Želimir Jelčić, Franjo Ranogajec*
PLIVA Croatia Ltd., TAPI Research and Development, Zagreb
*Ruđer Bošković Institute, Zagreb

Relaxation properties and glass transition by radiation crosslinking of unsaturated polyester resins

UDK 678.674
Authors review / Autorski pregled
Received / Primljeno: 20. 7. 2009.
Accepted / Prihvaćeno: 22. 3. 2011.

Abstract

Variations in the co-monomer, styrene content in the unsaturated polyester (UP) resin affect the thermal stability and the mechanical properties. These are governed by the phase behaviour of the mixture. Dynamic relaxation measurements by dielectric related methods show an increase in the phase separation of cured resin with an increase of styrene concentration. Dielectric permittivity was measured by stepwise changing of frequency during ^{60}Co γ-radiation curing at a constant temperature or by the simultaneous change of frequency and temperature after irradiation. Variations in the appearance of the glass relaxation due to varying degrees of immobilization of long range segmental motion in the uncrosslinked fraction by the introduction of the crosslinked phase by γ-radiation is made obvious by dielectric relaxation measurements of UP resins in the range of the gel fraction from zero up to 100%. A continuous shift of the glass transition of the resin and a change of the dielectric relaxation time distribution was observed as radiation crosslinking reaction proceeded. The shape of the dielectric spectrum bands indicated a heterogeneous nature of the transition which increased with the increasing degree of curing. In-source radiation curing of UP resins was studied by combining dielectric, thermal and charging current analyses. The *transition reaction times* corresponding to the maximum of the derivative (dε'/dt) curves, where ε' is the dielectric constant, regarded as the transition times at the corresponding frequency, are shorter for higher frequencies than for the lower ones. It is seen that the average relaxation time is shifted continuously by the reaction, while the temperature is constant and the frequency is changed as a parameter. Meanwhile the distribution of relaxation times is in-homogeneously broadened and the oscillator strength decreases. The α- and β-relaxations of UP resins shift to higher temperatures as the radiation dose (and crosslink density) increases. The relaxations, however, do not appear to be equally affected by the curing, β-relaxation being almost completely superposed by α-relaxation. The simulation of the dielectric spectra of the partially radiation crosslinked UP resins by the Geny-Monnerie model can be used for following the phase separation. The fragility index of the UP resins glass transition slightly changes as the styrene concentration increases indicating more fragility. The nuclear magnetic resonance (NMR) spin-lattice T_1 and spin-spin T_2 relaxation times can be described also by the terms from the Geny-Monnerie model that describes the polymer chain isotropic motion (4-bonds motion, θ) and by the shift from the ideal lattice (3-bonds motion in the ideal lattice, ρ). The thermally stimulated depolarisation currents of radiation and peroxy cured UP resins have been measured in the low temperature range. The study of the decrease of the current intensity as a function of the absorbed dose reveals important differences between the peaks of the spectrum; the low temperature peaks can be attributed to dipolar volume polarisation, and the high temperature peaks to an ionic space charge polarisation. The shift of the peaks may be indicative of plasticization of the polyester by styrene, and of restriction upon motions of the chain imposed by the crosslinks. The α_l-peak is a manifestation of the liquid-liquid (T_{ll}) transition, and here it corresponds to the thermally activated disintegration of phase separated structures, which were well documented in the inherently heterogeneous UP resins. From the T_{ll}/T_g ratio, it may be concluded that the liquid-liquid (T_{ll}) transition corresponds to the characteristic crossover temperature T_c derived in the random walk model. The charging current data above T_{ll} and below T_g are very well described by a simple Arrhenius law with the *same (or similar)* activation energy E_{low} suggesting that dynamic scaling continues to apply to the glass, with length ξ independent of temperature. The T_{ll}/T_g ratio, from TSD data, is found to be in the range of 1.06 to 1.21. It could be noticed that as the degree of cure increases the temperature at which maximum occurs shifts to higher values. The extent of cure can be detected as a systematic change in TSD current, as the height of the TSD peaks decrease by curing. TSD current measurements reveal the presence of high internal electrical fields due to space charges accumulated at the phase boundaries of glass fibres in filled UP resins. The compliance curves from thermomechanical measurements on partially radiation cured UP resins show transitions at increasing temperature by increasing the radiation dose, *i.e.* degree of crosslinking.

KEY WORDS:
phase separation
relaxation
styrene
unsaturated polyester(UP) resin

KLJUČNE RIJEČI:
fazno razdvajanje
nezasićena poliesterska (UP) smola
relaksacija
stiren

Relaksacijska svojstva i staklasti prijelaz ionizacijskim zračenjem umreženih nezasićenih poliesterskih smola

Sažetak

Toplinska postojanost i mehanička svojstva određeni su faznim ponašanjem nezasićenih poliesterskih (UP) smola, što je određeno vrstom i sadržajem komonomera. Dinamička relaksacijska mjerenja dielektričnim metodama upućuju na porast faznog razdvajanja umreženih smola s porastom sadržaja stirena. Dielektrična permitivnost mjerena je promjenom frekvencije u koracima za vrijeme ^{60}Co γ-ozračivanja pri stalnoj temperaturi ili istodobno s promjenom frekvencije i temperature nakon ozračivanja. Dielektrična relaksacijska mjerenja umreženih UP smola u rasponu γ-zračenjem umreženoga, geliranog udjela od 0 do 100 % omogućuju uvid u promjene staklaste relaksacije u neumreženoj fazi zbog porasta stupnja imobilizacije segmentnih gibanja dugog dosega. Porast staklišta i promjene razdiobe dielektričnih relaksacijskih vremena opaženi su pri ozračivanjem iniciranoj reakciji umreživanja smole. Oblik dielektričnog spektra indicira heterogenu narav prijelaza, koja raste s porastom stupnja umreženja. Umreživanje zračenjem UP smola praćeno je dielektričnim, toplinskim i strujnim metodama analize u samom polju zračenja. *Prijelazna reakcijska vremena*, koja odgovaraju maksimumu krivulja derivacije (dε'/dt) i time prijelaznim vremenima pri odgovarajućim vremenima, kraća su pri višima nego pri nižim frekvencijama. Srednja relaksacijska vremena pomiču se sa stupnjem reakcije, pri postojanoj temperaturi, a frekvencija se mijenja kao parametar. Razdioba relaksacijskih vremena nejednoliko se proširuje i oscilatorna snaga se smanjuje. Relaksacijski α- i β-procesi UP smola pomiču se prema višim temperaturama s porastom doze zračenja i gustoće umreženja. Relaksacijski procesi ipak nisu u jednakoj mjeri određeni umreživanjem, pri čemu je β-relaksacija u potpunosti prekrivena α-relaksacijskim procesom. Simulacija dielektričnih spektara djelomično zračenjem umreženih UP smola s pomoću Geny-Monnerieova modela omogućuje praćenje faznog razdvajanja. Indeks lomnosti staklastog prijelaza UP smola raste s porastom sadržaja stirena. NMR (nuklearna magnetna rezonancija) spin-rešetka i spin-spin T_2 relaksacijska su vremena opisana također članovima Geny-Monnerieova modela kojima se opisuju izotropna gibanja polimernog lanca (gibanja 4-veze, θ) i pomaci od idealne rešetke (gibanje 3-veze u idealnoj rešetci, ρ). Toplinski potaknute depolarizacijske (TSD) struje zračenjem i peroksidno iniciranih umreženih UP smola mjerene su u niskome temperaturnom području. Pad strujnog intenziteta kao funkcije apsorbirane doze zračenja upućuje na znatne razlike između maksimuma (TSD) spektra; niskotemperaturni maksimumi mogu se pripisati dipolnoj obujamnoj polarizaciji, a visokotemperaturni maksimumi ionskoj polarizaciji obujamnog naboja. Pomak maksimuma može indicirati omekšavanje poliestera stirenom te ograničavanje gibanja polimernih lanaca zbog umreženih točaka. Maksimum α_1 odražava prijelaz kapljevina-kapljevina(T_{ll}) te odgovara toplinski aktiviranom raspadu fazno razdvojenih struktura koje su dobro dokumentirane u inherentno heterogenim UP smolama. Prijelaz kapljevina-kapljevina(T_{ll}), prema omjeru T_{ll}/T_g, odgovara karakterističnoj temperaturi prijelaza T_c izvedenoj u okviru modela slučajnih koraka. Struja nabijanja iznad T_{ll} i ispod T_g može se vrlo dobro opisati jednostavnom Arrheniusovom jednadžbom s jednakom (ili sličnom) aktivacijskom energijom E_{low}, što upućuje na proširenje dinamičkog skaliranja na staklasto stanje, s duljinom ξ koja ne ovisi o temperaturi. Omjer T_{ll}/T_g, prema TSD podatcima, određen je u području od 1,06 do 1,21. Umreživanje pomiče temperature maksimuma prema višim vrijednostima. Doseg umreživanja može se pratiti mjerenjima TSD struje budući da visina TSD maksimuma opada s umreženjem. Mjerenje TSD struje staklenim vlakanima punjenih UP smola upućuje na visoka unutarnja električna polja zbog obujamnog naboja nakupljenog na faznim granicama. Krivulje popustljivosti, pri termomehaničkim mjerenjima, djelomično umreženih UP smola pokazuju prijelaze pri rastućim temperaturama s porastom apsorbirane doze zračenja, tj. stupnja umreženja.

Introduction

The crosslinking reaction of a UP resin system takes place with chemo-rheological changes that determine the kinetic behaviour of the system.[1-2] Initially, the reaction kinetic is controlled by the chemical reactivity of the functional groups, but later becomes controlled by diffusion and the degree of conversion levels off and tends to a limiting value. In these conditions, it is observed that the temperature of glass transition equals the temperature of the curing reaction, $T_g = T_{curing}$, and the properties of the system are those of the glassy state. The electrical techniques, such as dielectric relaxation spectroscopy, have been extensively used to study the molecular dynamics of the system during the crosslinking reaction using a wide interval of frequencies. The results of the author's investigations[3-5] on UP resins curing structure-property relationships are reviewed. The following topics are considered in particular: radiation curing, in-source following of the curing reaction, relaxation and dielectric properties. The molecular dynamics has been related to thermodynamic aspects of the reactive system by analyzing the variation of the relaxation time during the reaction progress. The objective has been to determine the relation between the dielectric response and the chemo-rheological events, such as gelation and vitrification, which occur during the network growth.

Unsaturated polyester resins

Unsaturated polyester resins (UPR) are defined as mixtures of hetero-chain pre-polymers containing repeating ester groups and aliphatic unsaturations sites in the backbone, with a vinyl monomer. Fundamental molecular parameters of UP pre-polymers are hydroxyl and carboxyl groups, Ordelt saturation extent(reaction of hydroxyl groups with double bonds), mass polydispersity index, short- and long-chain branch distribution, and composition of starting reactant.[6-7] Extensive research has been published on the curing of UP resins.[8-9] The chemical processes involved in the curing steps were investigated by several authors, using infrared spectroscopy(IR)[10] differential scanning calorimetry (DSC)[11] or NMR.[12] The kinetics of polyesterification reactions involving di-carboxylic acids and diols has been reviewed comprehensively by Fradet and Marechal.[13] Kinetic models have been reported for the cure of UP/styrene and mechanisms have been proposed for the microstructure formation.[14] During the cure of thermosetting resins, the glass transition temperature increases. The rate of reaction will slow down and eventually stop as the reactive groups are frozen in the matrix when the glass transition temperature approaches the isothermal cure temperature.[15] The structural change during UP resin crosslinking reaction is followed by early formation of spherical, sub-micrometer micro-gels.[16] The interaction of chemical kinetics with certain physical processes that take place during curing, such as the phenomena of gelation and vitrification and the possibility of forming different morphological or chemical structures increases the complexity of the curing study. The curing model is based on three steps: inhibition, initiation and propagation.[17] The alternative route of curing UP resin is radiation processing that has many advantages over the conventional processing methods: the initiation is homogeneous throughout the system and the rate of crosslinking is easily controlled by varying the dose rate. The effect of γ-ionizing radiation on an unsaturated polyester resin is described very early.[18-20] The copolymerization of unsaturated polyester with styrene results in the formation of a heterogeneous structure through strong intra-molecular reactions and phase separation.[21] Melot et al.[22] have combined dynamic mechanical spectroscopy(DMA) with high-resolution solid-state ^{13}C-NMR to characterize the molecular motions responsible for γ and β secondary relaxations in unsaturated polyester networks. The γ transition, which manifests itself at about -100 °C at 1 Hz, may be related to some motion of the phenyl groups in the styrene sequences. The β transition originates mainly from local modes of polyester units remote from the styrene crosslinks. Cook and Delatycky confirmed this assumption.[23] The variation of the β peak area as function of the crosslink content can be explained assuming the variation of the density of these mobile units. In that sense, the β transition may be assigned to mobility of network defects. The network structure also contributes to the phase segregation because its swelling capacity decreases with the increase of the crosslink density resulting in an exclusion of monomers, oligomers and polymers from it.[24] The major dielectric relaxation of UP resin was ascribed to the glass transition of the whole network, while the minor relaxation, at a lower temperature was ascribed to the polyester segments between crosslinks.[23 25] The complexity of the transition region was due to multiple relaxations, arising from the inhomogeneous network structure of crosslinked polyesters.

Uncrosslinked UP/ styrene mixtures

Dielectric measurements can be very informative giving the material dielectric constant, ε', and the dissipation factor, *tan* δ, over a wide frequency range from 100 up to 100 kHz. Dielectric permittivity real part ε'-*T* curves of uncrosslinked UP resins up to 30 wt.% of styrene are not highly structured. In the UP resins containing more than 30wt.% of styrene, the dielectric spectrum appears to be composed of two overlapping relaxation processes. The shoulder occurring in the region 220-230 K and signifying the presence of the β-relaxation decreases in the magnitude and is more separated from the α-relaxation as the styrene concentration increases until at the highest styrene concentration it can no longer be clearly distinguished. The overlap between the α- and β-relaxation precludes a detailed analysis of the variation in the position of the α-relaxation as a function of styrene concentration. The α-relaxation does not shift substantially by dilution, in contrast to the behaviour of the β-relaxation. At the highest styrene content (50 wt. %) low and high temperature dielectric transitions are separated.

The dielectric response of unsaturated polyester resin during cure

The determination of the degree of cure of an UPR has been studied previously by thermal, mechanical[25] spectroscopic[26] dielectric[27] and resistivity methods.[28] The dielectric response of thermoset during cure should be simultaneously described as a function of curing time and frequency domains where the dielectric constant relaxes.[29] The dielectric permittivity was measured by stepwise changing of frequency during ^{60}Co γ-radiation at the constant temperatures or by the simultaneous changes of frequency and temperature after irradiation. A continuous shift of the glass transition of the resin and a change of the dielectric relaxation time distribution was observed as radiation crosslinking reaction proceeded. The shape of the dielectric spectrum bands indicated a heterogeneous nature of the transition which increased with the increasing degree of curing.[30] Dielectric permittivity and differential temperature (ΔT) were simultaneously recorded during irradiation at the constant temperatures (*in-source* curing experiment). The permittivity ε' *vs.* reaction time curves show inflexions, which are defined as *transitions* that are shifted to shorter times by increasing frequency. The broadening of the transition and the decrease of the ε_o-value by curing is very appreciable. The lowest ε'(*t*) transition roughly corresponds to the exothermic DTA-peak, which is found to be highly asymmetric. With longer reaction time, at the side of this peak, further, very significant decrease in the dielectric permittivity is observed.

In-source radiation curing of UPR

In-source radiation curing of UP resins was studied by combining dielectric, thermal and charging current analyses.[31] The dielectric permittivity(by stepwise changing of frequency)[32] and charging current were measured throughout crosslinking (curing) of UPR that was initiated either thermally by adding benzoyl peroxide initiator to the system or by ^{60}Co-γ radiation at a preset dose rate in the specially designed cylindrical aluminium cell with coaxial electrodes connected by shielded polyethylene covered electrical cables to the dielectric relaxation spectrometer (DEA) and depolarisation analyzer (DPA). The cell was placed in a water thermostat close to the source at the place with the preset dose rate. The differential thermal analysis (DTA) could be performed simultaneously with the dielectric measurements during peroxy initiated and gamma radiation initiated curing (Figure 1). The poling charging current was measured during 60 seconds the poling voltage was applied. The charging voltage was kept constant (30 V) in all curing isothermal measurements.

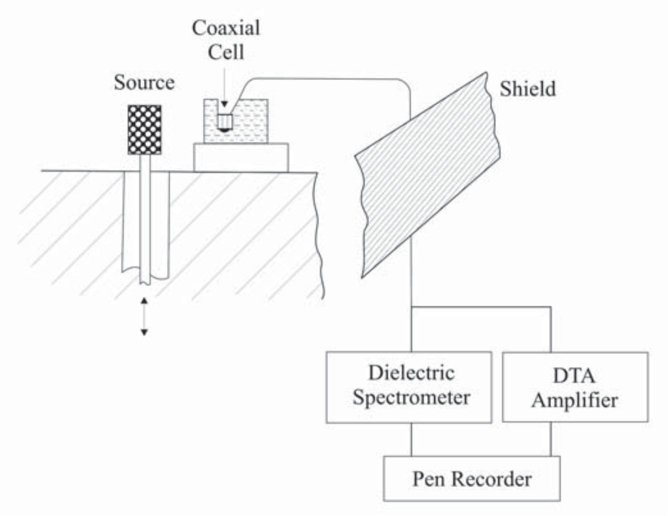

FIGURE 1 – Experimental arrangement for simultaneous in-source dielectric and thermal monitoring of the radiation curing reaction

The decrease in dielectric permittivity and in charging current throughout curing may be mainly associated with the partial immobilization of permanent carbonyl and hydroxyl dipoles attached to the oligoester chain. At a molecular level, as cure processed molecules will be created with ever increasing molar mass until an infinite network is formed.[33] Gelation corresponds to the point at which an infinite network is formed. Vitrification is the point at which the chains become close packed and there is insufficient volume for cooperative motion to occur. At a determined time scale[34] which may be of the order of 100s, the system vitrifies and the conversion levels off. The derivative of the highest frequency curve(dε'/d*t*) exhibits two maxima: the lower one is near the maximum of the DTA curve, the larger one is shifted considerably to longer reaction times. This behaviour has been observed by radiation curing as well as by peroxide initiated thermal curing (Figure 2).

Resin samples were cured by ^{60}Co-γ-radiation at 3.6 kGy/h dose rate to different levels and the polarisation current was measured at several temperatures. It was seen that the current *vs.* dose curves also show *transitions*. Beside the interrupted studies polarisation currents were measured during the reaction, too. This was done just by leaving the polarisation field on and measuring the current as function of the reaction time. A continuous decrease of the current by several decades was observed during radiation as well as thermal curing until a very low current level was reached. The polarisation spectra for interrupted measurements is shifted to longer times than the spectra obtained during the continuous measurements probably due to the post-cure by radical termination after irradiation. The values of the polarisation current decrease as the reaction proceeds. The observed drop of the polarisation current shows remarkable similarity to the dielectric spectra. The polarisation current has been measured for thermally and peroxide initiated curing, and for radiation initiated curing of samples, which contain the same amount of benzoyl peroxide, as well as for radiation initiated curing. In the experimental preset conditions, the radiation curing gives much higher crosslinking than the peroxide initiated one, because the threshold temperature for spontaneous thermal decomposition of benzoyl peroxide is about 60°C. The activation by irradiation of peroxy initiated reaction results in higher crosslinking efficiency. The comparison of the results obtained by different relaxation techniques shows that the shift of the transition temperature runs parallel with the increase of the crosslink density and also with the decrease of free non-reacted styrene content. There is a direct relation between the crosslink density measured by extraction, by polarisation current measurements and by the amplitude of the dielectric transition.

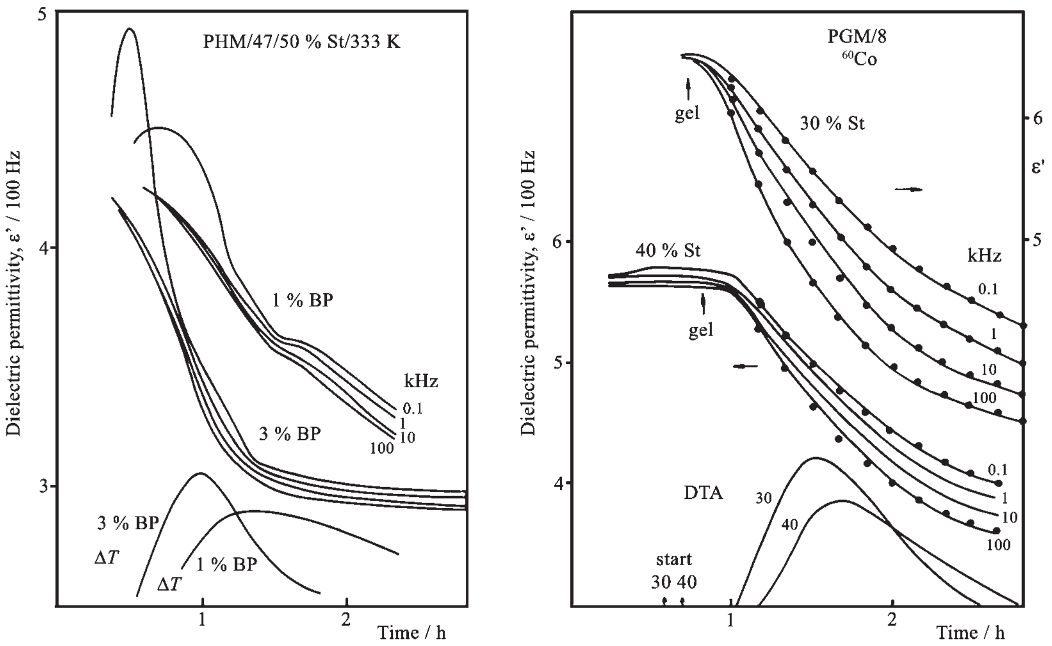

FIGURE 2 – Dielectric and DTA monitoring of initiator the curing reaction of unsaturated polyester. Left: Chemical initiation (isothermal curing at 60 °C with 1 wt.% and 3 wt.% of benzoyl peroxide (BP)); Right: *In-source* radiation curing of UP resins containing 30 wt.% and 40 wt.% of styrene. The points correspond to the simulation by the Geny-Monnerie type relaxation function (Equations 6-7).

From the variations of the viscosity with the temperature and more exactly with the normalized reduced T_g/T quantity, a classification of the glass forming liquids was proposed.[35] For the extremes of behaviour, glass forming liquids which exhibit an approximately Arrhenius temperature dependence of viscosity are defined as strong glass formers and on the contrary, those which exhibit a non-Arrhenius behaviour (for instance which could be described by Vogel-Tammann-Fulcher equation) are declared as fragile glass formers. Toward this end, Angell[36] has developed an energy landscape model based on the nature of structural evolution in a super-cooled liquid approaching the glassy state. The configurational states density comprising the potential energy hyper-surface of the material is the governing parameter.[37] Kinetic and thermodynamic aspects are introduced by the height of the energy barrier and the number of minima, respectively. According to this scheme, relaxation behaviour could be considered as strong or fragile, depending on the rate with which the associated properties are modified as the temperature passes through the glass transition region.[38] Fragile liquids exhibit steeper increase of relaxation times than strong liquids when approaching glass transition temperature in the T_g-normalized Arrhenius plots. Specifically, fragile glass formers have broader relaxation functions than strong glass.[39] The observed heterogeneity increment through adding more styrene monomer to the system is mainly attributed to the formation of tighter micro-gel structures. This microstructure is composed of distinct regions of densely crosslinked network distributed among a loosely crosslinked matrix.[40] Great dynamic heterogeneities of a thermoset resin system *via* formation of a complex structure were also reported by Wang and Ediger.[41] They actually found a bimodal distribution of local relaxation times due to slow and fast relaxing regions of their thermoset system. A typical frequency dependence of the measured *tan* δ at several temperatures in the glass transition region is obtained for the UPR with various styrene concentrations. Apparently, with the increase in temperature, the intensity of the glass transition peak enhances and shifts to higher frequencies. The characteristic time for local segmental relaxation was calculated by the frequency corresponding to the loss function peak, $\tau = 1/\omega_{max}$. The temperature dependence of the relaxation times for the UPR samples with various compositions was calculated and the shift factors above T_g, were successfully described by the WLF equation:[42]

$$\log a_T = -\frac{C_1(T-T_{ref})}{C_2+(T-T_{ref})} \qquad (1)$$

where C_1 and C_2 depend on the material type and on T_{ref}. WLF equation is equivalent to the Vogel–Fulcher–Tamman–Hesse equation (VFTH):[43-45]

$$\tau(T) = \tau_o \exp\frac{B}{T-T_o} \qquad (2)$$

where τ_0 is a pre-exponential factor and B and T_0 ($< T_g$) are specific adjustable parameters. B is a material parameter defining its relaxation activation energy while T_o is Vogel temperature representing the point, where relaxation time diverges to infinity. In the VFTH equation T_o is a diverging temperature, implying the physical impossibility of configurational changes in the solid (the configurational entropy, S_c, tends to 0 at that temperature), close to the so-called Kauzmann temperature and B/T_0 is a parameter which can be related with the fragility exhibited by the material: $B/T_0 > 30$ represents strong behaviour and $B/T_0 < 30$ is for fragile behaviour.[46]

Crosslinked UP/ styrene mixtures

The α- and β-relaxations of UP resins shift to higher temperatures as the radiation dose (and crosslink density) increases. The relaxations, however, do not appear to be equally affected by the curing, with the result that the β-relaxation has been almost completely superposed by the α-relaxation. Two relaxations have been already observed in the dielectric studies of crosslinked styrene - poly(propylene adipate maleate) resin.[47] The intensity of the β-relaxation decreases as the styrene concentration is raised.[48] The fact that the temperature of β-transition shifts to lower temperatures as the styrene concentration increases suggest that the motion of the relaxing units (presumably the polyester segments denoted by carboxyl groups) is becoming less restricted in non-cured UP resins. The intensity of the α- and β- relaxations decrease as the crosslink density (radiation dose) is raised. This suggests that a close connection exists between the β-relaxation in oligoester networks and the glass transition, since both relaxations involve the motion of polymer segments. Therefore, the dependence of T_β on crosslink density is a consequence of the decreasing flexibility of the oligoester segments. The data show three general trends: a) the curve is broad at low crosslink density and becomes broader as the crosslink density increases; b) loss maximum decreases with increasing crosslink density; c) the T_g increases with increasing crosslink density. The basic shape of the curves is similar and all show a maximum gel content around 30 wt. % of styrene. The gel fraction of cured resin is assumed to be proportional to ($T_{g,c}$-$T_{g,0}$) (where $T_{g,c}$ is the glass transition temperature of cured resin; $T_{g,0}$ being the glass transition temperature of non-crosslinked resin):

$$(T_{g,c} - T_{g,0}) \sim (gel)^{\nu} \tag{3}$$

The exponent ν is found in-between 2 and 3. Use of such empirical equations to obtain M_c values from the T_g shift on crosslinking yields only approximate results. The increase in T_g with crosslinking may be caused by two effects: a) the crosslinking can reduce the mobility of the polymer chains; and b) the resultant network effectively incorporates a copolymer of the starting oligoester and the crosslinking agent. An expression relates the T_g of a network to crosslink density by assuming the specific volume of the polymer at the glass transition to be a linear function of T_g:

$$T_g = T_{g,\infty} + k / M_c \tag{4}$$

where $T_{g,\infty}$ is the T_g of a polymer of infinite molecular mass, M_c is the molecular weight of network chains and k is material constant. The intensity of the loss peak at the glass transition temperature reflects the extent of mobility of the macromolecular chain segments at that transition temperature. Since crosslinking restricts the main chain mobility in the polymer, one would expect that the area under curves of loss ε" *vs.* temperature decreases with an increase in crosslink density. This trend will be reflected in the intensity of the loss peak heights, provided that all peaks are sharp and symmetrical. Loss maximum (dε'/dT) increases with M_c as expected, but only at low values of M_c. At high M_c the change in crosslink density has virtually no effect on loss maximum. The reduction in the intensity of the loss in polymers with partial crosslinking reflects the restraints imposed on the segmental mobility of the polymer chains by the crosslink points. The apparent activation energy of the main transition increases linearly with the temperature of the main transition. The meaning of E_a is not clear, beyond being the slope of Arrhenius plot (log f_{max} *vs.* 1/T) in its linear portion. One may properly conclude that the size of the moving unit in a given polymer increases as the temperature of the relaxation increases, at least when one is dealing with backbone motions in the carbon backbone polymers. E_a increases with T_g monotonically and hence the E_a values are not evidence *per se* for a mechanism. Gelation is accompanied by a large increase in viscosity. A specific chemical conversion is needed to vitrify at a fixed temperature. The components become less compatible with cure, and a phase separation point can be reached where oligoester-rich domains precipitate in the styrene-rich phase. Once gelation has occurred, the morphology is fixed. Long gel times promote complete separation. If gelation occurs prior to phase separation the oligoester is trapped in the network structure and no domains are formed. The resin cured from the lower temperatures T_L had a higher initial viscosity than the resin cured at higher temperatures $T_H > T_L$. The time to gel should follow Arrhenius behaviour causing the gel time at T_H to be much shorter than the gel time at T_L and a crossover in viscosity versus time (gelation is understood as an iso-viscous event). UP resins exhibited single glass transition, which normally occurred at considerably lower temperatures than T_g of the parent polymer. This is illustrated for UP resin formed from propylene glycol maleate (PPM/8) and styrene (Figure 3). Although T_g was still well defined at higher loadings of styrene, some broadening of transition did occur, especially at styrene loadings greater than 30wt.% where two resolved transitions occurred. The broadening of the transition indicates a greater variety of local relaxing environments and less genuine homogeneity at high styrene concentrations. The results indicate that styrene in excess of some critical concentration (about 30wt.%) was present as a second phase.

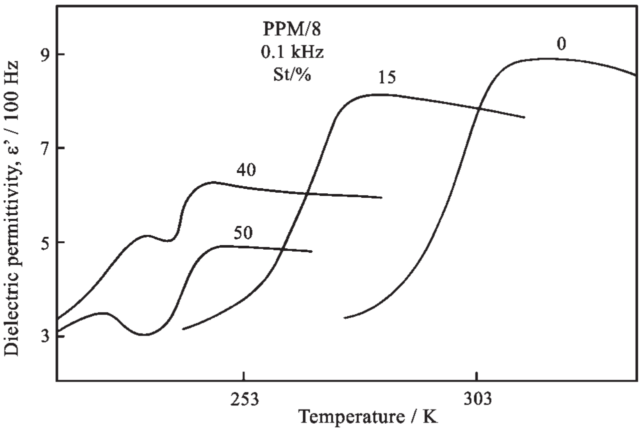

FIGURE 3 – Dielectric permittivity ε' (100 Hz) of propandiol based UPR resin (PPM8, 8 % maleate isomerisation) with different styrene content (0, 15, 40 and 50 wt.%)

The glass state structure could be influenced by the mode of formation of network. To understand this, it is necessary to study the structure that is formed during the crosslinking process. Aggregates formed in the reaction mixture are fixed by the curing reaction and then appear as the centres of inhomogeneous polymer structure. If the aggregation is caused by hydrogen bonding then the inhomogeneities would depend on temperature. In fact, the lower the curing temperature, the greater the size of aggregates and the viscosity of the reaction mixture. The diffusion effects are greater due to this fact, and so the crosslinking becomes more local. If the curing temperature is low the transition into the glassy state occurs at lower conversions.

Geny-Monnerie model

Macroscopic correlation function as derived by Geny and Monnerie[49] can be used for the description of dielectric permittivity:

$$\Phi(t) = \exp\left[-\frac{t}{\theta}\right] \cdot \exp\left[\frac{t}{\rho}\right] \cdot erfc\left[\sqrt{\frac{t}{\rho}}\right] \tag{5}$$

where *erfc* is the error complementary function. Terms θ and ρ are defined as *damping* time and diffusion time for conformation motion of a polymer chain, respectively, and thus have physical meaning. Laplace's transformation produces frequency dependent complex dielectric permittivity as function of θ and ρ. The real and imaginary terms can be then derived as:

$$\frac{\varepsilon'(z) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + \alpha z^{1/2} \left(\frac{\alpha}{2}\right)^{1/2} \left[1 + z^{1/2}\right]^{3/2}}{z + \alpha z^{1/2} + (2\alpha)^{1/2} z^{1/2} \left[1 + z^{1/2}\right]^{1/2}} \tag{6}$$

$$\frac{\varepsilon''(z)}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + \left(\frac{\alpha}{2}\right)^{1/2} \left[1 + z^{1/2}\right]^{1/2}}{z + \alpha z^{1/2} + (2\alpha)^{1/2} z^{1/2} \left[1 + z^{1/2}\right]^{1/2}} \tag{7}$$

where z is given as:

$$z = 1 + \left[\frac{\theta(T)}{\theta(T_0)} \right]^2 = 1 + \exp\left[\frac{2C_{1,0}(T - T_0)}{C_{2,0} + (T - T_0)} \right] \qquad (8)$$

where $C_{1,0}$ and $C_{2,0}$ are the WLF constants at the referent transition temperature T_0. In the first step, the maximum of the temperature derivatives (dε'/d*T*) are taken as the referent transition temperature T_0. By further iteration, a very good approximation can be achieved of the simulated (with four parameters: the referent transition temperature T_0, the WLF parameters C_1 and C_2, and $\alpha = \theta/\rho$) and the experimentally derived ε' *vs*. *T* curves (Figure 4). The value of α parameter defines the shape of Cole-Cole (ε'' *vs*. ε') diagram. The Debye limit is achieved by the slow diffusion process, for $\alpha = 0$. The Cole-Cole relaxation time distribution is given by $\alpha = \infty$ value, where $\alpha \sim 1$ value produces the Davidson-Cole relaxation time distribution.

The WLF C_1 parameters of hexanediol based UPR can be well described by the radiation dose and by the UPR chemical composition(styrene in wt.%, and maleate isomer content as %, $|R|=0.923$, $F_{signif}(2,8)=0.0004$, Figure 5):

$C_1 = 12.72 + dose$ (kGy) [-0.03489 · *maleate* (%) – 0.0423 · *styrene (wt.%)* (9)

Very good approximation is achieved for compatible systems, before the phase separation at 30 wt.% of styrene. WLF parameter $C_1 \cdot C_2$ is decreasing while the styrene concentration increases and the fumarate content increase in the unsaturated polyester oligomer structure. This fall is not as monotonous as it can be detected at the 30wt.% styrene concentration, close to the phase separation limit. Similar fitting can be done for the WLF reference temperature T_0 ($|R|=0.902$, $F_{signif}(2,8)=0.001$, Figure 6):

$T_0 = 251.46 + 4{,}007 \cdot dose$(kGy) - 1.276 · *styrene (wt .%)* (10)

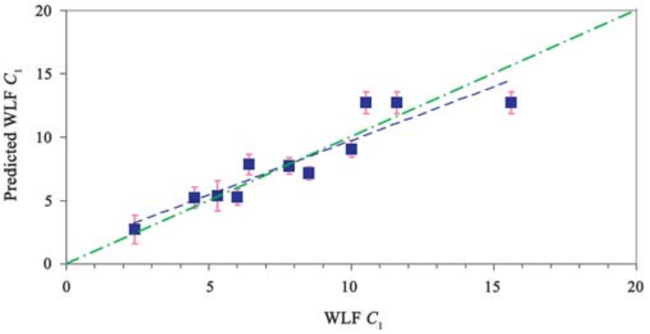

FIGURE 5 – Determined WLF C_1 parameters of hexanediol based UPR and predicted WLF C_1 parameters by the radiation dose and by the UPR chemical composition (styrene wt.% and maleate isomer content)

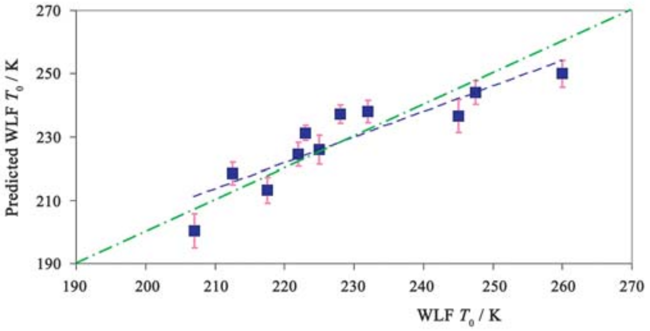

FIGURE 6 – Determined WLF T_0 parameters of hexanediol based UPR and predicted WLF T_0 parameters by the radiation dose and by the UPR chemical composition (styrene wt.% content)

The simulation of the dielectric spectra of the partially radiation crosslinked UPR can be used for following the phase separation. The WLF parameter C_1 decreases with the increase of absorbed radiation dose. This corresponds to the increase of part of fluctuation of free volume due to solvent (styrene) expulsion and to the phase separation that is induced by crosslinking. The lower limit of apparent activation energy derived from the Vogel model is given as $E_0 = C_1 \cdot C_2$, and the upper limit by

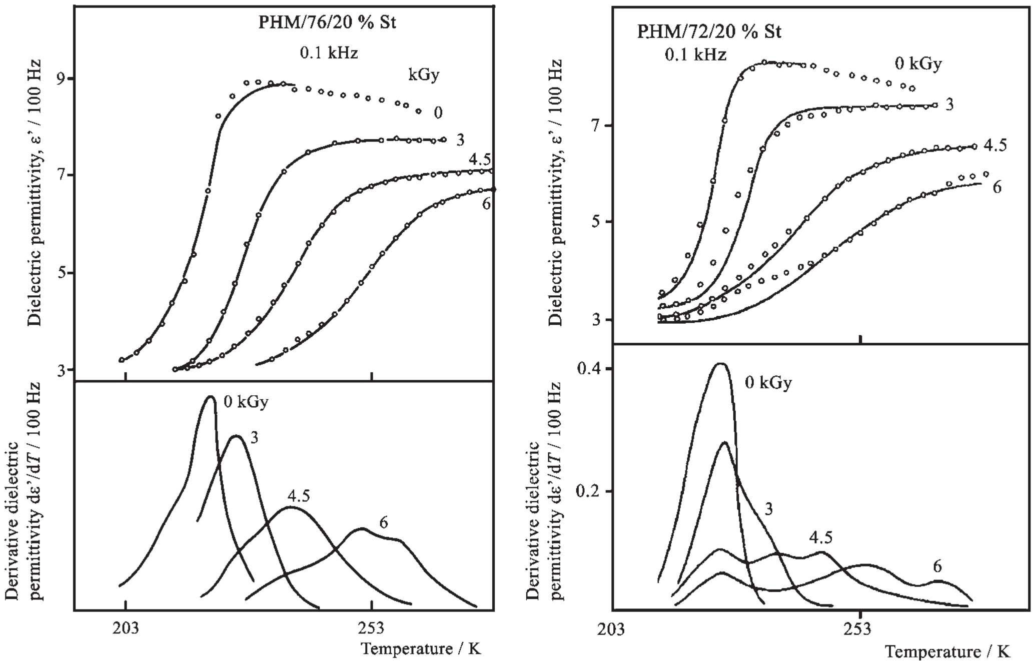

FIGURE 4 – Dielectric permittivity *e*' and its temperature derivative (d*e*'/d*T*) for 20 wt.% styrene UP resin hexanediol based UP resin (post-radiation curing measurement, radiation dose in kGy; 76 % (left) and 72 % (right) of maleate isomerisation)

$E^g(T_0) = C_1 \cdot RT_0^2/C_2$. The fall of Vogel's activation energies E_0 and $E^g(T_0)$ with the radiation dose (or partial crosslinking) is valid only by assuming a single relaxation time process; however, the dielectric spectrum widens due to the multiplicity of relaxation processes. The structure and dynamics of a network formed by radiation induced crosslinking of polyesters based on 1,6-hexanediol and 1,2-propylene glycol and maleic anhydride with styrene is studied by proton pulsed NMR spectroscopy.[50] The dependence of spin-lattice, T_1, and spin-spin, T_2, relaxation times on the structure of polyester chain, molar ratios of styrene to the polyester unsaturations and the radiation doses are analyzed in terms of network formation and structure, and their effect on molecular motion. Above the gel point, at temperatures above the glass transition, the presence of two T_2 components reflects the heterogeneity of the network structure in both resins. The glass transition temperature, determined from the T_2 relaxation measurements for UP resins continuously decreases with the increasing styrene content. Glass transition temperatures also increase with the increasing fumarate content. The processes of NMR relaxation directly represent the molecular dynamics by the spin-lattice T_1 and spin-spin T_2 relaxation times:

$$\frac{1}{T_1} = \frac{3}{10}\gamma_H^4 \hbar^2 r^{-6}\left[J(\omega_H) + 4J(2\omega_H)\right] \qquad (11)$$

$$\frac{1}{T_2} = \frac{3}{20}\gamma_H^4 \hbar^2 r^{-6}\left[3J(0) + 5J(\omega_H) + 2J(2\omega_H)\right] \qquad (12)$$

where $J(\omega)$ is a function of spectral density that describes the frequency distribution of vector motion between nuclei. The spin-lattice T_1 and spin-spin T_2 relaxation times can be described by the terms from the Geny-Monnerie model that describe the polymer chain isotropic motion (4-bonds motion, θ) and by the shift from the ideal lattice (3-bonds motion in the ideal lattice, ρ):

$$J(\omega) = \frac{\theta\left[1 + \left(\frac{\alpha}{2}\right)^{1/2}\left[1 + z^{1/2}\right]^{1/2}\right]}{z + \alpha z^{1/2} + (2\alpha)^{1/2} z^{1/2}\left[1 + z^{1/2}\right]^{1/2}} \qquad (13)$$

The NMR spin-lattice relaxation time T_1 is approximated similarly to the way the dielectric spectra was approximated (Figure 7). The experimental spectra can be described also by using the parameters derived by approximation of dielectric spectra. These approximations appear slightly narrow. This narrow approximation can be ascribed to narrower temperature range of dielectric spectra ($T_0 \pm 50$ K). The WLF parameters derived from the NMR relaxation times do not change too much. The radiation induced crosslinking of UP resins PHM/76 with 20 and 30 wt.% styrene, and of PHM747 with 20 wt.% styrene, decreases the free volume; however, the free volume increases by crosslinking due to the phase separation at concentrations higher than 30 wt.% styrene. The minimal free volume is thus observed at 30 wt.% styrene for the PHM/76 UPR and by 20 wt.% styrene for the PHM/47 UPR.

Fragility

Fragility is related to the magnitude of the decrease of log τ (or log a_T, if one deals with rheological data) with decreasing T_g/T and thus may be parameterised by the steepness 'index' *m:*

$$m = \left|\frac{d\log\tau}{d\left(\frac{T_g}{T}\right)}\right|_{T=T_g} = \left|\frac{d\log a_T}{d\left(\frac{T_g}{T}\right)}\right|_{T=T_g} \qquad (14)$$

Value m=16 corresponds to Arrhenius behaviour (strong limit) and for m>200 the systems reach the fragile limit.[51] The steepness index of many different materials is reported in some works.[52] Usually polymers appear at the fragile extreme of Angell's plot, although one can find also strong polymers.[53] It was found that m (that gives the deviation from the Arrhenius behaviour) could be correlated with the non-Debye (or non-exponential) behaviour (often parameterised by the stretched exponential β), for a series of glass forming liquids. Fragility m may be directly obtained from the VFTH or WLF parameters. When $T_{ref}=T_g$, m is given by:

$$m = \frac{\frac{BT_g}{2.303}}{(T_g - T_o)^2} = \frac{T_g C_{1g}}{C_{2g}} \qquad (15)$$

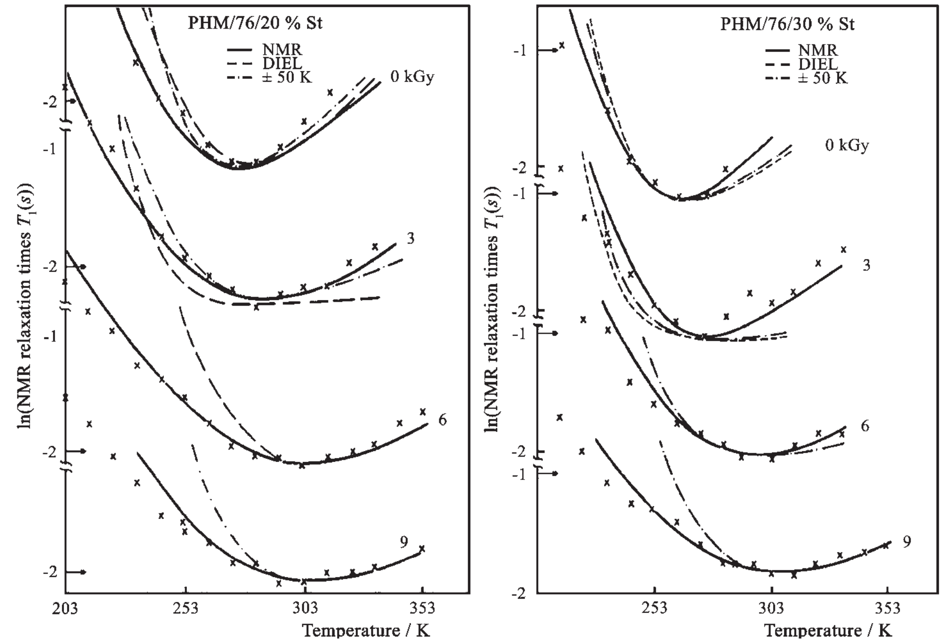

FIGURE 7 – Logarithmic NMR relaxation spin-lattice times T_1 for 20 wt.% (left) and 30 % (right) styrene UP resin hexanediol based UP resin (post-radiation curing measurement, radiation dose in kGy; 76 % of maleate isomerisation); x (crosses) experimental values, ─ (full line) fitting by the Eqs. 12 and 14; -. -(dashed-dot line) fitting by the Eqs. 12 and 14 in the limited range of ±50 °C around the T_1 minimum; - -(dashed line) fitting by the Eqs. 12 and 14, with the WLF parameters derived by the fitting of dielectric permittivity

where C_{1g} and C_{2g} are the coefficients of the WLF equation related to T_g. The usual value found for C_{2g} (≈50 °C) indicates that polymers with higher T_g values tend to be more fragile. Note that *m* may be also obtained directly from $E_a(T)$ plot:

$$m = \frac{E_a T_g}{\ln(10) R T_g} \qquad (16)$$

The fragility index of the UP resins slightly changes as the styrene concentration increases reflecting a character that becomes more fragile. Similar results have been reported by Saiter et al.[54] and Bureau et al.[55] on UPR with slightly different structures using dielectric analysis (DEA) and calorimetry, respectively. Recently, Alves et al.[56] used various techniques to study the fragility of their samples and figured out the disparity among the resulted data. Furthermore, the dynamic fragility obtained by DMA did not need to be the same as the thermodynamic fragility extracted from $\Delta c_p(T_g)$ in DSC. The cooperatively rearranging regions (CRR) concept, which was introduced by Adam and Gibbs[57] defined a subsystem size with independent configurational rearrangement capability. Modifying the Adam and Gibbs model, Dont[58] pointed out that at temperatures much higher than T_g the system contains elementary CRRs, and their number increases by temperature decrement. Finally, at a given temperature, namely crossover temperature, T_c, the system would be entirely filled by such as elementary CRRs. A number of evidences extracted from several experimental methods on many glass formers showed different relaxation mechanisms at above and below this temperature.[59-61] In other words, molecules at lower temperatures ($T<T_c$) move by crossing substantial potential energy barriers. However, at higher temperatures ($T>T_c$), thermal energies are comparable to the barrier heights and translational motion have a fundamentally different character. The change in relaxation mechanism coincided with the following different experimentally detectable events: *(a) departure from Vogel's behaviour; (b) the enhancement of translational diffusion rate in comparison to rotational motion, and (c) splitting of a single relaxation process into α and a slow β process.* It should be, however, mentioned that the crossover temperature is not identical with T_g. The T_c value scatters from ≈1.1 T_g in fragile liquids up to ≈1.6 T_g in the case of strong systems.[62] In most glass formers studied $\ln(\tau_\alpha(T_c))= -(6.5\text{-}7.5)$. The crossover temperatures for the UPR samples were estimated using the so-called random walk model (RWM) proposed by Arkhipov and Bässler.[63] In this model, the structural relaxation or transition from one configuration to another was considered as a structural unit jump within a complex energy landscape. In this framework, two temperature regimes of structural unit jumps are possible for fragile systems. The typical plot of calculated $\log(\tau)$ *vs.* (T_g/T), based on the Arkhipov and Bässler model, reveals the intersection of the two curves that locates an estimate of the characteristic T_c temperature. The characteristic T_c, or the temperature for the onset of significant intermolecular cooperativity increases with raising of styrene content. In other words, T_c could also be considered as the temperature below which the system packs completely by multiple CRRs. From Ngai's coupling model point of view[64] the degree of intermolecular cooperativity ($n_\alpha = 1-\beta_{KWW}$) increases enormously below T_c. Consequently, the onset of cooperativity in unsaturated polyester resin networks may move to higher temperatures (lower T_g/T) with raising of styrene content. On the other hand, the CRR size increment would be expected with decreasing temperature near the glass transition. Hempel et al.[65] reported in poly (*n*-alkyl methacrylate) series a systematic decrement of the number of particles[66] per CRR, $N_\alpha(T_g)$, when crossover temperature approaches T_g. $N_\alpha(T_g)$ of PE-S 60 is 1.7 times the number of particles per CRR at glass transition of PE-S 35. Therefore, the segmental relaxation in the tighter networks (with higher styrene content) is associated with the stronger intermolecular coupling. This effect could be correlated with either the increment of fragility index (*m*) or the magnitude of the strength parameter [$D= B/T_\infty = \langle U\rangle/(RT_\infty)$]. While fragility increases with enhancing the styrene content, the strength parameter shows the reverse trend. The strength parameter reflects the effectiveness of thermal energy at T_∞ to change the configurational state of a structural unit inside the CRR. The calculated values of the essential average barrier height[67] for a mole of structural units to relax, $\langle U\rangle$, at $T = T_g$ showed a decrement of the average barrier height with increasing the fragility of the system. In other words, systems with higher $\langle U\rangle$ showed signs of stronger behaviour. Apparently, this characteristic average energy controls the internal rearrangement capability of the structural units within the cooperative regions. The degree of freedom for the molecular relaxation of polyester chains increases inside each CRR by increasing the styrene concentration. However, the average energy required for rearrangement of a CRR, $N_\alpha(T_g)\langle U\rangle$, seems nearly constant for the UPR networks with different styrene content. As mentioned before, raising the styrene content is equivalent to decreasing the strength parameter. Kahle et al.[68] reported a correlation between the fragility index and the length scales of cooperativity (cube root of the mean volume of the CRR). Furthermore, a linear correlation between fragility and the size of cooperative units was found by Solunov[69] for some polymers and inorganic super-cooled liquids. Recently, Schroeder and Roland[70] suggested the existence of a critical cooperative length scale for segmental dynamics. The fragility enhancement in the networks with higher styrene content could be attributed to larger cooperative domain size of these networks (the average number of particles per CRR, $N_\alpha(T_g)$) in comparison with the average number of structural units between crosslinks, *v*, i.e. $N_\alpha(T_g) > v$. The Angell fragility concept was applied to samples with different crosslink densities.[71] Furthermore, the number of structural units per CRR[72] was estimated using RWM and the modified Adam-Gibbs's theory. The results showed that rising styrene content enhanced the crosslink density of the networks, which altered the intensity and broadness of the α-relaxation. The fragility index, a measure of temperature dependence of the relaxation times, was also increased by styrene content. Therefore, the segmental relaxation in networks with higher crosslink density could be associated with stronger intermolecular coupling. In addition, it was observed that the mean required energy for internal rearrangement of structural units within the CRR decreased as the fragility index increased, while the mean barrier height for repositioning of a CRR in cooperation to its local environment was nearly constant. The characteristic T_c, calculated based on applying the RWM for the UPR samples shifted to higher temperatures with making tighter networks. Fragility (from WLF parameters derived from the Geny-Monnerie simulation of dielectric measurements) can be relatively well described by the radiation dose and by the UPR chemical composition ($|R|$=0.782, $F_{signif}(1,9)$=0.004, Figure 8):

$$m = \frac{T_{0\cdot} \cdot C_{1g}}{C_{2g}} = 76.26 - 0.102\left[\mathit{maleate}(\%) \cdot \mathit{dose}(\mathrm{kGy})\right] \qquad (17)$$

An increase in T_g accompanied by an increase in the fragility index is a known feature of covalently bonded networks that show both an increase in T_g and *m* with increasing crosslink (or branching point) density.[73-74] While the exclusive increase in T_g upon crosslinking can also be rationalised by local stiffening of the polymer structure by introducing less flexible crosslinking agents, the correlated increase in T_g and *m* might be interpreted in terms of an increased degree of intermolecular cooperativity of the dynamic glass transition.[75] Indeed, an increase of the crosslinking density is producing stiffer chains, which means lower configurational entropy, according to the Gibbs–DiMarzio theory of glass transition.[76]

Liquid-like transitions

The liquid-liquid transition, T_{ll}, was observed by electrical, NMR and rheological methods.[77-79] However, these transitions can be re-interpreted by the characteristic temperature, T_c, or the temperature for onset of significant intermolecular cooperativity. These transitions were also interpreted by mobility changes. Another approach can be the length scale associated with dynamic heterogeneity and how it depends on temperature. Dynamic scaling[80] predicts relaxation times with the system specific temperature dependence, as the product of the universal cooperative length scale raised to the sixth power and a non-universal thermally activated process. The crossover to Arrhenius-type temperature dependence at high temperatures provides an experimental estimate of the caging temperature, T_A. The ratio of T_A/T_g corresponds to the ratio observed for the liquid-liquid transition temperature ratio to the glass transition temperature, T_{ll}/T_g. Dynamic scaling predicts that when a glass former is cooled too rapidly for an equilibrium to be established, the length scale of cooperative motion would fail to increase as it becomes increasingly difficult to bring a liquid to equilibrium at temperatures approaching critical T_c due to the large increase in relaxation times. Sufficiently close to T_c (and below T_c) the length scale for cooperative motion will be independent of temperature because the approach to equilibrium becomes extremely slow. For such low temperatures, the Arrhenius temperature dependence is predicted with activation energy E_{low}. The data above T_{ll} and below T_g are very well described by a simple Arrhenius law with the *same (or similar) activation energy* E_{low} suggesting that dynamic scaling continues to apply to glass, with length ξ independent of temperature (Figure 9). Dynamic scaling predicts that each glass would have a different relaxation time, but the temperature dependence observed at lower temperatures could be described by Arrhenius activation energy E_{low} (Figure 10).

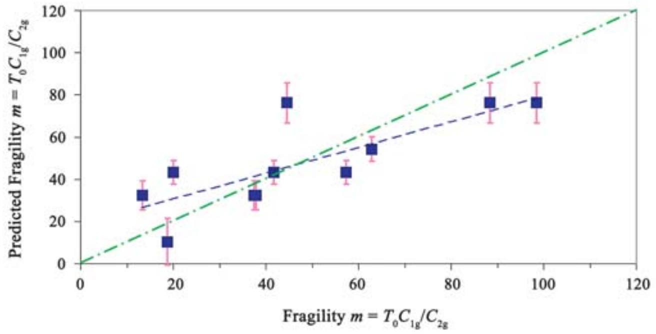

FIGURE 8 – Predicted and calculated fragility, *m* (from dielectric permittivity *e*' measurements) of hexanediol based UPR determined by the radiation dose and by the UPR chemical composition (maleate isomer content)

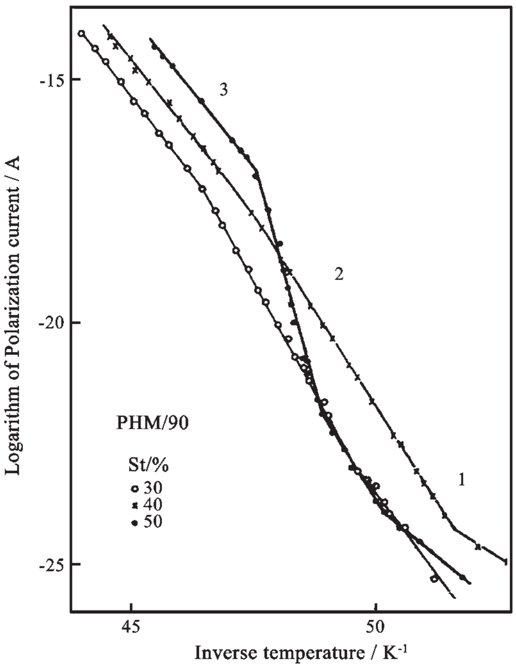

FIGURE 9 – Polarisation current of hexanediol (90% maleate isomer) based UP resin with 30, 40 and 50 wt.% of styrene; polarisation field 10kV/cm, at cooling rate 10 K/min. The ranges of linear Arrhenius segments correspond to glass (1), liquid-like (2) and liquid state (3)

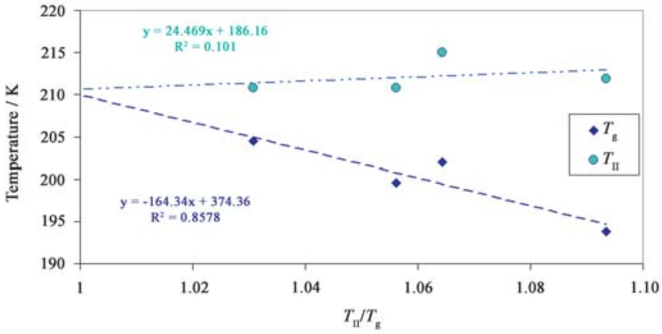

FIGURE 10 – Dependence of the liquid-like (T_{ll}) and glass transition (T_g) temperature for the hexanediol (90 % maleate isomer) based UP resin with 30, 40 and 50 wt.% of styrene samples on the reduced *window* (T_{ll}/T_g); data from Figure 9

Thermally stimulated current of unsaturated polyester resins

The dielectric properties of UP resins are mainly determined by inter- and intra-molecular hydrogen bonds. The electrical conductivity in the hydrogen bonded UP resin is usually relatively high. The motion in such systems, involved in the observed depolarisation current is a transfer of the hydroxyl group from a hydrogen bonding site to another, along hydrogen bond chains, subsequent proton exchange in the hydrogen bond leading to the proton conductivity. The dielectric depolarisation of hydrogen bond chains is considered as being due to orientational defects formed in hydrogen bond chains, i.e. in the array of coupled dipoles.[81] According to Hedvig[82] the dielectric depolarisation of hydrogen bonded chains could not be determined by the individual rotation of the H-bonds but by successive rotations. The dielectric depolarisation should depend very strongly on the physical structure. At transitions, especially at glass transition temperatures, in order to obtain large-scale mobility of the chains the hydrogen bonds must be broken. UP resins have been found heterogeneous and the studies by TSD technique are likely to give some insight into molecular interactions and the extent of mixing between the components.[83] Non-cured and cured UP resins with different weight proportions of oligoesters and styrene have been studied by TSD. These measurements revealed that the depolarisation currents decrease by curing UP resins. Thus, the extent of cure can be detected as a systematic change in TSD. The TSD spectra of UP resins are shown in Figure 11. The TSD spectra showed at least four current maxima at low temperatures. These peaks are designated β, α, α_1 and α_2, respectively. For the UP resin diluted with 40wt.% of styrene, two glass transitions, resulting from the micro-Brownian motion of the main chain backbone in separated phases β and α_1, and two liquid-like transitions have been observed. The α_1 peak observed at the higher temperature is associated with the space charge polarisation due to charge generation at the electrode-sample interface and also to motion of excess charge due to increased chain mobility. The structure of oligoester with polar end groups enhances the formation of free charge carriers, which accumulate at the electrode during polarisation formation. Their high concentration produces excess charges which on subsequent trapping give rise to α_1 peak during depolarisation. The temperature positions of the TSD peaks are changed, while their magnitudes are non-affected, except for β peaks, by changing composition of UP resins. For UP resins some part of conductivity can arise due to the proton transfer through the hydrogen bonds. The decrease of the depolarisation current by curing could then be ascribed to the disintegration of hydrogen bonds and molecular conformations favourable to proton charge carrier movements. The depolarisation current may arise either from a form of depolarisation due to movement of the protons between two equilibrium positions or from depolarisation involving very low frequency folding of the macromolecular chain about the hydrogen bonds. The depolarisation current increases drastically near the glass transition temperature T_g of non-cured resin, while at higher crosslink densities the variation is smaller.

These changes can be qualitatively interpreted using the model of hydrogen bond vibrations: depolarisation current at lower crosslink densities is related to proton jumps from one potential well to another while the part near vitrification corresponds to vibrational anharmonicity in one potential well. When a hydrogen bonded complex is formed rotations and translation of molecules in this complex are transformed into vibrational modes usually called hydrogen bond vibrations. Thus, it is possible that the gelation and crosslinking involve a rearrangement in the chain structure which renders the similar chain dipole orientations to become dissimilar. The hydrogen bond vibration modulates directly the chain-chain distance and can thus influence the proton jumps by the variation of activation energy, as it is observed at radiation doses larger than the gelation dose (3kGy). It may be argued qualitatively that the activation energy, which could roughly correspond to the height of the potential barrier of the double well, must considerably increase for increased inter-chain distances of hydrogen bonds. This is not observed at the glass transition temperature for cured resins. In fact, the inter-chain distance of the hydrogen bond shortens when going from the liquid to the gelled high elastic phase and thus the corresponding activation energy for depolarisation should decrease. For UP resins it is possible to visualize and verify a two dimensional - locally ordered structure due to inter- and intra-molecular interactions (for non-cured resins) and due to crosslink points (for cured resins). The cooling and curing result both in a small amount of aggregates dispersed throughout the solution or non-cured resin. During heating, a slight reduction in rigidity is accompanied by important displacements of the styrene molecules in sol phase where the macromolecules are in a meta-stable state. The α_1 peak which appears in the TSD spectrum is a transition corresponding most probably to the destruction of the aggregate structure of non-cured UP resin, and to the motion of the accumulated virtual charges at the interfaces of media having different permittivities and conductivities (the Maxwell-Wagner-Sillars effect) for partially cured UP resins. By taking into account that the polymer chains are not isolated but are in solution, having some interactions with styrene molecules, it is reasonable that the observed solvent induced shift of transition temperatures are influenced by the nature of the peripheral atoms of chain molecules, which creates van der Waals's type of screening. The chains should not be considered *infinite* in the solution. This implies that the solvent molecules have a shielding effect on the intermolecular interactions for partially cured and already gelled UP resins. Ultimately, as the mobility of the chain decreases by curing, the solvent screening becomes unable to compete with hydrogen bonding. By thermal disintegration of locally ordered structures at liquid-liquid transition in non-cured UP resins displacements of larger kinetic units, co-measurable with the chain length, are possible. For cured UP resins such as motions are impossible leading to decrease of a_1 peak intensity with curing. However, since the gelled samples can be considered to consist of aggregates of varying sizes and the oligoester molecules may perform the lattice-like motions, there is some hydrogen bonding left in the system. If the motions arising from the remaining unbroken intermolecular hydrogen bond of the gelled samples at higher temperatures are a randomly phased vibration without a unique frequency, it is reasonable to interpret the correlation time as the average period of the hydrogen bond vibration of the aggregated species. The temperature increase will have the effect of *softening* the hydrogen bonds. Therefore, as the crosslink density increases, one expects an increase in correlation time or decrease in the average vibration frequency. It could be noticed that as the state of cure increases, the following features are manifested: a) the temperature at which maximum occurs shifts to higher values. For an incompletely cured network many molecules have reacted at only one or two functional groups, so that the flexibility of mobile segments is not influenced by the neighbouring segments. However, as the degree of curing increases, the density of linkages between chain segments becomes sufficient to cause

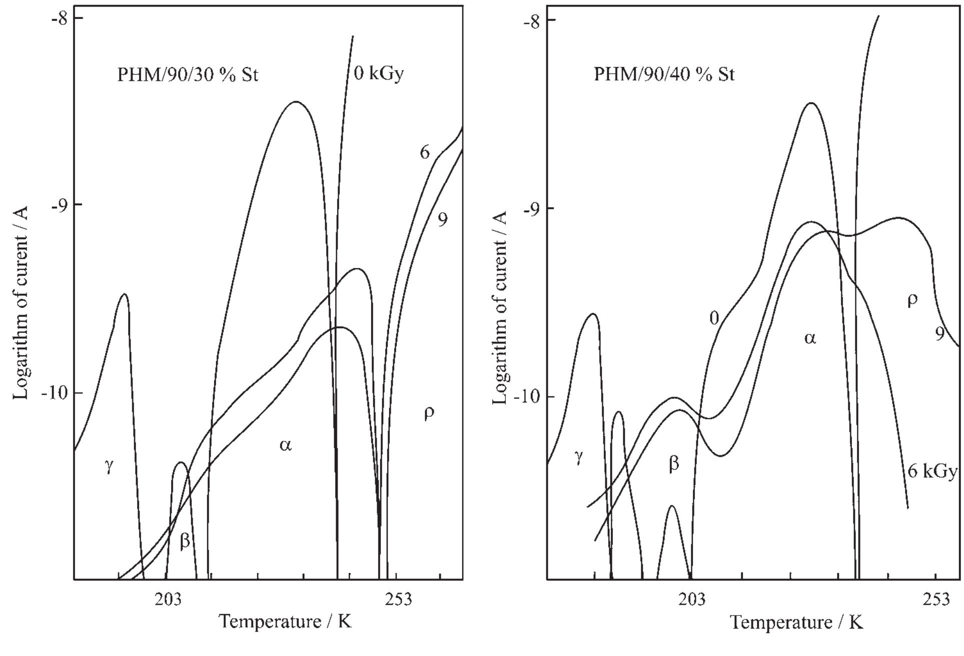

FIGURE 11 – Thermally stimulated discharging current of PHM/90 resin with 30 wt.% (left) and with 40 wt.% of styrene (right)

their mobility to begin to be restricted. It follows that the temperature at which such segments can exhibit their relaxation motions would rise as the cure approaches completion; b) the height of the peaks decreases. This is to be expected if the chain segments as part of the kinetic units are destroyed and immobilized as direct result of the crosslinking reaction; c) the T_{ll}/T_g ratio, from TSD data, is found to be in the range of 1.06 to 1.21. Thus, it is difficult to predict the value of this ratio. However, it is reasonable to conclude that the transition above T_g, α_1 observed by TSD, is the same transition as the one shown by various other techniques.[84]

Thermomechanical tests

The phase segregation in the cured UPR with an increase in styrene concentration and the dependence of glass transition temperature of UPR on styrene content were studied using dynamic mechanical tests.[85] It was found that the phase segregation was governed by the crosslink density and by the immiscibility of UP resin and polystyrene. Several structural series of unsaturated polyester networks which had different isophthalic acid - maleic anhydride ratios or different percentage rates of styrene incorporated in the network were studied by thermomechanical tests.[86] With the decreasing amounts of styrene incorporated in UPR the tensile *E*-modulus of cured UPR decreases, the tensile strength is reduced and the elongation at break is enlarged.[87] Thermomechanical measurements on partially radiation cured UP resins were done by applying the square shaped compression force load pulses and by measuring the isochronous compression compliance at 10 s loading time.[88].The compliance has a recoverable (elastic) term which can be separated from the non-recoverable (plastic) contribution term.[89] It is found that the compliance curves show transitions at increasing temperature by increasing the radiation dose, *i.e.* degree of crosslinking (Figure 12). As in case of dielectric spectra the temperatures corresponding to the maxima of the temperature derivative curves are regarded as the transition temperatures. The effective frequency associated to the isochronous creep compliances is 0.02 Hz. The temperature derivatives approximately represented the retardation time distribution. The transitions are shifted to higher temperatures, but also the amplitude of the creep compliance decreases and the transitions are broadened by crosslinking. High temperature limiting values (plateaus) of the elastic creep compliances are considerably reduced by crosslinking.

Filled UP resins

The importance of UPR is due to their important fields of applications, mainly in glass fibre reinforced plastics. Experimental results were reported on the electrical properties of glass-laminated UP resins.[90-91] Measurements of the poling current as function of temperature revealed two different activated processes (Figure 13). Above 50 °C the activation energy is 160 kJ/mol and has been associated with ionic conduction, possibly by protons, while at lower temperatures (below -70 °C) the activation energy is very low (less than 40 kJ/mol) and is associated with dipole - relaxation. It is concluded that the laminated UP resin undergoes a phase transformation between low and high temperatures, which gives rise to a completely different electrical response. This phase transformation can be associated with the glass transition of UP resin phase. In view of the low activation energy, giving rise to a polarisation peak, it is concluded that the low temperature range (glassy state) favours strictly localized motions of charges - most likely electrons. At higher temperatures, the behaviour corresponds to *dc*-conductivity and is associated with extended motions of charge carriers with limitations at contacts and at internal barriers. According to the air gap measurements, the pronounced dip found in the temperature dependence of the poling current (in the range from 20 to -30 °C) may be due to separation of conduction and dipole relaxation current. Thermally stimulated depolarisation (TSD) current measurements reveal the presence of high internal fields due to space charges accumulated at the phase boundaries of glass fibres.

Conclusions

Combined thermal, dielectric and polarisation charging techniques are successfully applied for monitoring crosslinking reaction of UP resins. The curing kinetics is complex because during the crosslinking reaction the viscosity of the system increases and the kinetics, which is initially controlled by the chemical reactivity of the functional groups, becomes controlled by the diffusion of these groups in the medium. Finally, the conversion levels off and the system attains the glassy state. At the beginning of the reaction, ε' decreases slightly, almost reaching the plateau value, followed by decay to a value of the so-called un-relaxed permittivity ε_∞, which tends to be practically constant for long curing times. The dipolar relaxation, analyzed by the peak of the maximum ($d\varepsilon'/dt$), was correlated with the thermal relaxation associated with vitrification, which is analyzed by the variation of the DTA signal. The continuous shift of glass transition of the resin was observed as crosslinking reaction proceeded. The simulation of the dielectric spectra of the partially radiation crosslinked UP resins by the Geny-Monnerie model can be used for following the phase separation. The fragility index of the UP resins glass transition slightly changes as the styrene concentration increases indicating more

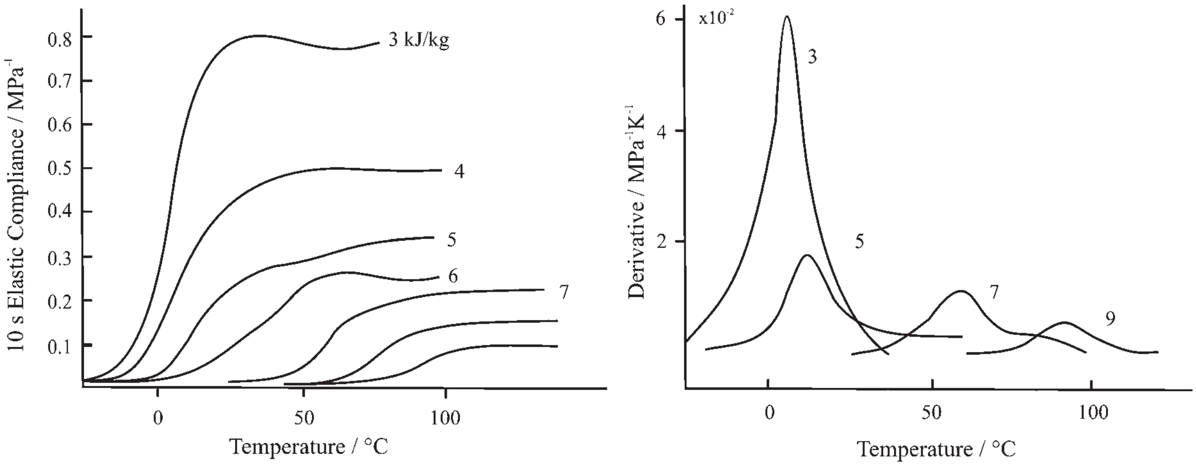

FIGURE 12 – Isochronous (10 s) elastic compression creep compliance (left) and derivative (right) curves for radiation cured UP resins as function of temperature (where numbers indicate radiation dose in kJ/kg)

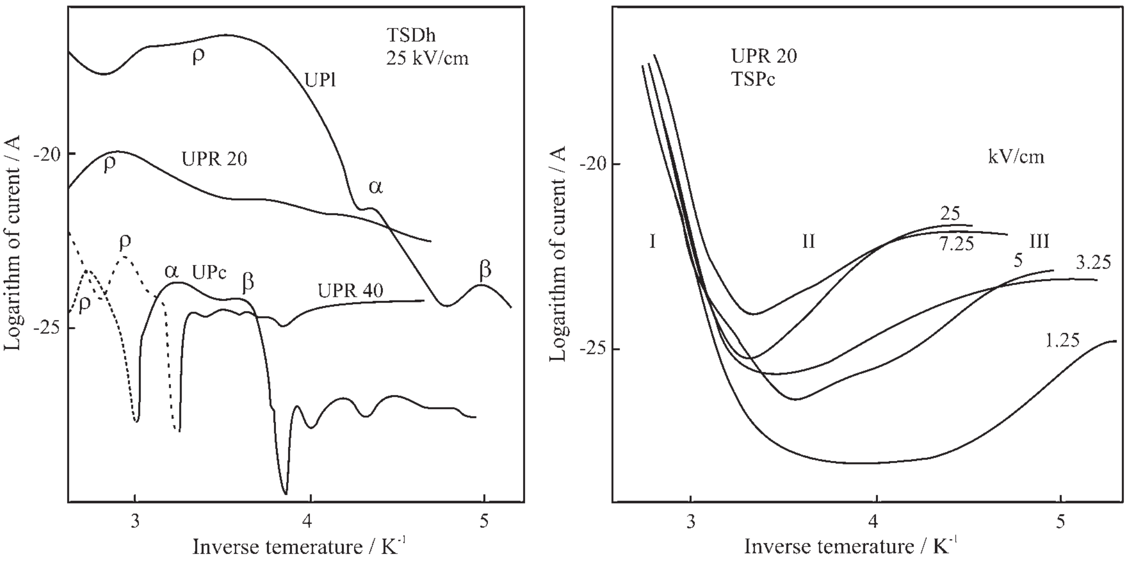

FIGURE 13 – Arrhenius-type plot of thermally stimulated poling current (TSP_c) during cooling cycle of reinforced UP resin (20 wt.% of glass fibres) under different *dc* electric fields; the numbers on the curves refer to the field strength in kV/cm) (left); Arrhenius-type plot of thermally stimulated discharge current (TSD_h) during heating cycle of liquid (UPl), cured (UPc) and reinforced UP resin (20 wt.% and 40 wt.% of glass fibres) (poled by 2.5 kV/cm) (right)

fragility. The NMR spin-lattice T_1 and spin-spin T_2 relaxation times can be described also by the terms from the Geny-Monnerie model that describes the polymer chain isotropic motion (4-bonds motion, θ) and by the shift from the ideal lattice (3-bonds motion in the ideal lattice, ρ). The shape of the polarisation charging current spectrum during the curing of UP resin shows the heterogeneous nature of vitrification process. The heterogeneity increases with the increasing of the degree of crosslinking. The UP resin exhibits a rather high concentration of carboxyl and hydroxyl end groups, which can ionize after disintegration of the existing hydrogen bonds. In addition, the investigated UP resin tends to phase-separate, and a large extension of interfaces must exist. It could be inferred, therefore, that the ionized protons can migrate in the non-ordered regions and accumulate at the interfaces, where the diffusion is more difficult. In this way interfacial polarisation of the Maxwell-Wagner-Sillars type could arise. However, it clearly results from the experimental facts described in this work that, at temperatures above T_g, another structural transition could be verified.

REFERENCES

1. Penczek, P., Czub, P., Pielichowski, J.: *Unsaturated polyester resins: Chemistry and technology*, Adv. Polym. Sci., 184(2005), 1-95.
2. Jelčić, Ž., Ranogajec, F.: *Radijacijsko umreživanja nezasićenih poliesterskih smola*, Zbornik radova GUMIPLAST 83, Sarajevo, 1983., 149-160.
3. Jelčić, Ž.: *Istraživanje radijacijskog umreživanja nezasićenih poliesterskih smola relaksacijskim metodama*, Master Thesis, University of Zagreb, Zagreb, 1981.
4. Jelčić, Ž.: *Dielektrična relaksacija nezasićenih poliesterskih smola*, Dissertation, University of Zagreb/ Institute *Ruđer Bošković*, Zagreb, 1984.
5. Jelčić, Ž.: *O primjeni ionizirajućeg zračenja za umrežavanje nezasićenih poliesterskih smola*, Proceedings *Ojačani poliesteri*, Novi Sad, Društvo plastičara i gumaraca, Zagreb, 1981, 5-01-05.
6. Andreis, M., Veksli, Z.; Meic, Z.: *Polyesterification and isomerization of maleic anhydride and 1,6-hexane diol as studied by 1H and 13C n.m.r.*, Polymer, 26(1985), 1099-1104.
7. Yang, Y. S., Pascault, J. P.: *Modeling of unsaturated polyester prepolymer structures. II. Hydroxyl and carboxyl functionalities*, J. Appl. Polym. Sci., 64(1997), 147-156.
8. Lucas, J. C., Borrajo, J., Williams, R. J. J.: *Cure of unsaturated polyester resins: 1. Heat of copolymerization and glass transition temperature*, Polymer, 15(1993), 3216-3219.
9. Caba, K., Guerrero, P., Mondragon, I., Kenny, J. M.: *Comparative study by DSC and FTIR techniques of an unsaturated polyester resin cured at different temperatures*, Polym. Int., 45(1998), 333-338.
10. Cristobal, L. V., Perdomo Mendoza, G. A.: *Unsaturated polyesters 2. Polyester from maleic anhydride and 1,3-propylene glycol*, Polym. Bull., 23(1990), 577-581.
11. Abadie, M. J. M., Sakkas, D.: *A kinetic investigation of the cross-linking of unsaturated isopthalic polyester using DSC I. Isothermal investigation,* Eur. Polym. J., 28(1992)8, 873-879.
12. Grobelny, J.: *Cross polarization/magic angle spinning 13C n.m.r. study of crosslinked polyesters*, Polymer, 38(1997), 751-757.
13. Fradet, A., Marechal, E.: *Kinetics and mechanisms of polyesterifications I. Reactions of diols with diacids*, Adv. Polym. Sci., *43*(1982), 51-142.
14. Ramis, X., Salla, J. M.: *Time-temperature transformation (TTT) cure diagram of an unsaturated polyester resin*, J. Polym. Sci., Polym. Phys. Ed., 35(1997), 371-388.
15. Eisenberg, P., Lucas, J. C., Williams, P. J. J.: *Unsaturated polyesters: influence of the molar mass on the cure with styrene and the properties of the resulting networks,* J. Appl. Polym. Sci., 65(1997), 755-760.
16. Hsu, C. P., Lee, L. J.: *Free-radical crosslinking copolymerization of styrene unsaturated polyester resins. 1. Phase separation and microgel formation*, Polymer, 34(1993), 4496-4505.
17. Delahaye, N., Marais, S., Saiter, J. M., Metayer, M.: *Characterization of unsaturated polyester resin cured with styrene*, J. Appl. Polym. Sci., 67(1998), 695-703.
18. Charlesby, A., Wycherley, V.: *The irradiation of unsaturated polyester resins*, Int. J. Appl. Rad. Isotopes, 2(1957), 26-34.
19. Sedzierski, K.: *Radiation curing of unsaturated polyester resin*, Polymer 17(1976), 261.
20. Jelčić, Ž., Hedvig, P., Ranogajec, F., Dvornik, I.: *Dielectric and thermal analysis of radiation curing of unsaturated polyester resins*, Rad. Phys. Chem., 20(1982), 309-314.
21. Hsu, C. P., Lee, L. J.: *Free-radical crosslinking copolymerization of styrene/ unsaturated polyester resins. I: Phase separation and microgel formation*, Polymer, 34(1993), 4496-4505.
22. Melot, D. , Escaig, B., Lefevre, J. M., Eustache, R. P., Lauprêtre, F.: *Mechanical properties of unsaturated polyester resins in relation to their chemical structure. I. Secondary relaxations and local motions*, J. Polym. Sci., Polym. Phys. Ed., 32(1994), 249-260.
23. Cook, W. D., Delatycki, O.: *Low-temperature relaxations in styrene-crosslinked polyester networks*, J. Polym. Sci., Polym. Phys. Ed., 13(1975), 1049-1056.
24. Sanchez, E. M. S., Zavaglia, C. A. C., Felisberti, M. I.: *Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties*, Polymer, 41(2000)2, 765-769.
25. Yang, Y.-Sh.: *Viscosities of unsaturated polyester resins: Combining effects of prepolymer structure, resin composition, and temperature*, J. Appl. Polym. Sci., 60(1996), 2387-2395.
26. Grunden, B. L., Sung, Ch. S. P.: *Cure characterization of unsaturated polyester resin by fluorescence spectroscopy***,** J. Appl. Polym. Sci., 94(2004)6, 2446-2450.

27. Jelčić, Ž., Hedvig, P., Ranogajec, F., Dvornik, I.: *Study of crosslinking of unsaturated polyester resins by dielectric spectroscopy*, Proc. 5th Symp on Radiation Chemistry, Tihany, Akademiai Kiado, Budapest, 1983, 805-811.
28. Jelčić, Ž., Hedvig, P., Ranogajec, F., Dvornik, I.: *Study of radiation crosslinking of unsaturated polyester resins by relaxation methods*, Angew. Makromol. Chem., 130(1985), 21-40.
29. Jelčić, Ž., Ranogajec, F.: *Dielektrična spektroskopija polimernih materijala i mogućnost identifikacije i karakterizacije polimernih materijala*, Zbornik radova Savjetovanja *Identifikacija polimernih materijala*, Društvo plastičara i gumaraca, Zagreb, 1983, 121-131.
30. Jelčić, Ž.: *Pregled teorijskih pristupa relaksacijskoj spektroskopiji polimera*, Polimeri 4(1983), 265-267.
31. Jelčić, Ž., Ranogajec, F., Pucić-Miličić, I.: *In-source analysis of radiation curing of unsaturated polyester resin by charging current technique*, Int. J. Rad. Appl. Instr., Part C. Rad. Phys. Chem., 36(1990), 461-466.
32. Jelčić, Ž., Brajković, N.: *Dielektrična spektroskopija i toplinski potaknuta depolarizacija omekšanog poli (vinil-klorida)*, Polimeri, 13(1992), 183-189.
33. Mijovic, J., Kenny, J., Maffezzoli, A., Trivisano, A., Bellucci, F., Nicolais, L.: *The principles of dielectric measurements for in situ monitoring of composite processing*, Compos. Sci. Technol., 49(1993), 277-290.
34. Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M., Ramos, A. R.: *Isobaric volume and enthalpy recovery of glasses. II. A transparent multiparameter theory*, J. Polym. Sci., Polym. Phys. Ed. 34(1979), 2467-2532.
35. Angell, C. A.: *Perspective on the glass transition*, J. Phys. Chem. Solids, 49(1988), 863-871.
36. Angell, C. A., Ngai, K. L., McKenna, G. B., McMillan, P. F., Martin, S. W.: *Relaxation in glassforming liquids and amorphous solids*, J. Appl. Phys., 88(2000), 3113-3157.
37. Roland, C. M., Santangelo, P. G., Ngai, K. L.: *The application of the energy landscape model to polymers*, J. Chem. Phys., 111(1999), 5593-5598.
38. Bohmer, R., Ngai, K. L., Angell, C. A., Plazek, D. J.: *Nonexponential relaxations in strong and fragile glass formers*, J. Chem. Phys., 99(1993), 4201-4209.
39. Saltzman, E. J., Schweizer, K. S.: *Universal scaling, dynamic fragility, segmental relaxation, and vitrification in polymer melts*, J. Chem. Phys., 121(2004), 2001-2009.
40. Wen, M., Scriven, L. E., Mc Cormick, A. V.: *Kinetic Gelation Modeling: Structural Inhomogeneity during Cross-Linking Polymerization*, Macromolecules, 36(2003), 4140-4150.
41. Wang, C. Y., Ediger, M. D.: *Spatially heterogeneous dynamics in thermoset resins below the glass-transition temperature*, J. Polym. Sci., Polym. Phys. Ed., 38(2000), 2232-2239.
42. Williams, M. L., Landel, R. F., Ferry, J. D.: *The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids*, J. Am. Chem. Soc., 77(1953), 3701-3707.
43. Vogel, H.: *Das Temperaturabhänigkeitgesetz der Viskosität von Flüssigkeiten*, Phys. Z., 22(1921), 645.
44. Fulcher, G. A.: *Analysis of Recent Measurements of the Viscosity of Glasses*, J. Am. Chem. Soc., 8(1923), 339.
45. Tamman, G., Hesse, W.: *Die Abhängigkeit der Viscosität von der Temperatur in die unterkühlten Flüssigkeiten*, Z. Anorg. Allg. Chem., 156(1926), 245-257.
46. Angell, C. A.: *Why C1 = 16-17 in the WLF equation is physical - and the fragility of polymers*, Polymer, 38(1997), 6261-6266.
47. Lenk, R. S., Padget, J. C.: *Dynamical mechanical properties of unreinforced cast, cured polyesters upon basacid*, Eur. Polym. J., 11(1975), 327-329.
48. Shinyashiki, N., Matsumura, Y., Miura, N., Yagihara, S., Mashimo, S.: *Dielectric Study of Water Structure in Polymer Solution*, J. Phys. Chem., 98(1994) 13612-13615.
49. Gény, F., Monnerie, L.: *Dynamics of macromolecular chains. V. Interpretation of the dielectric relaxation data*, J. Polym. Sci., Polym. Phys. Ed., 15(1977), 1-9.
50. Andreis, M., Veksli, Z., Ranogajec, F., Hedvig, P.: *1H n.m.r. relaxation of radiation induced crosslinking in polyester-styrene systems*, Polymer, 30(1989), 1498-1507.
51. Böhmer, R., Ngai, K. L., Angell, C. A., Plazek, D. J.: *Nonexponential relaxations in strong and fragile glass formers*, J. Chem. Phys., 99(1993), 4201-4209.
52. Huang, D., McKenna, G. B.: *New insights into the fragility dilemma in liquids*, J. Chem. Phys., 114(2001), 5621-5630.
53. Santangelo, P. G., Ngai, K. L., Roland, C. M.: *Temperature Dependence of Relaxation in Polypropylene and Poly(ethylene-co-propylene),* Macromolecules, 29(1996), 3651-3653.
54. Saiter, A., Bureau, E., Zapolsky, H., Marais, S., Saiter, J. M.: *Application of random walk model to the glass transition of unsaturated polyester resins cured with different styrene contents,* J. Non-Cryst. Solids, 307-310(2002), 738-743.
55. Bureau, E., Chebli, K., Cabot, C., Saiter, J. M., Dreux, F., Marais, S., Metayer, M.: *Fragility of unsaturated polyester resins cured with styrene: influence of the styrene concentration*, Eur. Polym. J., 37(2001), 2169-2176.
56. Alves, N. M., Gomez Ribelles, J. L., Gomez Tejedor, J. A., Mano, J. F.: *Viscoelastic Behavior of Poly(methyl methacrylate) Networks with Different Cross-Linking Degrees,* Macromolecules, 37(2004), 3735-3744.
57. Adam, G., Gibbs, J. H.: *On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids*, J. Chem. Phys., 43(1965), 139-146.
58. Garwe, F., Schönhals, A., Lockwenz, H. Beiner, M., Schröter, K., Donth, E.: *Influence of Cooperative a Dynamics on Local b Relaxation during the Development of the Dynamic Glass Transition in Poly(n-alkyl methacrylate)s*, Macromolecules, 29(1996), 247-253.
59. Ngai, K. L.: Correlation between the secondary β-relaxation time at Tg with the Kohlrausch exponent of the primary α relaxation or the fragility of glass-forming materials, Phys. Rev., E 57(1998), 7346-7350.
60. Alves, N. M., Mano, J. F., Gomez Ribelles, J. L., Gomez Tejdor, J. A.: *Departure from the Vogel behaviour in the glass transition-thermally stimulated recovery, creep and dynamic mechanical analysis studies*, Polymer, 45(2004), 1007-1017.
61. Wang, C. Y., Ediger, M. D.: *Anomalous translational diffusion: A new constraint for models of molecular motion near the glass transition temperature*, J. Phys. Chem., B 104(2000), 1724-1728.
62. Novikov, V. N., Sokolov, A. P.: Universality of the dynamic crossover in glass-forming liquids: A *magic* relaxation time, Phys. Rev., E *67*(2003), 031507.
63. Arkhipov, V. I., Bässler, H., Khramtchenkov, D.: *Random-Walk Approach to Dynamic and Thermodynamic Properties of Supercooled Melts. 2. Coupling of Structural Units and Susceptibility Spectra*, J. Phys. Chem., 100 (1996), 5118-5122.
64. Leon, C., Ngai, K. L.: *Rapidity of the Change of the Kohlrausch Exponent of the α-Relaxation of Glass-Forming Liquids at TB or Tb and Consequences,* J. Phys. Chem., 103(1999), 4045-4051.
65. Hempel, E., Kahle, S., Unger, R., Donth, E.: *Systematic calorimetric study of glass transition in the homologous series of poly(n-alkyl methacrylate)s: Narayanaswamy parameters in the crossover region*, Thermochim. Acta, 329(1999), 97-108.
66. Korus, J., Hempel, E., Beiner, M., Kahle, S., Donth, E.: *Temperature dependence of a glass transition cooperativity*, Acta Polym., 48(1997), 369-378.
67. Richert, R., Bässler, H.: *Dynamics of supercooled melts treated in terms of the random-walk concept*, J. Phys: Condens. Matter, 2(1990), 2273-2288.
68. Kahle, S., Korus, J., Hempel, E., Unger, R., Höring, S., Schröter, K., Donth, E.: *Glass-Transition Cooperativity Onset in a Series of Random Copolymers Poly(n-butyl methacrylate-stat-styrene),* Macromolecules, 30(1997), 7214-7223.
69. Solunov, C. A.: *Cooperative molecular dynamics and strong/fragile behavior of polymers*, Eur. Polym. J., 35(1999), 1543-1556.
70. Schroeder, M. J., Roland, C. M.: S*egmental Relaxation in End-Linked Poly(dimethylsiloxane) Networks*, Macromolecules, 35(2002), 2676-2681.
71. Taheri Qazvini, N., Mohammadi, N.: *Dynamic mechanical analysis of segmental relaxation in unsaturated polyester resin networks: Effect of styrene content*, Polymer, 46(2005)21, 9088-9096.
72. Saiter, A., Saiter, J. M., Grenet, J.: *Cooperative rearranging regions in polymeric materials: Relationship with the fragility of glass-forming liquids*, Eur. Polym. J., 42(2006)1, 213-219.
73. Kramarenko, V. Y., Ezquerra, T. A., Šics, I., Balta-Calleja, F. J., Privalko, V. P.: *Influence of cross-linking on the segmental dynamics in model polymer networks*, J. Chem. Phys., 113(2000), 447.
74. Fedderly, J. J., Lee, G. F., Lee, J. D., Hartmann, B., Dušek, K., Dušková-Smrčková, M., Šomvársky, J.: *Network structure dependence of volume and glass transition temperature*, J. Rheol., 44(2000), 961-972.
75. Schönhals, A., Schlosser, E.: *Dielectric relaxation in polymeric solids Part 1. A new model for the interpretation of the shape of the dielectric relaxation*, Colloid-Polym. Sci., 267(1989), 125-132.
76. Gibbs, J. H., DiMarzio, E. A.: *Nature of the Glass Transition and the Glassy State*, J. Chem. Phys., 28(1958), 373-383.
77. Jelčić, Ž., Ranogajec, F., Pucić-Miličić, I.: The *Liquid-Like Transitions of Unsaturated Polyester Resin by Conductivity Measurements*, Proc. 8th Int. Conf. Dielectric Liquids, Pavia, 1984, 140-145.
78. Jelčić, Ž., Pucić-Miličić, I., Ranogajec, F.,: *The Liquid-Like Transition of Radiation Cured Unsaturated Polyester Resins by Poling Current,* Proc. 6th Symp. On Radiation Chemistry, 1986, P. Hedvig, L. Nyikos and R. Schiller(Eds.), Akademia Kiado, Budapest, 1987, 551-555.
79. Jelčić, Ž., Ranogajec, F., Pucić-Miličić, I.: *Liquid-Like Transitions in Unsaturated Polyester Resin by thermally Stimulated Polarization and Depolarization Measurements*, IEEE Trans. El. Ins., EI-20(1985)2, 459-463.

80. Erwin, B. M., Colby, R. H.: *Temperature Dependences of Relaxation Times and the Length Scale of Cooperative Motion for Glass-Forming Liquids*, J. Non-Cryst. Solids, 225(2002), 307-310.
81. Jelčić, Ž.: *Toplinski potaknuta depolarizacija vlaknima ojačanog poli(etilen-tereftalata),* Zbornik radova Savjetovanja *Vlaknima ojačani polimerni kompoziti,* Društvo plastičara i gumaraca, Zagreb, 1992, 8/1-8/4.
82. Hedvig, P.: *Dielectric Spectroscopy of Polymers*, Akademia Kiado, Budapest, 1977.
83. Jelčić, Ž.: *Termički stimulirana depolarizacije polimera*, Polimeri, 8(1987), 265-268.
84. Boyer, R. F., Miller, R. L., Park, C. N.: *Regression analysis studies of polymer transitions. I. Volume-temperature data on amorphous polymers*, J. Appl. Polym. Sci., 27(1982), 1565-1588.
85. Sanchez, E. M. S., Zavaglia, C. A. C., Felisberti, M. I.: *Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties*, Polymer, 41(2000), 765-769.
86. Mortaigne, B., Vivien, B.: *Influence of the styrene-maleate ratio on the structure-property relationships of unsaturated polyester networks*, Polym. Adv. Technol., 7(1996), 813-821.
87. Rot, K., Huskić, M., Makarovič, M., Ljubič Mlakar,T., Žigon, M.: *Interfacial effects in glass fibre composites as a function of unsaturated polyester resin composition*, Composites, Part A: Appl. Sci. Manuf. 32(2001), 511-516.
88. Jelčić, Ž., Ranogajec, F.: *Pulsna termomehanička analiza radijacijskog umrežavanja nezasićene poliesterske smole*, Polimeri, 5(1984), 49-51.
89. Jelčić, Ž.: *Pregled najnovijih teorijskih pristupa viskoelastičnosti polimera*, Polimeri, 9(1988), 147-150.
90. Jelčić, Ž., Ranogajec, F.: *Thermally stimulated depolarization of radiation cured unsaturated polyester resin-glass micronodules composites*, *Polymer Composites*, B. Sedlaček,(Ed.) W. de Gruyter, Berlin, 1986, 363-371.
91. Jelčić, Ž., Ranogajec, F., Babić, L., Ivanović, Z.: *Thermally Stimulated Current In Glass-Laminated Unsaturated Polyester Resins*, Polym. Comp., 12(1991), 384-390.

CONTACT

Dr. sc. Želimir Jelčić
PLIVA Croatia Ltd.
TAPI Research and Development
Prilaz baruna Filipovića 25
HR-10000 Zagreb, Croatia
E-mail: zelimir.jelcic@pliva.hr

Uspjeh tvrtke *Šestan-Busch* na *Sajmu vojne opreme i naoružanja IDEX 2011* u Abu Dhabiju

Abu Dhabi pokazao se dobrim izborom za predstavljanje i poslovanje hrvatskih tvrtki. Sada je kao druga, tvrtka *Šestan-Busch*, proizvođač zaštitne opreme za vojsku, policiju, službe sigurnosti i sl. iz Preloga, na navedenom sajmu sklopila posao.

Prva hrvatska tvrtka koja je u 2011. uspješno izlagala u Abu Dhabiju bio je *Tehnix* iz Donjega Kraljevca. Na *Sajmu industrije obnovljivih izvora energije i zaštite okoliša* sklopili su ugovore vrijedne 5,5 milijuna eura.

Prema riječima direktora tvrtke *Šestan-Busch* Alojzija Šestana, dogovorena je proizvodnja prvih 7 000 kaciga za egipatsku vojsku, kao i proizvodnju 15 000 kaciga za Ujedinjene Arapske Emirate, proizvodnji kaciga za Kuvajt, Indiju i Saudijsku Arabiju. Posebno ga je, dodaje, razveselio komentar stručnjaka iz Južnoafričke Republike, koji su rekli da je *prelоška kaciga* u usporedbi s njihovom proizvodnjom *rolls-royce* te su pokazali veliko zanimanje za proizvode ove tvrtke.

Uskoro slijede novi poslovni pregovori u Kuvajtu, a s partnerom iz Indije priprema se ponuda za velik posao u državi koja se nezaustavljivo razvija. Sklopi li se još barem jedan ugovor, kapaciteti tvrtke u Prelogu, u kojoj danas radi 40 ljudi, bit će popunjeni do kraja godine. A ako se posao dodatno razgrana, tvrtka *Šestan-Busch* morat će zaposliti i nove radnike.

Predstavljanje *hrvatske* kacige zamjeniku vrhovnoga zapovjednika oružanih snaga Ujedinjenih Arapskih Emirata generalu Sheiku Mohammedu bin Zayedu all Nahyanu (*Foto*: MORH)

Čini se kako bi i ostale međimurske tvrtke mogle imati koristi od jednoga od najvećih sajmova vojne opreme. Među njima je čakovečki *Čateks*. Naime, tvrtka *Kroko International* sklopila je ugovore o opremanju kuvajtske specijalne policije. Riječ je o 40 000 policijskih odora, 10 000 komada odjeće specijalne namjene i 5 000 protubalističkih prsluka. *Čateks* se već specijalizirao za proizvodnju materijala za vojne odore kakve nose vojnici u više zemalja.

Gordana BARIĆ