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Crosslinked films from epoxy-functionalized latexes: relationship between crosslinking and film properties

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SUMMARY: Homogeneously epoxy-functionalized latexes were synthesized using free-radical emulsion copolymerization of methyl acrylate and glycidyl methacrylate, with semi-continuous addition of an emulsified mixture of the monomers. Intra-particle crosslinking was controlled by the addition of either a transfer agent or a difunctional monomer. The films derived from those latexes were crosslinked by the addition of various amounts of piperazine just before film formation. This water soluble diamine reacts with the epoxy groups at room temperature and plays the role of a crosslinking agent during the coalescence process. The amount of unreacted epoxy groups in the films was measured after 10 days by infra-red spectroscopy. Conversion of the amine group was derived and correlated with the initial amine over epoxy molar ratio ρ. The effect of ρ on swelling of the films and on their mechanical properties was studied. The properties were compared with those of films with intra-particle crosslinking only.

Introduction

Coatings from film forming latexes are obtained through a now widely accepted film formation mechanism that can be divided in three general steps1-3). Namely polymer particles concentrate upon water evaporation until they contact each others via an irreversible process. Further evaporation of residual water from the film voids induces particle deformation. With proper temperature and moisture conditions the original particle membranes collapse to form hydrophilic islands while major chain diffusion occurs between adjacent particles thus leading to a homogeneous film. Crosslinking inside the particles has been shown to reduce both kinetics and final extent of the chains interdiffusion4). However, the ultimate mechanical properties and solvent resistance of the films, which are the main targets of the latex-based coating industry, are highly dependent

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on the degree of chains interdiffusion$^{5,6)}$. Therefore, improvement of the film ultimate properties requires a proper balance between high crosslink densities (for higher moduli and solvent resistance) and high degree of chain diffusion (for lower brittleness). One of the current strategies is based on the use of the so-called post-crosslinkable latexes$^{5)}$. Two major systems can be distinguished based either on reversible crosslinking via polar/ionic interactions at the particles interfaces$^{7-10)}$ or on irreversible crosslinking through covalent bonding between reactive groups introduced within the particles during the polymerization process$^{5)}$. Among the latter systems one can further distinguish between self-crosslinkable latexes$^{11-18)}$, blends of co-reactive latexes$^{19-21)}$ or the addition of an external crosslinking agent into a reactive latex$^{21-24)}$.

There is a large variety of chemical functions that can be used for crosslinking purposes$^{5)}$. Among them, epoxy groups have been widely applied. The room temperature crosslinking reaction of epoxy functionalized latexes was previously reported by Okubo et al.$^{21)}$, by O'Brien et al.$^{23)}$, by Magnet$^{24)}$, and more recently by Geurts et al.$^{19,20)}$. In those studies, crosslinking was either performed by the addition of an amine functionalized second latex$^{19-21)}$ or induced by the addition of BF_3 etherate $^{21)}$ or of a water soluble diamine$^{23,24)}$. In the first case (blend of two reactive latexes), the reaction was shown to take place in a thin interfacial layer due to slow polymer-polymer interdiffusion and comparatively fast chemical reaction. In the latter cases, no surface concentration dependency was observed which was explained by the possible diffusion of the crosslinking agent inside the particles. Moreover, a significant increase of solvent resistance and tensile strength were observed.

In this work, homogeneously functionalized reactive latexes were prepared by methyl acrylate and glycidyl methacrylate emulsion copolymerization. The influence of particles pre-crosslinking on the film formation process as well as its effect on ultimate solvent resistance and mechanical properties of the film was first studied and used as a reference system. Room temperature post-crosslinking was obtained by adding various amounts of a hydrosoluble diamine, piperazine, to an un-crosslinked latex and to a pre-crosslinked one. The piperazine-induced crosslinking was investigated and compared with the former situation of intra-particle crosslinking. The study of its effect on the film formation process in relation with the film final properties is the main purpose of this work.

Experimental part

Reagents

Methyl acrylate (MA) and glycidyl methacrylate (GMA) were used as provided by Elf Atochem. Diethyleneglycol dimethacrylate (DEGDMA) was used as purchased from Aldrich and dodecanethiol (RSH, from Aldrich) was distilled before use. Sodium persulfate initiator was recrystallised twice before use. Anionic and nonionic poly(ethylene oxide) ($\overline{DP}_n$= 25) nonyl phenol surfactants were used as purchased from Witco, respectively Rewopol NOS25® (cmc = 1 g·dm^{-3} at 25°C, sulfate end-group) and Rewopal HV25® (cmc = 0.115 g·dm^{-3} at 25°C, hydroxy end-group). Ion-exchanged water was used in all recipes.

Emulsion copolymerizations and latex characterization

Emulsion copolymerizations of MA and GMA were carried out according to a semi-continuous process in a conventional 3 dm^3 thermostated glass reactor. Monomer-starved conditions were applied in order to maintain a constant copolymer composition leading to a homogeneous functionalization in the whole particle volume. Typical recipe (latex L4, Tab. 1) is the following: part of the water (216 g) and of the emulsifiers (NOS25® = 0.2 g and HV25® = 0.2 g) were first introduced into the reactor. Stirring speed was set at 150 rpm and nitrogen bubbling was started. After heating to 70°C, part of the initiator aqueous solution was introduced in one shot (10 wt % of the solution composed of water = 27 g and $Na_2S_2O_8$ = 2 g). After 5 minutes, the remaining initiator solution and the aqueous emulsion of the monomers, composed of water (248 g), NOS25® (2 g) HV25® (2 g), $NaHCO_3$ (0.8 g), MA (380 g), GMA (20 g, 5 wt-% of monomers) were continuously fed in two separate streams into the reactor during 4 hours. This corresponds to a rate of 2.78 10^{-2} g.s^{-1} monomer feed, which is far below the maximum polymerization rate. Once the addition was completed, the system was maintained at 70°C for 1 more hour in order to reach complete conversion of the monomers. Sodium hydrogenocarbonate was used to maintain the pH at 7 in order to avoid epoxy groups hydrolysis. In this situation, the epoxy content of latex L4 is 94 % of the original amount, as determined by infra-red spectroscopy.

For some experiments, crosslinking was controlled by the addition of various amounts of DEGDMA. For other experiments, molar masses were reduced by using dodecanethiol (RSH) as a transfer agent (See experimental conditions in Tab. 1). Both compounds were mixed with the monomers and thus continuously fed into the reactor.

Average particle diameter (D) and size distribution were measured by Quasi Elastic Light Scattering (QELS, MALVERN ZetaSizer 4).

Tab. 1. Experimental conditions and latex characteristics for the synthesis of latexes with various intra-particle crosslink densities (on the basis of the experimental conditions for latex L4)

Latex	[RSH], g (mol·dm^{-3})*	[DEGDMA], g (mol·dm^{-3})*	Solid content, wt %	D, nm	pH	Preserved epoxy groups, from FTIR, wt %
L4	0	0	44.8	190	6.9	94
TR2	0.2 (2.4 10^{-3})	0	45.1	187	7.2	93
TR3	0.4 (4.8 10^{-3})	0	45.2	192	7.0	95
TR4	0.8 (9.5 10^{-3})	0	44.6	189	7.3	92
TR5	1.6 (1.9 10^{-2})	0	45.3	193	6.7	82
TR6	3.2 (3.8 10^{-2})	0	44.7	175 unstable	6.5	81
R1	0	2.2 (2.2 10^{-2})	44.8	190	7.0	94
R2	0	4.35 (4.3 10^{-2})	45.5	189	7.3	95
R3	0	8.7 (8.6 10^{-2})	44.9	192	6.4	93
R4	0	17.4 (0.173)	46.0	189	7.2	94

* concentration in the monomer phase

Film formation and characterization

Films were formed at 30°C under normal pressure and 50% relative humidity, and film properties were measured after 10 days.

The epoxy content was measured in films by infrared spectroscopy (FTIR, NICOLET 605X) based on the 912 cm^{-1} epoxy absorption band after subtraction of a reference poly(methyl acrylate) spectrum. Calibration curves based on GMA were used for quantitative analysis.

Isothermal swelling measurements were performed by immersion of film samples (1 cm x 2 cm, 2 mm thick) in 50 cm^3 acetone during more than one week in order to quantify the weight fraction of insoluble material ($\varphi_i = W_2/W_0$) as well as the swell ratio ($\tau_s = (W_1 - W_2)/W_2$). W_0 represents the weight of the film before swelling, W_1 represents the weight of the swollen film and W_2 represents the weight of the dried film after swelling and elimination of the soluble part. According to the Flory-Rehner theory[25,26)], the average molar mass between crosslinks ($\overline{M}_c$) can be calculated from:

$$\overline{M}_c = -\frac{d_p \cdot V_s \cdot \left(F_2^{1/3} - \frac{F_2}{2}\right)}{ln(1-F_2) + F_2 + \chi F_2}$$

using[27)] : $\chi = 0.34 + \frac{V_s}{RT}(\delta_s - \delta_p)^2 = 0.341$ (T = 298 K)

$F_2 = \dfrac{W_2}{W_2 + \frac{d_p}{d_s}(W_1 - W_2)}$ - the volume fraction of crosslinked polymer

d_p : polymer density ($d_p = 1.29\ g \cdot cm^{-3}$) ; d_s : acetone density ($d_s = 0.79\ g \cdot cm^{-3}$).
$\delta_s = 19.8\ (J \cdot cm^{-3})^{1/2}$ and $\delta_p = 20\ (J \cdot cm^{-3})^{1/2}$ solubility parameters of acetone and poly(methyl acrylate), respectively
$V_s = 73.42\ cm^3 \cdot mol^{-1}$ (molar volume of acetone).

Extensiometry measurements (INSTRON 4301) were performed at 25°C under 75 % relative humidity at slow crosshead speed of 10 $mm \cdot min^{-1}$. Among the five samples tested the two extreme ones were disregarded and thus, the average maximum stress and elongation at break were calculated on the basis of three samples.

Results and discussion

Effect of intra-particle crosslinking on film formation and properties

Latex L4 obtained by the typical recipe described above leads to slightly crosslinked films. Preliminary experiments had shown that a spontaneous consumption of the intra-particle epoxy groups occurred during polymerization and that a direct relationship existed between the amount of consumed groups and the crosslink density of the films. The involved reaction is the hydrolysis of the epoxy group which leads to a diol able to further react with another epoxy group. In order to obtain a model system with completely soluble polymer, a chain transfer agent was used to limit the effect of the epoxy side-reaction to chain branching only. On the other hand, in order to control the intra-particle crosslinking, an additional difunctionnal monomer was used.

In the first case, increasing amounts of a conventional chain transfert agent, dodecanethiol (RSH), were added to latexes based on the recipe of L4 (Tab. 1). Thiol group can react with epoxy but this was not observed for the lowest concentrations of RSH (latexes TR2-TR4). This side reaction was evidenced for the highest concentrations only (TR5 and TR6), since the amount of unreacted epoxy groups decreased from 94 % to 82 % and 81 % respectively. For the last two cases, no insoluble polymer was recovered and, for instance, for latex TR5 the number average molar mass, measured by size exclusion chromatography, was 35 000 $g \cdot mol^{-1}$ with a broad molar mass distribution ($I_p = 4.4$). At the highest concentration of RSH (latex TR6), particles became less stable with a large content of coagulum. Values of τ_s and φ_i are reported in Tab. 2 as a function of the amount of transfer agent. It appears that the gel point can be located between the latexes TR4 and TR5 for which respective concentrations of transfer agent are $9.5\ 10^{-3}\ mol \cdot dm^{-3}$ and $1.9\ 10^{-2}\ mol \cdot dm^{-3}$ in the organic phase.

To control crosslink density in the particles, the difunctional monomer, DEGDMA, was used at different concentrations on the basis of L4 recipe (Tab. 1). Neither particle diameter nor ratio of preserved epoxy was modified by the use of this monomer. In contrast, swell ratio τ_s and fraction of insoluble material φ_i were drastically influenced as shown in Tab. 2. For instance, φ_i reached 93 % for the highest concentration. In these experiments, crosslinking is the consequence of a spontaneous reaction of the epoxy groups and of polymerization of DEGDMA.

The theoretical average molar mass between crosslinks can be calculated, assuming that all the consumed epoxy groups as well as all the added DEGDMA molecules are involved in crosslinking with formation of an ideal homogeneous network with tetrafunctional crosslinks :

$$\overline{M}_{c\,(th)} = \frac{W_p}{2\left(N_{epoxy} + N_{DEGDMA}\right)} \tag{1}$$

The reverse is proportional to a crosslink density (expressed in moles of crosslinks per g of polymer):

$$\frac{1}{\overline{M}_{c\,(th)}} = \frac{2 \cdot N_{epoxy}}{W_p} + \frac{2 \cdot N_{DEGDMA}}{W_p} \tag{2}$$

with : W_p = weight of polymer (g)
N_{epoxy} = mole number of crosslinked units resulting from epoxy reaction
(N_{epoxy} = half the mole number of reacted epoxy groups)
N_{DEGDMA} = total mole number of DEGDMA in the latex

The theoretical values can be compared with the experimental ones $\overline{M}_{c\,(s)}$ which are derived from swelling measurements and calculated using the Flory-Rehner theory. They are reported in Tab. 2 for the latexes R1 to R4 and it appears that $\overline{M}_{c\,(s)}$ is much higher than $\overline{M}_{c\,(th)}$. The crosslink density, $1/\overline{M}_{c\,(s)}$, is plotted versus ($2 \cdot N_{DEGDMA}/W_p$) in Fig. 1. As expected from equation (2) a linear relationship is observed. However the slope (0.09) is much smaller than the theoretical value of 1 calculated when assuming that all the DEGDMA double bonds are participating in crosslinking. A possible explanation would be that only part of this monomer is really active (9 % in this case). Since monomer-starved conditions are applied during the synthesis, internal viscosity of the particles is very high due to high polymer to monomer ratio throughout the polymerization. Therefore, the second double bond of an incorporated DEGDMA unit may be kept unreacted because diffusion of macroradicals towards its location would be hindered. However, as much as 91 % of the added DEGDMA bearing an unreacted double bond does not seem reasonable and no residual double bond was effectively detected by infra-red spectroscopy. Another explanation would be that crosslink density is in fact close to its theoretical value (complete conversion of both double bonds of DEGDMA) but that swelling measurements lead to unexpectedly high values of τ_s and thus to overestimated average molar mass between crosslinks. Similar conclusions were also drawn by Zosel in the case of poly(n-butyl methacrylate) latex crosslinked with methallyl methacrylate$^{4)}$.

Tab. 2. Characteristics of the films with various intra-particle crosslink densities.

Latex	Preserved epoxy groups , wt %	τ_s	φ_i	$\overline{M_c}$ (s) From swelling	$\overline{M_c}$ (th) theoretical
L4	94	13	0.75	89 300	47 300
TR2	93	14	0.68	101 500	-
TR3	95	18	0.52	156 200	-
TR4	92	26	0.30	292 600	-
TR5	82	soluble	0	-	-
TR6	81	soluble	0	-	-
R1	94	11	0.81	67 000	15 020
R2	95	10	0.86	56 800	9010
R3	93	8	0.89	38 500	4980
R4	94	6	0.93	23 300	2630

The main reason is that $\overline{M}_{c\,(th)}$, calculated using the Flory-Rehner equation, does not properly describe the structure of the network formed in the polymer film. The network is not homogeneous as crosslinks cannot be randomly distributed in the film owing to the fact that only intra-particle crosslinking takes place and that particles are connected to their neighbours by chain diffusion through the interfaces and formation of entanglements.

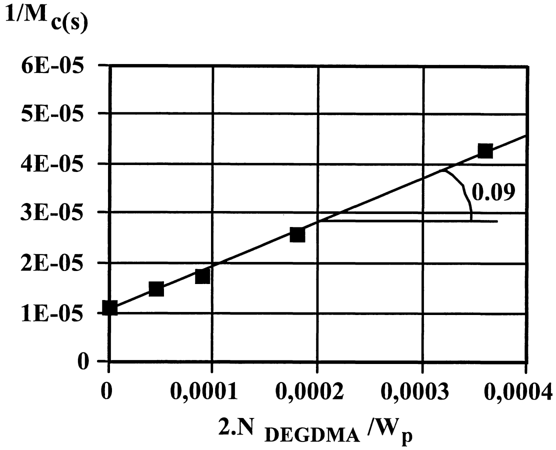

Fig. 1: Crosslink density derived from swelling measurements versus the amount of added DEGDMA ($2.N_{DEGDMA}/W_p$) for films L4, R1, R2, R3 and R4

Expectedly, upon immersion into a good solvent, films should disintegrate and lead back to the individual swollen particles. However, this behaviour is not observed since, as mentionned by Zosel$^{4)}$, it would require an unprobable cooperative and complete disentanglement. Nevertheless, it is likely that this situation leads to a different swelling ability between the particle crosslinked cores and the uncrosslinked interphase leading thus to films with higher swelling than expected. In other words, intra-particle crosslinking leads to films with poor solvent resistance.

Uniaxial elongation experiments were performed above T_g for films obtained from seven latexes with various intra-particle crosslink densities. Stress-strain curves are plotted in Fig.2. Film TR5 has a typical behaviour of non crosslinked rubber with high strain and low stress at break. In comparison, when crosslink density is increased but still kept relatively low (TR4, TR3, TR2, L4), strain at break decreases and tensile strength increases to reach a maximum value for the more crosslinked films TR2 and L4. For films derived from the DEGDMA crosslinked latexes R3 and R4, there is still the expected decrease of maximum strain but now tensile strength decreases with increasing crosslink density. When the polymer is less crosslinked than TR2 or L4, the coalescence process is not hindered. Adjacent particles are strongly connected to each others by chain interdiffusion and entanglements formation. Similarly to homogeneously crosslinked elastomers, tensile strength increases when overall crosslink density is increased. In contrast, when high intra-particle crosslink densities are reached, it is known that coalescence process is slowed down and that formation of entanglements is prevented owing to the presence of short dangling chains[4)]. Thus, cohesion between particles is poor and breaking is supposed to occur in the inter-particle domain.

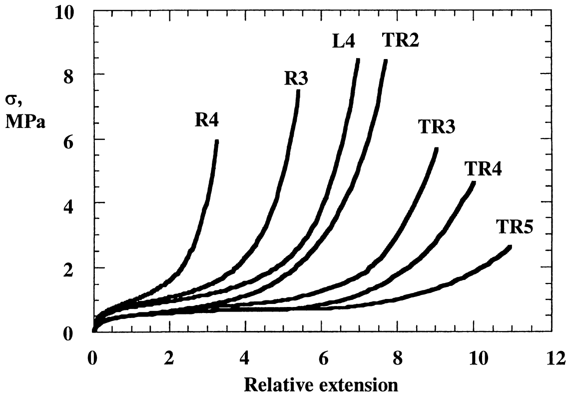

Fig. 2: Stress-strain plots for films derived from latexes with various intra-particle cross-link densities: TR5, TR4, TR3, TR2 (with a transfer agent), L4 (crosslinked via epoxy side-reaction), R3 and R4 (crosslinked with DEGDMA)

Effect of post-crosslinking on film formation and properties

A water-soluble diamine, piperazine, was added to latexes just before film formation in order to induce crosslinking by reaction with the epoxy groups at room temperature. The behaviour of two latexes of the previous series was studied with various amounts of piperazine, in concentration lower than the stoichiometry. The ratio ρ indicates the mole number of added amine groups (two times the mole number of piperazine) to the mole number of preserved epoxy. The first latex is TR5 (series N, Tab. 3) in which polymer is completely soluble and the second one is L4 (series P, Tab. 4), which is crosslinked by spontaneous reaction of the epoxy groups.

For both series, the fraction of unreacted epoxy groups in the films was measured after 10 days by IR spectroscopy and the values are reported in Tab. 3 and 4 together with the derivated conversion of the amine groups and the results of swelling measurements (τ_s and φ_i).

Tab. 3 : Characteristics of the films from latex TR5, crosslinked with piperazine (Series N)

Film	ρ = [NH]/[epoxy]	Epoxy groups consumed by reaction with –NH, %	Conversion of the amine groups, %	τ_s	φ_i	$\overline{M_c}$ (s) From swelling	$\overline{M_c}$ (th) Theoretical
N0	0	0		soluble	0	-	-
N1	0.15	12	80 (?)	soluble	0	-	-
N2	0.23	36	100	soluble	0	-	-
N3	0.45	48	100	11.3	0.77	70 100	7 700
N4	0.61	56	92	3.5	0.87	9 050	6 200
N5	0.80	62	78	3.0	0.90	6 900	5 600
N6	1.21	86	86*	1.8	0.94	2 800	4 030

* based on $\rho = 1$ which corresponds to the maximum amount which can be converted

Tab. 4. Characteristics of the films from latex L4, crosslinked with piperazine (Series P)

Film	ρ = [NH]/[epoxy]	Epoxy groups consumed by reaction with -NH, %	Conversion of the amine groups, %	τ_s	φ_i	$\overline{M_c}$ (s) From swelling	$\overline{M_c}$ (th) Theoretical
P0	0	0		13	0.75	89 300	47 300
P1	0.13	12	90	10	0.78	56 800	16 430
P2	0.26	22	85	8.5	0.81	42 800	10 650
P3	0.35	30	86	6	0.87	23 300	8 300
P4	0.53	42	79	3	0.90	6 900	6 250
P5	0.70	48	69	2	0.94	3 400	5 550
P6	1.06	56	56*	1.5	0.99	2 050	4 840

* based on $\rho = 1$ which corresponds to the maximum amount which can be converted

When the latex is not initially crosslinked (series N), reaction between epoxy and amine is quantitative until a ratio $\rho = 0.45$. For higher amounts of piperazine, the extent of reacted epoxy is lower than ρ indicating incomplete reaction, and conversion of the amine after 10 days slightly decreases when ρ is increased. For the film N6 where $\rho = 1.21$, 86 % of the epoxy groups have reacted and since particles are homogeneously functionalized, this indicates that crosslinking takes place not only in a superficial shell but inside the particles. When particles are initially crosslinked (series P), the reaction is never quantitative and amine final conversion is always lower than for the corresponding uncrosslinked latex. For instance, when $\rho = 1.06$, only 56 % of the epoxy groups have reacted.

From swelling measurements, it is obvious that the addition of piperazine leads to the formation of crosslinked films. For the uncrosslinked latex, gelation occurs when ρ is set between 0.23 and 0.45 (see Tab. 3) and in the case of the pre-crosslinked one, the insoluble polymer fraction varies from 0.75 to 0.99 when ρ is increased from 0 to 1.06 (Tab. 4). Moreover in both cases, for the higher values of ρ, swelling of the films is drastically reduced since very small values of τ_S are observed. On the basis of this swell ratio, $\overline{M_c}_{(s)}$ can be calculated. Results are reported in Tab. 3 and 4 together with the theoretical values $\overline{M_c}_{(th)}$, calculated with the assumption that two consumed epoxy groups are involved in a crosslink. In Fig. 3, experimental and theoretical crosslink densities (respectively $1/\overline{M_c}_{(s)}$ and $1/\overline{M_c}_{(th)}$) are plotted versus the fraction of epoxy groups which have reacted with the diamine. Interestingly, two behaviours can be observed depending on the fraction of consumed epoxy groups. Indeed, for reacted epoxy ratios smaller than approximately 0.4, there is no insoluble polymer in films derived from uncrosslinked particles and there is a slow increase of the measured crosslink density ($1/\overline{M_c}_{(s)}$) for pre-crosslinked particles: values and slope are both smaller than the theoretical ones. For values of reacted epoxy larger than 0.4, there is a strong increase of $1/\overline{M_c}_{(s)}$ with the fraction of consumed epoxy groups for both film series: slope is larger than that of the theoretical curve and, especially for films of the series P, values are also larger than the theoretical ones.

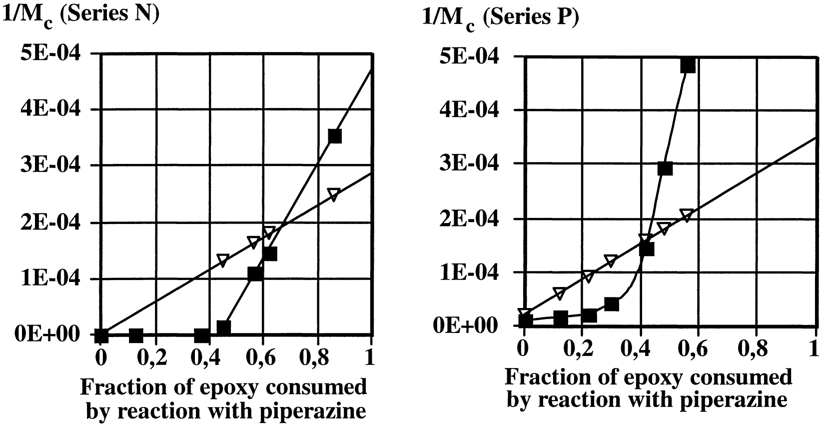

Fig. 3: Experimental (þ) and theoretical (V) crosslink densities derived from swelling measurements versus the fraction of epoxy groups which have reacted with piperazine. Series N corresponds to the uncrosslinked latex TR5 and series P to the spontaneously precrosslinked latex L4

Complementary informations are provided by stress-strain curves plotted in Fig. 4 and 5 for the films crosslinked with the larger amounts of piperazine. For the initially uncrosslinked latex (films N), when ρ is increased, tensile strength increases while elongation at break decreases. In contrast to intra-particle crosslinking, piperazine-induced crosslinking results in an increase of tensile strength of the films when high enough crosslink densities are reached. This is the indication of a good cohesion in the inter-particle region. Films behave as homogeneously crosslinked rubber.

Surprisingly, for the pre-crosslinked latex (films P), an increase of the amount of piperazine leads to a decrease of the mechanical properties i.e. a decrease of both tensile strength and elongation at break and therefore a decrease of fracture energy. Mechanical properties are close to those observed for the highly pre-crosslinked latex films using DEGDMA.

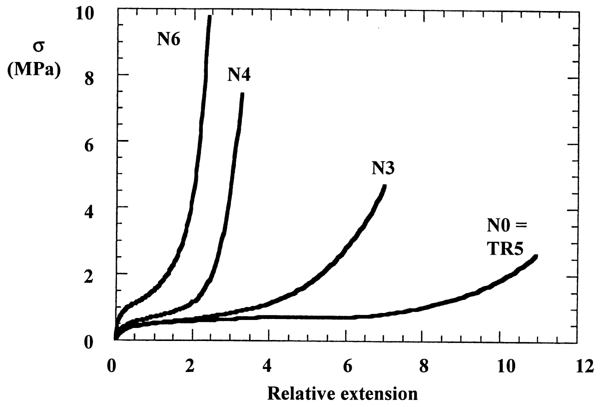

Fig. 4: Stress-strain plots for films of the series N: N0, N3, N4 and N6 with various amounts of added piperazine

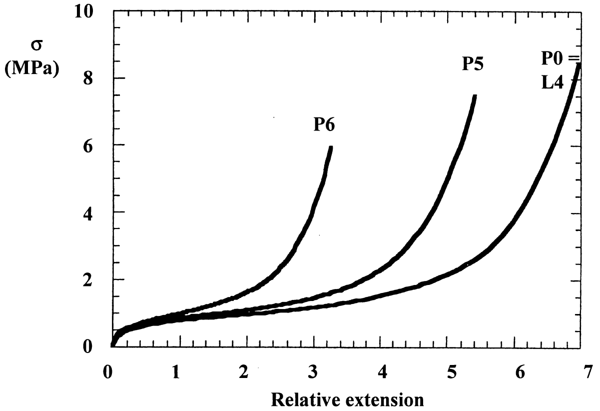

Fig. 5: Stress-strain plots for films of the series P : P0, P5 and P6 with various amounts of added piperazine

To summarize, for series N, when ρ is lower than 0.45, reaction of the diamine is quantitative indicating that the diffusion processes are not hindered. The reaction does not lead to insoluble material which might be due to the low average molar mass of the polymer. In contrast, for higher ratios of added amine, reaction is still not quantitative after

10 days and final conversion of the amine decreases when ρ is increased. This means that the diffusion processes are progressively slowed down which can be explained by the simultaneous formation of a dense network. In that situation, swelling of the films is drastically reduced with respect to that of films with only intra-particle crosslinking. Therefore, it is reasonable to consider that crosslink density is not homogeneous but decreases from the boundary to the core of the particles. Crosslinking also takes place inside the particles since the reaction concerns as much as 86% of the epoxy groups for the highest value of ρ. The existence of this dense network at the periphery of the particles prevents swelling as well as extraction of the polymer located in the inner part which explains why swelling ability of the film is drastically reduced beyond a certain extent of the crosslinking reaction. Moreover, tensile strength is also increased indicating a good cohesion in the inter-particle domain. This means that interdiffusion of the chains through the particles boundaries occurs sufficiently before complete gelation of the system.

For series P, because of the initial intra-particle crosslinking, diffusion and coalescence processes are slowed down even for low amounts of piperazine, resulting in lower yields of amine consumption. In that case it can be supposed that the epoxy groups in the inner part of the particles are not involved. The decrease of tensile strength with the increase of crosslink density may indicate that, for pre-crosslinked particles, piperazine-induced crosslinking essentially takes place at the interface owing to slow diffusion processes. This leads to poor cohesion of the films.

Conclusion

The addition of a water-soluble crosslinker to a functionalized latex enables the formation of crosslinked films with improved mechanical properties and solvent resistance. It has been shown that for initially uncrosslinked particles the crosslinking reaction is not restricted to a thin interfacial layer but concerns also the inner part of the particles. In this case, the system leads to crosslinked films combining high crosslink density and good cohesion owing to large chain interdiffusion in the interparticle domain. In contrast, the combination of intra-particle crosslinking and post-crosslinking leads to improved solvent resistance but to a degradation of the mechanical properties explained by a poor cohesion of the films.

Acknowledgements

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