Abstract

Ionizing radiation offers clean and easily regulated way of initiating polymerization and crosslinking reactions, independent of the reaction temperature but only very few methods can be used for in-situ reaction monitoring. The advantages and limitations of electrical conductivity as a method for reaction monitoring are discussed on crosslinking of unsaturated polyester (UP) resin as an example. The results are compared to nonelectrical methods like extraction analysis and differential scanning calorimetry (DSC). The knowledge gathered over the years about the various aspects of UP crosslinking by us and other authors is reviewed and reinterpreted according to newer approaches, taking into account not only the influence of microgel formation in various reaction conditions but also reaction induced phase separation, its influence has been shown to depend on polyester composition. The importance of determining the extent of post-irradiation crosslinking that is rarely studied is shown. The correct approach to interpretation of reaction conductivity data is presented and the need to avoid use of logarithms of original data if not based on a particular physical background is stressed.

The application of electrical conductivity method to study of crosslinking of UP resins led to discovery of liquid-liquid transitions that were investigated in greater detail. In addition to viscometry and DSC, the structural background of those transition, the decrease of short-range or local order based on inter-and intramolecular hydrogen bonding was confirmed by spectroscopy, particularly near-infrared spectroscopy. The details on those transitions, mostly on less known upper liquid-liquid transition, that should be investigated in all polymers, especially those with lower glass transition temperature, are presented.

KEY WORDS:

differential scanning calorimetry
electrical conductivity
extraction analysis, hydrogen bonding
liquid-liquid transitions
microgels
near-infrared spectroscopy
post-irradiation crosslinking

radiation crosslinking
reaction-induced phase separation
unsaturated polyester resins

Radiation crosslinking and liquid-liquid transitions in unsaturated polyesters

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Dedicated to Franjo Ranogajec, Ph.D., on the occasion of his 70th birthday
Posvećeno dr. sc. Franji Ranogajcu za njegov 70. rođendan

Sažetak

Ionizirajuće zračenje omogućuje čistu inicijaciju polimerizacije i umrežavanja koja se može lako regulirati neovisno o temperaturi, no samo vrlo rijetke eksperimentalne metode omogućuju in-situ praćenje reakcije. Opisane su prednosti i ograničenja mjerenja električne vodljivosti kao metode praćenja reakcija na primjeru umrežavanja nezasićenih poliesterskih smola. Rezultati su uspoređeni s neelektričnim metodama kao što su ekstrakcijska analiza i diferencijalna pretraživačka kalorimetrija (DSC). Spoznaje do kojih smo mi i drugi autori dolazili godinama o različitim aspektima umrežavanja nezasićenih poliesterskih smola prikazane su i reinterpretirane prema novijim pristupima, a i izbjegavanje logaritmiranja podataka ukazuju na potrebu za implementacijom funkcija za pravilan izraz identifying formalni težnji za vrijeme reakcije i istaknuta nužnost izbjegavanja logaritmiranja ako za to ne postoji jasna fizička osnova.

Primjena metode električne vodljivosti u proučavanju umrežavanja nezasićene poliesterske smole dovela je do otkrića prijelaza tekuće-tekuće, koji su detaljnije istraženi. Uz viskozimetriju i DSC, primjerom spektroskopskih metoda, osobito spektroskopijom u bliskome infracrvenom području, potvrđeno je da je strukturna osnova tih prijelaza smanjenja lokalne rešenosti kratka dosega koja se zasniva na među- i unutarmolekulnim vodikovim vezama. Izneseni su detalji o tim prijelazima, prije svega manje poznatome gornjem prijelazu tekuće-tekuće, koje bi trebalo istražiti u svim polymerima, a osobito onima s nižom temperaturom staklišta.
Introduction
The paper reviews a part of the research on crosslinking and structural transitions in unsaturated polyester (UP) resins performed at the Laboratory for Radiation Chemistry and Dosimetry. The unsaturated polyester resins belong to the most widely used thermosetting resins and are being increasingly applied for various industrial and other purposes because they are relatively inexpensive and have balanced properties. The crosslinking reaction of UP resins is rather complex, and not yet completely known. The study of the crosslinking reaction is often complicated by the limitations of experimental techniques to monitor reactions in the bulk especially if during the course of the reaction the liquid system solidifies. Ionizing radiation offers clean and easily regulated way of initiating crosslinking reaction but in-situ monitoring of radiation-induced reactions is further complicated by the need for radiation protection of both the equipment and the experimenter(s). These reasons motivated our research on methods that are able to overcome these obstacles as such as based on changes in the electrical properties, especially changes in electrical conductivity. Since it is not such a common technique, more details on electrical conductivity both as a method of monitoring the reaction course and for polymer characterization will be given. The investigation of UP crosslinking and their properties led to additional results, discovery and study of liquid-liquid transitions in those resins.

Radiation crosslinking of unsaturated polyester resins
The unsaturated polyester (UP) resins consist of polyester coils swollen to some extent in a solvent, styrene in most cases, that is also a crosslinking agent (a reactive solvent). Styrene yields a homogeneous mixture with polyester in the range of concentrations, undergoes (relatively) low homopolymerization, has low evaporation rate and a low cost. The UP resin samples investigated were mostly commercial resins (Chromoplast, produced by Chromos-resins factory, Zagreb) that consisted of poly(propylene glycol maleate) and poly(neopentyl glycol maleate) based polyester (in some cases iso-phthalic or ortho-phthalic units were included) diluted with fumarate, to which styrene was added in different concentrations. 

The crosslinking reaction and structural transitions were monitored by a number of experimental techniques, electrical conductivity method being the main method that was complemented by differential scanning calorimetry, DSC, extraction analysis (determination of gel content including UV-VIS spectrophotometric determination of styrene content), viscometry, FTIR and NMR. The experimental details can be found in our previously published papers.

The reaction between styrene and polyester double bonds is spontaneous and highly exothermic so an initiator, usually hydroquinone or its derivative has to be added to prevent crosslinking during storage of the resin. The reaction is started by addition of initiators (sometimes called catalyst although they change during reaction) and sometimes accelerators. The initiators are usually organic peroxides, in quantities ranging from 1 to 3% by the weight of polyester resin. In the presented work no initiator was used since ionizing radiation was applied to start the crosslinking reaction. Unlike initiator, ionizing radiation offers homogeneous and constant initiation, independent of the temperature or sample thickness. The UP resin crosslinking is a heterogeneous free radical copolymerization whose course can be divided into the following periods: induction period, propagation period that has a kinetically controlled diffusion controlled part including gel effect and vitrification. During the whole course of crosslinking, the contribution of each free radical reaction step can vary during (periods of) crosslinking, for example the initiator can be exhausted or diffusion can reduce radical propagation and/or termination. During the induction period, the initiator scavenges free radicals obtained by decomposition of initiator, heating or by ionizing radiation or radicals formed by reaction of those reactive species with styrene or polyester giving stable radicals and there is no crosslinking. When the inhibitor is used up, the propagation period of crosslinking begins. In case of UP resins three types of reactions occur: copolymerization of styrene and polyester - inter- and intramolecular reactions, styrene homopolymerization and polyester homopolymerization.

Obviously, it would be correct to use the term crosslinking reactions instead of using the term crosslinking reaction. For network formation the most significant reactions are those between styryl and ester radicals. Homopolymerization of styrene results in short polystyrene chains that may graft onto polyester resulting in branching on polyester coil that somewhat increases its size but consumes double bonds without network formation except in case when polystyrene chain forms a link between polyester coils. Homopolymerization of polyester double bonds is usually less likely because of steric hindrances and excluded volume effect but may become significant in special conditions (at the end of the reaction and/or at higher temperature). In kinetically controlled propagation period of crosslinking reaction, steps of free radical reactions: initiation (depending on initiator type or concentration) propagation and termination occur simultaneously until diffusion reduces the possibility for two free radicals to meet. At that moment there is practically no termination and propagation rate significantly increases what is called the Trommsdorff or gel effect and is a characteristic of free radical (co)polymerizations. If three-dimensional network is being formed, such as in the case of crosslinking, the gel effect can occur very early in the reaction. The specific features of the UP resin crosslinking arise from microstructure formation that is due to the fact that the reaction starts in the system where long chains already exist. Intramolecular cyclization caused by formation of styrene bridges on primary polyester chains results in globular formations of submicrometer range, microgels, that appear early in the reaction. The formation of microgels causes slight decrease of the reacting system viscosity prior to gelation. Microgels have permanent shape, surface area and solubility and can be clearly identified on scanning electron microscope (SEM) micrographs. Longer polyester chains have greater tendency to form coils so that the possibility of intramolecular crosslinking and microgel formation increases with molecular mass of the polyester. Further reaction leads mostly to branching on the microgel surface and increases in size until bigger particles - microgel clusters, appear. Obviously, intermolecular reaction is essential for macroscopic network formation while intramolecular copolymerization of styrene and polyester only uses up double bonds and reduces the extent of network formation. Intramicrogel reactions delay intramolecular crosslinking and the gel effect in UP resin occurs at relatively high conversion. The link between microgels usually includes one or more styrene molecules. Linking by polyester homopolymerization is possible but, as already mentioned, very unlikely in most reaction conditions. On gelation separate microgels cannot be detected anymore; particles with diameter about an order of magnitude larger emerge instead and the intermolecular reaction becomes predominant. The resulting network has inhomogeneous structure both inside and outside of microgels and a part of double bonds remains unreacted inside the microgels so that the conversion in such systems never reaches 100%. It is of no surprise that Hsu et al. detected stable styryl radicals and radicals on the ends of a polyester chain by ESR in post-gelation period and in the cured sample.
The reaction temperature influences the extents of intramicrogel and intermicrogel crosslinking. Huang et al.16,19 found that at low temperatures (40°C) intramicrogel crosslinking is only slight, producing less compact microgels than in higher temperature reactions. The remaining styrene molecules diffused into the microgels causing further crosslinking and/or branching later in the reaction. At low temperatures homopolymerization of styrene was about ten times slower than the reaction between styrene and polyester which contributed to increased intermicrogel crosslinking. At medium temperatures, 70 to 90°C, intramicrogel crosslinking was extensive in the early stage of reaction and conversion of polyester double bonds was higher than that of styrene. At even higher reaction temperatures, intramicrogel crosslinking predominated in the greatest part of propagation period reducing the extent of intermicrogel reaction. Radiation-induced reactions can be carried out at lower temperatures, even below room temperature, so the concepts of Huang et al. can be applied although they studied peroxy-initiated UP resin crosslinking. Molar ratio of styrene to polyester double bonds is probably the most important factor that influences the course of UP resin crosslinking, microgen formation, as well as the final conversions. Polar polyester and non-polar styrene are not compatible in every molar ratio which greatly depends on the structure of the polyester chain. To overcome that, the aromatic units are sometimes added to polyester chain but it increases styrene swelling which is favourable for intramicrogel crosslinking resulting in more compact microgels, less intermicrogel crosslinking and delayed formation of three-dimensional network. The best results are achieved when molar ratio of styrene to polyester unsaturations is about 2/1. In this case the copolymerization is azeotropic and styrene dilution and swelling effects are commensurate so the rates of intermicrogel and intramicrogel crosslinking are about the same resulting in more homogeneous structure of the final product. If the styrene/polyester ratio significantly differs from 2/1, the phase separation occurs prior or during the reaction resulting in styrene-rich and UP-rich phases; in the latter case it is called reaction-induced phase separation (RIPS). RIPS is not yet completely explained but can be easily understood since on the appearance of microgels the two-component system (polyester coils + styrene) becomes three-component and the miscibility of such systems is greatly reduced. Because of this some extent of RIPS is very likely in most crosslinking reactions that include intramolecular cyclization although this is difficult to prove. RIPS begins at very low reaction conversion (<1%) and at gelation (~10% conversion) blocks the mass transfer between the phases completely.20 In another paper Huang et al.21 showed that the resulting phases differed in styrene to polyester molar ratio; the styrene rich phase had molar ratio of unsaturations 40/1 while polyester rich one had ratio 2.5/1 so that crosslinking reactions obviously had different courses and conversions in each phase. We also detected RIPS in the same cases of UP resin radiation crosslinking; sometimes it was even possible to separate the liquid part from gel.7

Monitoring of crosslinking by dc-electrical conductivity

Although polymers are generally considered insulators, their electrical conductivity is in most cases still high enough for reaction monitoring. This is especially true for thermosetting resins since their conductivity is in the semiconductor range prior to reaction. When DC electrical field is applied across a dielectric one, the resulting current is a sum of: - bulk (ionic) conductivity - diffusion of ionic carriers. It is generally accepted that the greatest part are ionic impurities brought into the polymer during its preparation or processing.22,23 More recent investigations have shown that the intrinsic charge carriers, protons from the hydrogen bonds of functional groups on (macro)molecules and traces of moisture are the main carriers while the role of impurity ions is overrated.24 - The polarization current - caused by dipolar reorientation and accumulation of opposite charges at the electrodes and possible interfaces in the polymer.25,26 - Electrode injection may contribute at higher electrical field strengths but not at the field strengths usually used for reaction monitoring. Polymers like the unsaturated polyesters that have functional groups, such as carboxyl and hydroxyl, that can dissociate and release protons have higher electrical conductivity compared to other polymers. Another source of protons might be residual water that is present in traces in polyesters because it cannot be completely removed during a polycondensation synthesis reaction. 

Electrode polarization - accumulation of opposite charges at the electrodes and dipole reorientation causes gradual decrease of current with time that depends on sample thickness and the electrical field strength. Polarization can be reduced by choosing the appropriate material for electrodes: aluminium electrodes were shown not to be completely blocking for the epoxy system27 and we used such electrodes as well. In reaction monitoring the electrical field can and should be applied a while before the start of the reaction; in thermosetting systems the steady state conduction is usually attained in less than 100 s at room temperature; at higher temperatures this period becomes shorter. Anyway, the conductivity decrease during the reaction is much greater than the one due to polarization effects which is usually marginal.

The bulk electrical conductivity, σ, is very sensitive to changes in microviscosity, η, of the system which is defined by the Stokes law:

$$\sigma = \frac{Z \cdot \varepsilon_0 \cdot \mu}{\eta}$$  \hspace{1cm} (1)

$$\mu = \frac{e}{6(\Pi \cdot \tau \cdot \eta)}$$  \hspace{1cm} (2)

where $\varepsilon_0$ is the permittivity of free space, Z is the number of charge carriers, $\varepsilon$ is the charge and $\mu$ is the mobility of charge carriers. During crosslinking the mobility of charge carriers is reduced because the diffusion of ions decreases as the viscosity of reacting system increases, leading to preferred association into ion-pairs thus reducing the number of charge carriers. The conductivity decreases more or less steeply, its slope depending on the reaction rate (Fig. 1) and its first derivative is very helpful for detecting subtle changes related to different reaction periods. The first derivative during radiation crosslinking was zero during the induction period, in the first part of propagation period where the rate is controlled by the law of mass the 1st derivative increased; it reached maximum that corresponds to the maximum crosslinking rate and/or the gel effect (in some UP resins two separate maxima were observed).2 The 1st derivative decreased when diffusion limitations set in; on macrogelation and/or vitrification of the reacting system it is again zero because conductivity became constant. When the crosslinking is completed the conductivity assumes a constant value which may be several orders of magnitude lower than prior to the reaction.28

The formation of three-dimensional network increases the viscosity until a continuously connected structure is formed with formally infinite viscosity which is by the majority of authors considered to be a gelation point.25,26 If the glass transition temperature of the cured resin is higher than the reaction temperature, vitrification precedes gelation but even in the vitrified system at least some of the crosslinking reactions continue (due to the much longer reaction times of those reactions, different methods have to be applied to detect the corresponding changes). 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observed the inflection point on electrical conductivity curve that corresponds to the highest rate of mobility decrease and tried to correlate it to gelation but usually it seemed that the inflection lagged behind the gelation or vitrification determined by other experimental techniques, most likely because the logarithms of conductivity data were used (more on that later). We observed vitrification at the point at which the first derivative of conductivity became zero.

The electrical conductivity method along with very few other, mostly (di)electric methods, can be used to monitor reactions in thicker systems. Day37 showed by dielectric spectroscopy that the crosslinking rate and the conversion of a resin on the surface was different than the conversion in the deeper parts which has implications on processing. At the surface the reaction began earlier but proceeded slower than in the middle part of the sample where it began later but was faster due to the released heat of the reaction that could not be dissipated because of poor thermal diffusivity. Day found this effect to be significant for samples thicker than 5mm; his experiments were performed at a single temperature, 423K. We also investigated the effects of sample thickness measuring the changes of electrical conductivity on thermal initiation of crosslinking on the selected temperatures between 95 and 120°C. The plots of the first derivative of conductivity in 6mm thick samples revealed two separate rate maxima in the propagation phase while in 1.5 mm thick samples there was a single propagation maximum. It is very likely that the heat released during the first propagation period that could not be transferred out of the sample enhanced intramicrogel reactions by supplying the energy to overcome the steric hindrance and allowing the remaining polyester groups to react either with styrene or to homopolymerize. It can be expected that at lower reaction temperatures heat released during crosslinking influences the reaction rate even more. In radiation crosslinking of 6mm thick UP resin samples at room temperature the contribution of reaction heat to crosslinking enhancement was again observed: the gel appeared at higher doses compared to 1.5mm thick samples and contained more styrene while the corresponding DSC thermograms revealed polyester homopolymerization (later), similar to thin samples crosslinked at higher dose rate.

The main limitation of (di)electrical monitoring of reaction course is that the change of the electric properties cannot be directly related to chemical change. To determine the extent of crosslinking of UP resins and to correlate it to the electrical conductivity change of fully or partially cured (which is easily achieved in case of radiation initiation) samples, extraction was performed. The solubility of the network is inversely proportional to the extent of the crosslinking reaction. The disadvantage of gel determination is that in the early stages of the reaction there is no measurable quantity of gel. In later stages of the reaction the gel content increases and then levels off at about 90%, depending on the reactivity of the resin. The unreacted styrene content in the solution was measured by UV spectrophotometry and monitored during the whole reaction course. The changes in electrical conductivity and the corresponding styrene and gel content changes are shown in Figure 2. Due to the previously described specific features of UP resin crosslinking it is clear that styrene concentration may decrease somewhat differently than gel content increase. Unextracted resin samples and the gel obtained on extraction can be further investigated by various methods (FTIR, SEM). Considering FTIR, it must be stressed that if samples are prepared in the form of KBr disks, the microscopic inhomogeneity of microgels may cause macroscopic effects resulting in irreproducible spectra. The methods that we used to correlate the electrical and chemical changes and the corresponding advantages and limitations are listed in Table 1.

![FIGURE 1](image1.jpg) The decrease of electrical conductivity (blue line) during the radiation initiated crosslinking of UP resin (dose rate 0.345kGy/h at 17°C) and the change of 1st derivative of conductivity (violet symbols)

![FIGURE 2](image2.jpg) The radiation-initiated crosslinking of UP resin (dose rate 0.4kGy/h at 67°C): the decrease of electrical conductivity (blue line) versus dose, the corresponding changes in free styrene content (orange symbols) and increase in gel content (green symbols, the values on the axes are reversed to make the comparison easier) in samples irradiated in the same conditions are shown (the styrene content was determined from normalized UV absorption at 291.5nm.)

Effect of electrical field strength
When polymerization or crosslinking is monitored by any experimental method that applies electrical field across the sample, the influence of the field on the reaction should be expected. This issue is relatively seldom discussed; most authors do not even specify the field strength they used. Depending on the reacting system, the field can increase or decrease the reaction rate, in some cases even
change the reaction mechanism from radical to ionic.38 In the case of UP resin crosslinking the slope of the conductivity curve, i.e. the rate of reaction showed pronounced dependence on the electrical field strength in both radiation and thermally initiated reactions.3 When conductivity changes of the samples irradiated at the same dose rate but at different field strengths were compared an increase in the reaction rate with the field strength increase was observed and confirmed by extraction: the gel appeared at the lower dose and its final content was higher in the samples crosslinked at higher field strengths. The favourable effect of the field was noted both in the case of thermal and radiation initiation of crosslinking. The polyester chain is polar and obviously oriented under the influence of the electrical field in a manner that improved contact between the reaction sites.

The two propagation slopes (detected as maxima in the 1st derivative of conductivity) behaved differently under the influence of the electrical field.4 In the kinetically controlled propagation period the field did not influence the reaction rate because there were enough double bonds available to the reaction; the system was liquid; the diffusion of monomers was easy. On the other hand, in the second part of propagation the remaining double bonds were mostly buried inside the microgels and less available to the reaction; the viscosity was much higher and the diffusion of monomers was greatly reduced. In such conditions, the orientation that increased the accessibility of reaction sites had much more significance and the reaction rate increased with field strength increase (changes in mechanism of conductivity or electrode effects were excluded). The influence of the electrical field on the vitrification was also observed: the stronger the field, the earlier the system reached vitrification. Since the samples for extraction were at first chosen according to the changes of conductivity and the total doses were different at each electrical field strength and dose rate, the experiments were repeated in such a way that all samples were irradiated to the same total doses. Their residual reactivity was determined by DSC and the same behaviour was noted again. In case of UP resin crosslinking the electrical field obviously brings the reactants closer together which is similar to the effect of increased pressure observed by Huang et al.19.

A very interesting interplay was observed between the influence of the electrical field and the dose rate that is in fact the rate of initiation on UP resin crosslinking.3 The measurements were carried out at three field strengths: 2.5, 25 and 250kV/m and at three dose rates 3.05, 0.354 and 0.096kGy/h. Although the reaction time became shorter when the dose rate was increased, the total dose needed for the completion of crosslinking became higher. The effect of electrical field was the most pronounced at the lowest dose rate because the concentration of reaction sites was low and better contact promoted by electrical field had greater significance. At the same time due to low concentration of primary radicals (those directly produced by radiation), their recombination that is not effective for crosslinking was negligible. On the other hand, at the highest dose rate high initiation rate contributed to intramolecular reaction and microgel formation is very high while a large part of primary radicals are likely to recombine. Much less gel was formed at the corresponding doses implying significant styrene homopolymerization and no influence of the electrical field strength was observed. Obviously, the favourable influence of electrical field on UPE resin crosslinking was inversely related to dose rate. In another set of experiments the samples were irradiated to the same total dose at each dose rate under a medium electrical field and without it. The residual reactivity that is inversely proportional to the reaction extent determined by DSC as a non-electric method was the highest in samples irradiated at the highest dose rate while electrical field strength had the most influence on the samples irradiated at the lowest dose rate.

**Evaluation of the conductivity data**

To get kinetic information from the electrical conductivity data, the logarithm of electrical conductivity is commonly plotted against reaction time/dose instead of conductivity itself. Even nowadays the works of Warfield et al.28,29 and Kagan et al.40 are cited but no physical basis for using of the logarithm of conductivity was ever presented. They proposed equation (3):

\[
\frac{d\sigma}{dt} = \frac{(\ln \sigma - \ln \sigma_0)}{(\ln \sigma_\infty - \ln \sigma_0)}
\]

where \(\sigma\) is conductivity at time \(t\), \(\sigma_0\) is initial conductivity; and \(\sigma_\infty\) is final value of conductivity at the end of the reaction. Lane et al.,41 Day,42 Mijovic et al.43 cited an article of Keinle et al.44 published in 1934 where such proportionality was not explicitly stated and in no other chemical method are the logarithmic data used as values in the calculation of reaction rates.45 This approach is still in use although some authors noticed discrepancies between reaction events and extents determined by the electrical methods and other experimental techniques.24,42,43 but did not recognize that the use of data in the logarithmic form is the source of the problem. The data in the logarithmic form are skewed, greater significance is given to lower values, noise is increased and curves shifted to higher reaction times/doses which is best seen in Figure 3 where the logarithmic form of the conductivity data presented in Figure 1 is plotted. The most dramatic differences are seen in the first derivative plot where all the structure corresponding to reaction periods is lost. As a result of logarithm application, the sensitivity of the electrical conductivity method is significantly reduced, the values at the end of the reaction may be so high and scattered that it is difficult to notice the levelling off and/or the two maxima in thermally initiated reaction cannot be detected. Because of that, the logarithms should be avoided in the interpretation of reaction changes of electrical conductivity and otherwise used only when there is a clear physical basis for that.

Our approach was to use untransformed conductivity data which enabled us to correctly determine the boundary conditions for the calculation of reaction extent.

### TABLE 1 - Some advantages and disadvantages of experimental methods used in the research of the UP resin crosslinking

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td>Electrical conductivity</td>
<td>Sensitive, can be applied in various conditions (radiation), changes in aggregate state are no obstacle</td>
<td>No information on chemical change</td>
</tr>
<tr>
<td>Extraction</td>
<td>Gives insight into the crosslinking course, especially if the solution is analyzed by spectroscopy</td>
<td>Generally time-consuming</td>
</tr>
<tr>
<td>DSC</td>
<td>Sensitive</td>
<td>No information on chemical change, only small sample size</td>
</tr>
<tr>
<td>FTIR</td>
<td>Chemical information</td>
<td>Only thin films can be investigated; Difficult preparation of (partially) crosslinked samples</td>
</tr>
<tr>
<td>NMR (solution)</td>
<td>Chemical information</td>
<td>Difficult preparation of (partially) crosslinked samples</td>
</tr>
<tr>
<td>SEM</td>
<td>Morphology</td>
<td>Difficult preparation of (partially) crosslinked samples</td>
</tr>
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\[
\sigma_t = \frac{(\ln \sigma_\infty - \ln \sigma_0)}{(\ln \sigma_\infty - \ln \sigma_0)} (3)
\]

\[
\frac{d\sigma}{dt} = \frac{(\ln \sigma_\infty - \ln \sigma)}{(\ln \sigma_\infty - \ln \sigma_0)}
\]

\[
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\]

\[
\frac{d\sigma}{dt} = \frac{(\ln \sigma_\infty - \ln \sigma_0)}{(\ln \sigma_\infty - \ln \sigma_0)}
\]
FIGURE 3 - The same electrical conductivity data as in Figure 1 but plotted as natural (and decimal, on additional y axis) logarithm of conductivity vs. dose (blue line), and the change of the corresponding 1st derivative of logarithm of conductivity (violet symbols).

$$\frac{d\sigma}{dt} = \frac{\sigma_i - \sigma_f}{\sigma_i - \sigma_0} \quad (4)$$ (Symbols are the same as in equation 3). By using equation 4 we not only avoided the above mentioned errors but attained full sensitivity of the electrical conductivity method. This made possible to reveal additional information on the course of crosslinking of unsaturated polyester resin like the influence of the upper liquid-liquid transition, $T_{lp}$ (it will be discussed later in detail) on radiation crosslinking of UP resin. The reaction was initiated at the selected temperatures in the range from 20 to 72°C while $T_{lp}$ is at about 32°C for the investigated resin. Above the $T_{lp}$ transition polyester coil becomes looser, styrene molecules more easily penetrate the coil and more polyester double bonds became available to crosslinking. It can be expected that such change would influence the crosslinking rate. The reaction was monitored by the electrical conductivity method and its rates were calculated using both equations (3) and (4); the Arrhenius plots were plotted as shown in Figure 4. When the conductivity data in the logarithmic form were used, the reaction rate can be fitted linearly to give single straight line with significant scatter. On the contrary, original conductivity data gave two linear segments with much less scattering corresponding to two different reaction rates. The linear segments intersected in the temperature range of the upper liquid-liquid transition and the obtained temperature is in good correlation with that temperature determined by other experimental methods. The activation energy of crosslinking was lower above the $T_{lp}$ temperature as expected on breaking of intramolecular interactions. The use of untransformed data also revealed vitrification and how it is influenced by the upper liquid-liquid transition: vitrification occurred at constant dose on temperatures below $T_{lp}$ and its dose linearly decreased with temperature if crosslinking was performed in the temperature range above $T_{lp}$. In this manner full sensitivity of electrical conductivity method to both reaction and structural changes was obtained.

Post-irradiation reaction and reaction-induced phase separation

Post-irradiation reaction is defined as continuation of polymerization, crosslinking or degradation after the irradiation is terminated and is caused by the free radicals formed under the irradiation that are trapped and stabilized in macromolecules or in the network.\textsuperscript{46,47} The post-reaction course largely depends on the polymer under consideration and should be studied as a part of any investigation of radiation effects on polymers but it is rarely done. In the partially crosslinked UP resins irradiated and kept at room temperature the post-irradiation changes were observed up to 5 days after the irradiation.\textsuperscript{6,9} The extent of post-irradiation crosslinking depended on the period of the crosslinking reaction at which the irradiation was terminated. These results emphasize the importance of monitoring the post-irradiation changes in polymers because of the impact on the final properties, especially if the polymers are used for the preparation of composites and nanocomposites as is often the case of UP resins. The study of post-irradiation crosslinking was used also to compare the sensitivity of three very common experimental techniques used to monitor crosslinking: extraction analysis, FTIR spectroscopy and DSC. The DSC was most sensitive and provided additional information on the course of radiation and post-radiation reaction from the shapes of the DSC thermograms and the residual heats. The extraction analysis is also very sensitive and able to detect the post-effect but was time consuming. Since the samples were irradiated in bulk and KBr disks were prepared of the resulting gel, it was very difficult to obtain macroscopic homogeneity, not to mention microscopic inhomogeneity that is a consequence of the UPE resin crosslinking, so that FTIR spectroscopy was not appropriate for monitoring of its post-irradiation changes of UP resin.

Both radiation and post-irradiation crosslinking reactions were highly influenced by the structure of the polyester.\textsuperscript{5,9} As previously said, a part of flexible maleate and fumarate units in polyester chain is often replaced by rigid ortho-phthalic or iso-phthalic units to increase the compatibility with styrene.\textsuperscript{14} Such polymers have lower degree of unsaturation compared to the polyester of the same molecular mass containing only maleic acid residues. Its microgels formed on crosslinking are not that compact so its shrinkage is reduced. We found that it applies only to the UP resins containing iso-phthalic units in polyester chain while the crosslinking behaviour of the resins containing ortho-phthalic units significantly differed (other components being the same which was confirmed by NMR). In fact, the presence of ortho-phthalic units seems to reduce the styrene-polyester compatibility resulting in the reaction-induced phase separation (RIPS). RIPS caused the appearance of double peaks in DSC thermograms (Fig. 5, left, resin A) that were first ob-
served in a study of residual reactivity of some partially crosslinked UP samples in which it was possible to separate liquid and gel parts. The thermograms of gels had one distinct reaction peak at about 180°C, while the thermograms of unreacted resin and liquid parts showed wide double exotherms. The exotherm of uncured resin had a shoulder at about 150°C while the higher temperature maximum was in the same range as in gels. Although most authors assign such double peaks to initiator effects, in this case none was added. Because of that we concluded that the lower-temperature peak was caused by copolymerization of styrene and polyester and styrene homopolymerization (those reactions occur at similar temperatures and are virtually indistinguishable in DSC). The lower temperature peak in DSC thermograms of resin containing ortho-phthalate decreased faster during the post-irradiation period which is consistent with the ESR-findings of Hsu et al. that found that the decay of radicals was higher in styrene-rich phase during postcure after RIPS because of lower crosslinking density. The higher-temperature peak and the only peak in thermograms of gels obviously resulted from polyester homopolymerization. The appearance of double peaks and distinctive polyester homopolymerization peak at about 150°C in thermograms of UP resins is a strong indication of RIPS. The lower extent of radiation and post-irradiation crosslinking that begins at a higher dose for ortho-phthalate-containing resin can be seen in Figure 5, right, as delayed and lower gel content increase with the dose compared to iso-phthalate-containing resin. Iso-phthalic units in polyester obviously did improve compatibility with styrene resulting in single-peak DSC thermograms of intermediate temperature (Figure 5, left, resin I), higher reaction extents and more homogeneous surface appearance on SEM micrographs compared to coarser surface structure of ortho-phthalate-containing resin, i.e. signs of macroscopic RIPS were not observed. In thermograms of UP resins containing iso-phthalate double peaks may appear only in extreme reaction conditions like at very low temperature where the compatibility with styrene might be reduced increasing the probability of RIPS. In rare cases where the decomposition of initiator(s) produces an additional peak, it appears at temperature lower than that of styrene reactions, i.e. below 80°C.

**Liquid-liquid transitions**

Electrical conductivity of polymers exponentially depends on temperature:

$$\sigma = \sigma_0 \cdot \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} (5)

The activation energy of electrical conductivity, $E_a$, is denoted apparent because the real nature and concentration of charge carriers is unknown and should not be confused with activation energy of (crosslinking) reaction. The apparent activation energy of conductivity is usually determined by stepwise measuring conductivity at different temperatures. Stepwise heating and taking readings on levelling-off of current works best, but is time consuming although time needed for levelling off decreases with temperature. The same information can be obtained from electrical field dependence of conductivity measured at various temperatures. Both approaches were used on unirradiated i.e. unreacted UP resin samples and on those irradiated to various doses covering the whole crosslinking course observing the corresponding increase of the apparent activation energy. To confirm the linear, Arrhenius type dependence and to exclude other temperature-conductivity relationships like Vogel–Fulcher–Tammann–Hess, the regression analysis was performed and the residuals for both types of temperature dependencies were compared. Only the Arrhenius-type plot with two to three linear segments that differ in slopes gave random residuals which is a proof of the appropriate temperature dependence. Such plot is shown in Figure 6 where these dependencies are shown for two UP resins that differed in the length of aliphatic chain of diol.

In fact, in the temperature range above the glass transition temperature there are two changes of apparent activation energy of electrical conductivity in UP resins which means that structural changes occurred. Since all measurements on UP resins were performed in the temperature range above glass transition temperature $T_g$, of UP resins, the change(s) of activation energy can only be caused by breaking interactions that give rise to liquid-liquid transition(s): lower liquid-liquid transition ($T_{ll}$) and upper liquid-liquid transition ($T_{ul}$).

The later transition should not be confused with liquid-liquid phase separation and/or upper critical solution temperature (UCST) that occur in systems with at least two components while liquid-liquid transitions were determined in a number of pure polymers like polystyrene or PMMA.

The scale of transitions in amorphous polymers is shown in Figure 7. The fact that random residuals were obtained only if electrical conductivity was plotted as separate Arrhenius type segments plots (three if the corresponding temperature range of measurement

**FIGURE 5** - The crosslinking thermograms of UP resins A (containing ortho-phthalic units) and I (containing iso-phthalic units) (left), and the changes in gel content with dose on radiation crosslinking of resins A and I (right)
covers both liquid-liquid transitions) is the strongest argument against the opposition\textsuperscript{51,52} to the concept of short-range or local order in polymer melts and existence of those transitions. The opponents mainly cited Flory’s concepts that allowed no organization in amorphous polymers above the \( T_g \), whatever, although this may be a misrepresentation of Flory’s ideas. Each of the linear segments has a corresponding apparent activation energy: \( E_{a2} \) below the \( T_l \) transition temperature, intermediate activation energy, \( E_{a3} \), and \( E_{a4} \), the activation energy above the \( T_p \) transition.

At glass transition temperature, \( T_g \), the viscoelastic glass becomes a viscoelastic melt (Figure 7). Below \( T_g \), large scale molecular motion is restricted and above it liquid-like motion begins\textsuperscript{53} but at temperatures not much above \( T_g \), polymers do not flow. Boyer and coworkers\textsuperscript{54} explain this by the constraints due to secondary valent forces: Van der Waals and London forces in non-polar polymers and dipole interactions and hydrogen bonds in polar polymers. Those interactions include a couple of bonds and short-range order is based on them. Each coil interacts with the neighbouring coils and intercommunication by short-range order spreads throughout the sample causing the macroscopic effect. The flow starts on breaking of intermolecular short range interactions at lower liquid-liquid transition temperature \( T_l \) that is approximately 1.2\( T_g \) (in K). The fact that \( T_l \) is sensitive to variations in molecular mass and disappears on dilution and on crosslinking confirms its intermolecular nature. Residual local order based on intramolecular interactions, mostly at polymer chain ends, breaks at the upper liquid-liquid transition temperature \( T_{ll} \) that is 30-50K higher than \( T_l \). By breaking of intra- molecular interactions the coil ends become free to rotate. Because of its intramolecular nature, the \( T_{ll} \) transition is almost unaffected by changes in molecular mass or crosslinking.

Both \( T_{ll} \) and \( T_{hp} \) transitions are weak and influenced by thermal history of the sample. Their intensity is greater in polar polymers, especially those that can form hydrogen bonds. Their existence may sometimes be masked by some other processes such as liquid crystal transformation. Thermal decomposition of polymers with high \( T_g \) starts at temperatures below liquid-liquid transitions. As glass transition, liquid-liquid transitions are in fact relaxations and their temperature depends on the frequency of measurement. The liquid–liquid transitions are also called slow processes\textsuperscript{54} because the polymer coil needs a certain amount of time to achieve the corresponding configuration, so transitions are detected much easier by low frequency measurements. It may also be the reason why it is difficult to observe them in experiments with a temperature ramp or flow, while we easily observed them in the quasi steady-state experiments such as the electrical conductivity measurement.

The transition intensity is determined as a percent of the slope change in the Arrhenius plot and has to be above threshold value of 10% if there is a transition.\textsuperscript{55} When the readings of conductivity were taken at fixed preset times after the application of the electrical field and the apparent energy of electrical conductivity was calculated, we found that the intensity of the \( T_g \) was the lowest for the conductivity measurements taken at the shortest times. The intensity of \( T_g \) increased with time because of its slow nature to which the polarization process contributed since the orientation of polar functional groups in the polyester chain increased the local order in proportion to the electrical field strength.\textsuperscript{2} Above \( T_g \), the decrease of the local order increased the mobility of the charge carriers and reduced the structure strength resulting in a decrease of the apparent activation energy of conductivity or flow (in measurements of temperature dependence of viscosity). The Arrhenius plot of viscosity is very similar to the inverse plot of electrical conductivity although the viscosity measurement includes the flow of material while electrical conductivity does not. The downside of viscosity measurements is that it cannot be measured on samples crosslinked above gelation point, while conductivity is not the subject of such limitations. The temperatures of \( T_g \) transitions in various UP resins determined by viscosity and conductivity (the temperatures of \( T_g \) transition determined in two UP resins are listed in Table 2) were almost identical and the corresponding intensities of liquid-liquid transitions was between 15 and 30%.

One of the advantages of radiation initiation of the UP resin crosslinking is that in the temperature range below spontaneous thermal initiation, the reaction can be interrupted at any moment and the temperature dependence of electrical conductivity measured to calculate its apparent activation energy. This procedure can be repeated at chosen doses and changes of \( E_a \) plotted against the reaction time or dose. As the three-dimensional network reduces the mobility of charge carriers, the overall conductivity decreases, and the apparent activation energies both below and above the \( T_{ll} \) increase with dose i.e. reaction extent and then level off. However, the \( T_{ll} \) transition was detected along the entire reaction course and was not affected by styrene concentration or maleate to fumarate ratio in the polyester. The \( T_{ll} \) temperature determined from the intersection point of those two linear segments was in agreement with other experimental methods in Table 2). Assuming that the conductivity attains its final value at the vitrification point, the vitrification time or dose is determined from the intersection point of linear increase of \( E_a \) and its final value(s). The vitrification dose
was very sensitive to reactivity of the resin; it increased with the increase in the furmarate content while the concentration of styrene monomer had no influence in the investigated concentration range (20-50%). Crosslinking reactions performed at temperatures below the \( T_l \) transition had approximately constant vitrification doses while for reactions at temperatures above the \( T_l \) transition, vitrification dose decreased linearly. Obviously, the decrease in local order on breaking of the intramolecular interactions was favourable for crosslinking. Poly(hexanediol maleate), PHM, resins had significantly higher vitrification dose than poly(propandiol maleate), PPM, resin. The three dimensional networks in PHM resins is looser because double bonds in the polyester chain are further apart and the crosslinking density has to be higher than in PPM resin to result in the vitrification of the reacting system. The vitrification dose does not depend on the styrene content.

The differential scanning calorimetry (DSC) is generally accepted as the main method for detection and investigation of structural transitions in polymers but liquid-liquid transitions can be detected only upon careful analysis of thermograms. The readings of other experimental methods were taken after samples achieved the thermal equilibrium at a preset temperature so it is difficult to compare those results with the ones determined by DSC where the temperature changes linearly and the sensitivity of DSC decreases if the heating rate is decreased. The corresponding endothermic changes of the thermogram slope in the DSC traces of UP resins recorded at various heating/cooling rates were analysed and the corresponding \( T_l \) transition temperatures were determined from the intersection point of the tangents on the DSC trace above and below it. Since the temperature of any transition increases linearly with the heating or cooling rate extrapolation to a zero temperature point of the tangents on the DSC trace above and below it is possible. The readings of other absorption intensities with temperature are shown in Figure 8.

The IR absorption intensities decrease with temperature increase unless there is a structural transition, in which case an increase of absorption intensities related to that transition occurs (the increase of absorption intensities is seen as negative values on the subtracted spectra in Figure 8). Particularly intense changes in NIR spectra of the investigated resins were detected at 1430nm and between 1900nm and 2100nm corresponding to the absorptions of free and hydrogen bonded hydroxyl groups than in MID-IR. The disadvantage of NIR is the relatively complicated and somewhat uncertain assignation of the absorptions since they arise from various overtones and combinations of those in the MID-IR region. The NIR spectra of the UP resins were recorded at successively increasing temperatures. Two of those spectra, which were recorded well below and above the \( T_l \) transition and the spectra obtained by subtraction of higher-temperature spectra from lower-temperature spectra are shown in Figure 8.

![Figure 8 - NIR absorption spectra](image)

**TABLE 2 -** \( T_l \) transition temperatures and the apparent activation energies above and below it, of UP resins determined by different experimental techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>PPM</th>
<th>PHM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_l, K )</td>
<td>( E_{a1}, \text{kJ/mol} )</td>
</tr>
<tr>
<td>Electrical conductivity*</td>
<td>304</td>
<td>49.3</td>
</tr>
<tr>
<td>Viscosity *</td>
<td>304</td>
<td>58.2</td>
</tr>
<tr>
<td>DSC (heating) **</td>
<td>318</td>
<td>324</td>
</tr>
<tr>
<td>Rate of crosslinking</td>
<td>321</td>
<td>-1.95</td>
</tr>
<tr>
<td>NIR</td>
<td>303</td>
<td>310</td>
</tr>
</tbody>
</table>

*uncrosslinked samples, **extrapolation to zero heating rate, ***heating rate of 0.1K/min

\( \rho \), vitrification dose
temperature determined from the changes of the above mentioned absorptions was 33°C while in PPM resin $T_{II}$ transition occurred at 37°C reflecting the influence of alkyl chain length on the strength of intramolecular hydrogen bonding. The slopes of temperature dependencies of absorption maxima caused by carbon-carbon and carbon-hydrogen bonds shown in Figure 9, right, also changed somewhat at the transition temperature since the decrease of local order influenced the whole polyester coil.

The absorptions involved in H-bonding not only increased in intensity but also shifted to lower frequencies at the temperature of $T_{II}$ transition confirmed that this transition was caused by the reduction of hydrogen bonding strength. Shifts of the peak wavelengths of the IR absorptions at the phase transition temperatures have been encountered in numerous cases. A shift toward lower wavelengths, such as can be seen for absorptions at 1430, 1910, and 2090nm, especially if there is an inflection point, implies a change in conformation or interaction. The absorption at 1910nm had the greatest shift to lower wavelengths at the $T_{II}$ temperature; the shift was reproducible in heating and cooling cycles which confirms the change of H-bonding. The hydroxyl group absorption in the PHM at 1430nm also shifted in the temperature range of the $T_{II}$ temperature, similarly to 1910nm absorption. The absorption at 1945nm shifted only slightly which is an argument for its assignment to the carbonyl group that has fixed configuration, instead of its usual assignation to hydroxyl absorption and vice-versa. The intensities and positions of carbon–hydrogen and carbon–carbon absorptions that are not involved in H-bonding changed insignificantly at the $T_{II}$ temperature. The breaking of H-bonding and the decrease of local order increases the concentration and mobility of protons and other charge carriers which causes the observed decrease of the apparent activation energy of conductivity.

Various configurations of hydrogen bonds between carboxyl and/or hydroxyl end groups of polyester are possible. Two possibilities are shown in Figure 10. End groups can be connected to each other or a water molecule (remaining after polycondensation reaction) may be inserted. In the latter case the formation of relatively stable six-member rings is possible, which would contribute to local order below the $T_{II}$ and its intensity. At temperatures above $T_{II}$ such structures are broken and the movement of chain ends becomes easier.

Since intermolecular interactions are broken on dilution it is the easiest way to discriminate $T_{II}$ from $T_{I}$. On increasing the concentration of a solvent the $T_{II}$ temperature decreases until the transition disappear while it is generally accepted that the upper liquid–liquid transition is almost unaffected. Since we confirmed that in UP resins hydrogen bonding is the main interaction that short range order is based on, we tried to influence it at both inter- and intramolecular level by adding solvents with various affinity towards H-bonding. The absorptions involved in H-bonding not only increased in intensity but also shifted to lower frequencies at the temperature of $T_{II}$ transition. The increasing concentration of a solvent the $T_{II}$ temperature decreases until the transition disappear as can be seen in Figure 11 where the effects of addition of n-butanol are shown. On addition of some solvents like p-dichlorobenzene the $T_{II}$ temperature even increased, possibly because such solvents take part in H-bonding with end groups of the polyester chain and contribute to the local order. In such cases the intensity of $T_{II}$ increased as well. Other solvents that are either poor solvents for polyester or cannot form H-bridges did not influence the $T_{II}$ transition. This is the reason why the presence of styrene that is reactive solvent in UP resins had no effect on the appearance, temperature range, or intensity of the $T_{II}$ since it is a poor solvent for polyester and it cannot take part in hydrogen bonding.

The only other parameter that we found to influence the $T_{II}$ transition in UP resins is the nature of the polyester. The alkyl chain length between two ester groups is greater in PHM resins compared to PPM resin, resulting in more loosely packed PHM coils and lower energy needed for the chain ends to achieve freedom of motion and lower the $T_{II}$ temperature. In crosslinked samples the three-dimensional network impairs movement of polymer coil so $T_{II}$ becomes weaker as the crosslinking density increases and then it disappears. Since most part of a crosslinking reaction occurs on the coil surface, the behaviour of intramolecular interactions is almost unchanged and the $T_{II}$ can be detected even in completely crosslinked samples but its intensity is somewhat reduced and its temperature is slightly increased because the polyester chain is constrained by the network and more energy is needed for the $T_{II}$ to occur.

**FIGURE 9** - The temperature dependence of the normalized absorption intensities (to corresponding intensities at 14°C) of the PPM resin: carbonyl and hydroxyl absorptions (left), absorptions of carbon-hydrogen bonds (right) (The $T_{II}$ transition occurred at the greatest absorption intensity.)
be taken about the method and especially about heating or cooling with Tg below room temperature (in those with high Tg these tran-

ting. It distorts the conductivity curves that as a consequence differ
.

The liquid-liquid transitions should be looked for in any polymer

Some approaches to interpretation of experimental data like using

FIGURE 11 - The Arhenius plots of temperature dependencies of
electrical conductivities of the PPM resin and the same resin to

Concluding remarks

Although a part of our results was published before the microgel

type with T, below room temperature (in those with high Tg these trans-

The liquid-liquid transitions should be looked for in any polymer with T, below room temperature (in those with high Tg those trans-

REFERENCES


5. Pucic, I., Ranogajec, F.: Investigation of upper liquid-liquid transition in un-


16. Dulek, K.: Special features of network formation by chain crosslinking copoly-


17. Hsu, C. P., Lee, L. J.: Free-radical crosslinking copolymerization of styrene un-


26. Friedrich, K., Vinh Tung, C., Boiteux, G., Seytre, G., Ulanski, J.: Buildup of ther-


28. Warfield, R. W., Petree, M. C.: Use of electrical resistivity in study of polymeri-


Održan sastanak Plastics Europe Mediterranean

Jedna od ocjena s nedavno održanog sastanka Vijeća udruženja Plastics Europe Mediterranean je da je kriza europskoga industrijskog sektora prozila zenit.

U Rimu je početkom ožujka 2010. održan sastanak članica udruženja Plastics Europe Mediterranean na kojem su predstavnici strukovnih udruženja i tvrtki iz Bugarske, Grčke, Hrvatske, Italije, Rumunjske, Srbije i Turske razmijenili podatke i iskustva o utjecaju krize na nacionalne industrijalne proizvodnje i prerade plastike. Kretanja u zemljama Plastics Europe Mediterranean uvelike prate kretanja u ostalom dijelu Europe. Eurostatov podaci o zemljama Europske unije pokazuju da je proizvodnja kemijske industrije u EU-27 u 2010. godini smanjena za 11,4 %.

Ovdje izlaganje održao je Vittorio Maglia, glavni analitičar Federchimicae, talijanskog saveza kemijske industrije. Maglia je rekao kako je nedvojbeno da je vrhunac europske industrije u industrijskom sektoru dostignut potkraj 2009. godine. To se, međutim, ne može reći za gospodarstvo općenito, posebice ne za financijski sektor, u kojem su moguća daljnja negativna kretanja, u prvom redu povećanje nelikvidnosti koje će dovesti do daljnje povećanje nezaposlenosti. Blagi pozitivni pomaci europskoga industrijskog sektora ne mogu se temeljiti na razvoju novih proizvoda i presećenju proizvodnje u europske (ali i izvaneuropske) zemlje povoljnijega poslovnog okružja.

Na sastanku su dvije točke bile posvećene posebno osjetljivim temama: aktualnom europskom zakonodavstvu i očekivanim promjenama u području dodira plastike s hranom i unutarnjim izvozom europske i izvozom europske proizvode na izvoz iz zemalja u Europsku uniju. Ova sastanka je, u svrhu uočavanja tih promjena, potpuno propisana "PlasticsEurope Mediterranean".

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