phenomena are likely [22]. For the amorphous materials it is also possible that the effects are related to conductive impurities, injected space charges and other electrode effects.

ρ-peak is clearly originates from the motion of space-charges that first took part in the conduction, and were accumulated in the polymer close to the electrodes during the formation. The ρ-peak, therefore, depend on the nature of the electrode and on the presence of impurities such as absorbed water [21]. It is now also clear why the ρ-peak always appear above the dipolar α-peak, the latter arise from local displacements of charges, whereas the former arise from the gross motion of charges over macroscopic distances.

It is observed also, Figure 1, that beyond the ρ-peak the current rises again. This rising may be due to the spurious current found in all bilaterally metallized polymers whether charged or uncharged [10]. It is found that [22] at temperatures well above T_g many uncharged metallized polymers generated a parasitic current. This current is not caused by thermoelectric effects. One can attribute this to a weak electrochemical potential which arises in spite of the presence of identical electrodes. This explanation is supported by the fact that the temperature dependence of this current runs parallel to that of the conduction current [10].

To accurately determine whether a transition is of dipolar nature or not, the peak intensity (I_m) was plotted *versus* the polarizing field, Figure 2. A linear dependence was obtained for the α-relaxation. Even though the intensity of the ρ-relaxation peak is strongly dependent on E_p, the data deviate from linearity, which indicates that it is not due to a dipolar relaxation and is probably due to trapped charges at interfaces.

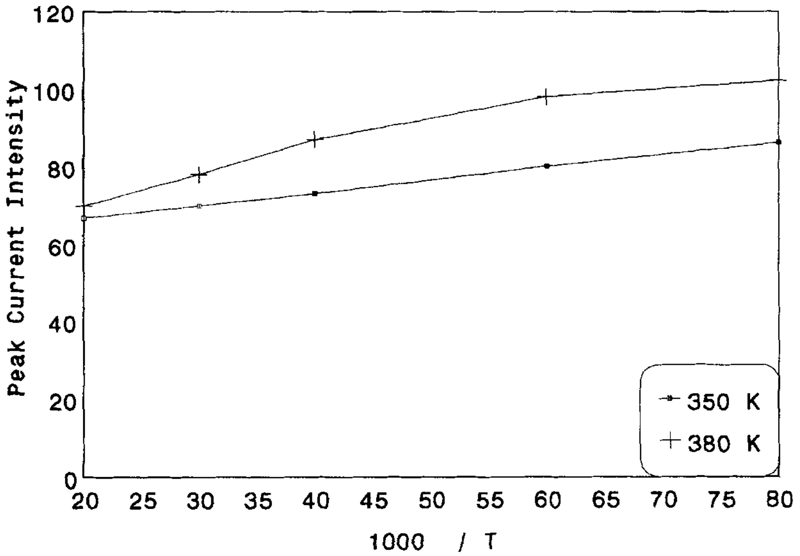

FIGURE 2 Variation of the peak current intensity with the polarizing field.

On the other hand, the linear dependence of I_m on E_p, Figure 2, is not always definitive test for the relaxation nature. This is because Maxwell-Wagner charging at buried interfaces is sometimes 100% efficient and can look like a dipolar process [10]. TSDC spectra taken at three different polarization fields are given in Figure 3 for CPVC-PES blend. A strong dependence on E_p is seen at all temperatures. To determine the exact dependence with E_p, the same data are plotted as current divided by E_p as shown in Figure 4 which exhibits that α and ρ peak intensities are well normalized by this procedure. Minor deviation was observed for $E_p = 10\,\text{kV/cm}$ due to ohmic conductivity which starts at temperatures above 360 K. Ohmic conductivity is spontaneous current flow: it is independent of E_p and can be easily subtracted.

By fractional integration of thermal peak cleaning (tpc) spectrum one can obtain Bucci plots using [10]

$$\ln \tau(T) = \ln\left(\int_{T_0}^{T} I(T)dT\right) - \ln I(T) \qquad (4)$$

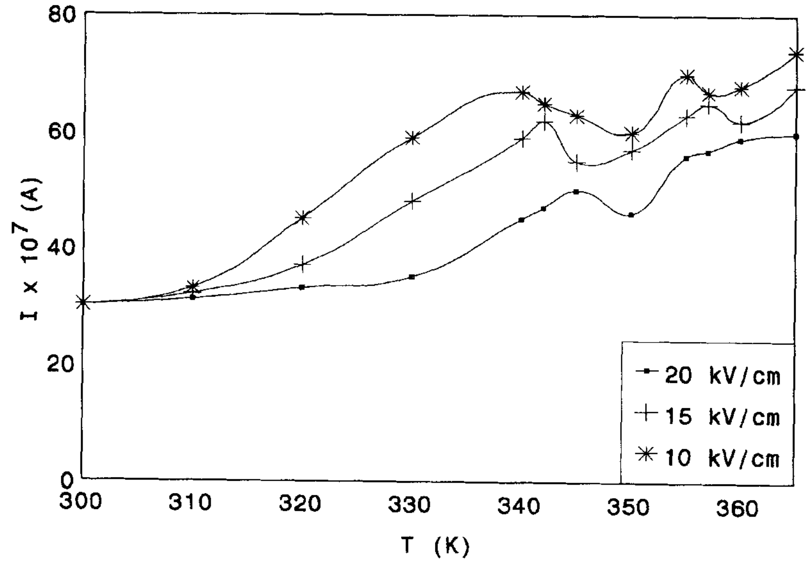

FIGURE 3 Dependence of the current on absolute temperature at different polarizing fields (20, 15, and 10 kV/cm).

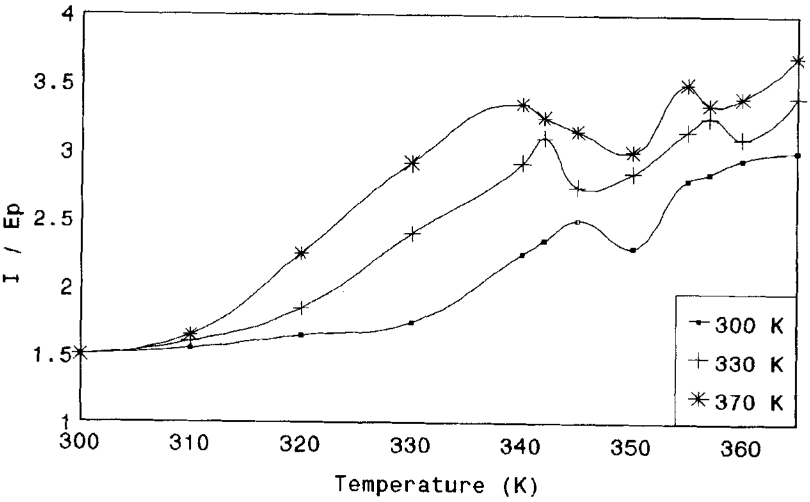

FIGURE 4 Variation of I/E_p with temperature for CPVC–PES blend.

Bucci plots are shown in Figure 5, with the slopes proportional to the activation energy (E_a). Unlike other techniques, such as the ac dielectric techniques, the relaxation dynamics are determined at any temperatures by the tpc method giving a characterization of E_a over the complete temperature range. The apparent activation energies are plotted in Figure 6 showing a maximum at $T_g = 390\,\mathrm{K}$.

TPC spectrum can be analyzed by fitting directly using the Frohlich method [23, 24]. This analysis of tpc spectrum taken in the vicinity of T_g for the blend is shown in Figure 7. The single E_a Frohlich fit (using the theory developed by Frohlich [23, 24]).

$$I(T) = P_0/\tau_o \exp\left(- E_a/RT - S/\tau_o \int_{T_0}^{T} \exp(-E_a/RT')\right) dT' \quad (5)$$

where P_0 is a constant related to the initial polarization, T_0 is the initial temperature of the polarization scan and R is the universal gas constant. To facilitate Frohlich fitting for the obtained spectrum, an

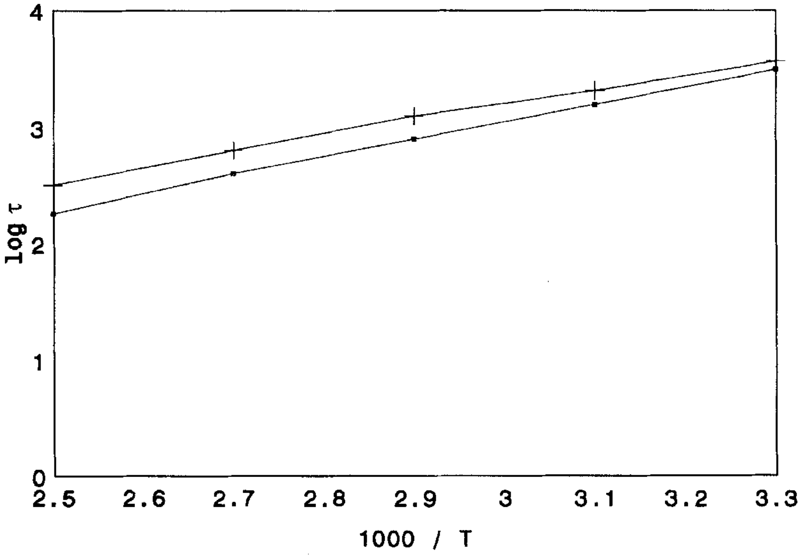

FIGURE 5 Bucci plot of the calculated relaxation time τ *vs* $1/T$ for a thermally cleaned TSDC spectrum.

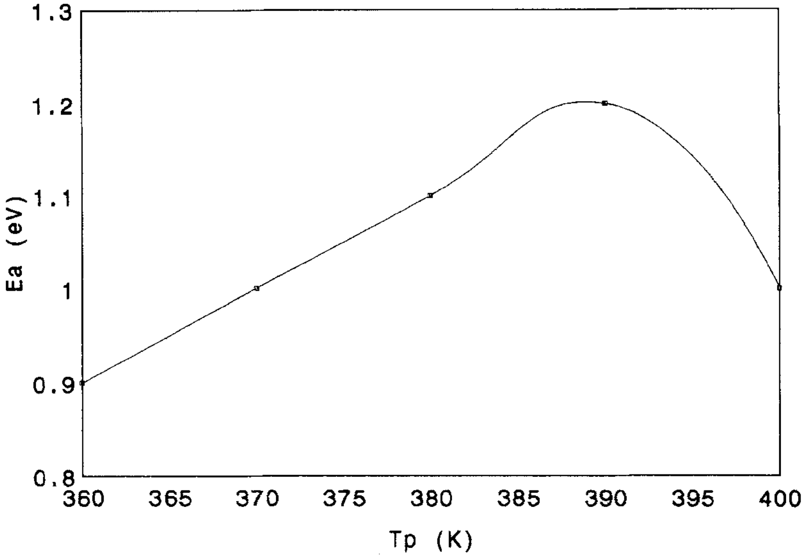

FIGURE 6 Variation of activation energy with the polarizing temperature for CPVC–PES blend.

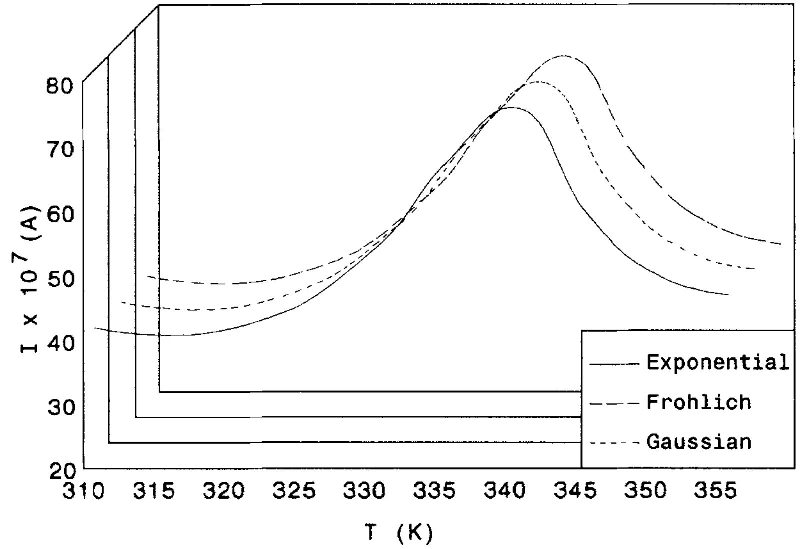

FIGURE 7 Frholich fit of TSDC taken in the vicinity of T_g for CPVC–PES blend.

appropriate form of the integral on the right hand side of Eq. (5) is used [25]. Using a single E_a value in Eq. (5) generates tpc spectrum which is quite asymmetric as a function of temperature while the experimental data are quite symmetric. This can be caused by assuming that there is a slight breadth to the distribution of activation energies [24]. It is also possible to generate symmetric tpc spectra by inputting a few narrowly spaced but discrete values of E_a:

$$I(T) = \sum_{i=1}^{n} a_i I(T, E_{a,i}) \tag{6}$$

when n values is 2 or 3, a_i are normalized weighting factors, $E_{a,i}$ is the i-th activation energy and $I(T, E_{a,i})$ is calculated using Eq. (5). The main value of E_a obtained by this fitting was shown to be the same as that calculated by using the Bucci method.

The obtained fitting of E_a by Frohlich method gives a low value of E_a. A Gaussian fit is also shown in Figure 7, illustrating the asymmetry on the low temperature side of the peak which indicates a low E_a process. A fit was performed using Eq. (6) with three values of $E_{a,i}$ and three values of a_i to account for the asymmetric nature of the spectrum. As expected, the fitting values of the normalized amplitudes indicate an asymmetric distribution which is given in Table I. The values of $E_{a,i}$ which corresponds to the peak intensity region, are still close together with a deviation less than ±1%. Because numerical analysis is performed, the Bucci analysis by fractional integration is more sensitive to asymmetric nature of the spectrum in terms of extracting the low E_a process. The Frohlich method weight the data around the peak quite heavily and is rather intensive to the low temperature tail.

TABLE I Frohlich analysis of thermally cleaned spectra

T_p	$E_{a,1}(eV)$	$a_1\%$	$E_{a,2}(eV)$	$a_2\%$	$E_{a,3}(eV)$	$a_3\%$	$E_a(eV)$ *Bucci*
360	9.25	20	9.35	35	9.6	45	0.91
370	9.6	20	9.71	35	9.82	45	0.93
380	1.02	30	1.09	40	1.13	51	1.02
390	1.14	30	1.21	40	1.28	51	1.16
400	1.23	37	1.36	45	1.4	59	1.23

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