

Rheological and Thermogravimetric Studies of the Crosslinking Process of Functionalized Acrylic Latexes

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ABSTRACT: Acrylic latexes are among one of the most widely used binders in the chemical bonding of textile nonwovens. This article investigates the crosslinking process of functionalized acrylic latices to understand the binder behavior during the processing of nonwovens and in the final product. Two techniques are used: rheology, to follow the structural development within the latex polymer, and thermogravimetry, to investigate the reaction through the weight loss resulting from the formation of evolving side products. The work has been carried out on latices functionalized by two crosslinking agents: *N*-methylol acrylamide

(NMA) and *N*-methylol methacrylamide (NMMA). The results highlight the importance of the nature of the crosslinking agent, especially, its hydrophilic character, and the influence of the pH of the latex dispersions on the crosslinking mechanism, as well as on the final mechanical properties of the latex films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1117–1123, 2006

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INTRODUCTION

Nonwovens (NW) are, among technical textiles, the class of materials that represents the biggest sales progression: they are used in a wide range of applications from disposable to durable including hygiene, medical, automotive, transport, and civil engineering. In chemically bonded NW, the fibers are bonded together by means of a latex binder, which is usually crosslinked to ensure semipermanent or permanent properties in the final product.

Acrylic latices are among the predominant binders since they can be designed to provide either stiffness or softness, and also confer excellent properties to the NW. These latices consist in general of three or four monomers. One indeed associates very often with the basic monomers one or more monomers known as "functional" in relatively small quantity and whose role is primarily to functionalize the basic copolymer, for instance, to improve the mechanical properties of the latex film. During the crosslinking treatment at high temperature of the chemically bonded NW, bond formation between the polymer macromolecules will

lead to a stiff three-dimensional structure: the viscoelastic properties of the latex will therefore change. The chemical and mechanical properties of the crosslinked polymer are thus different from those of the uncrosslinked one.^{1–4} From a chemical point of view, crosslinking brings an improvement in the strength to solvents and to high temperatures.^{5,6} From a mechanical point of view, crosslinking brings an increase in the breaking resistance and in the Young's modulus, as well as a reduction in the elongation at break.^{7,8}

Self-crosslinking of the majority of acrylic latices is obtained via *N*-methylol groups, usually present in the form of *N*-methylol acrylamide (NMA).⁶ Generally, this monomer is copolymerized with the basic monomers to form latices able to be crosslinked upon heating. The methylol functions can then undergo self-condensation by heat treatment⁹ or by combined effects of a heat treatment and an acid catalysis.^{10,11}

The mechanism of the condensation of methylol groups occurs in two stages (Fig. 1).^{12–14} The first stage leads to the formation of an ether bond (compound I) by elimination of a water molecule, and the second stage, to that of a methylene bond (compound II) by elimination of a formaldehyde molecule.

In a previous study,¹⁵ we worked with commercial latices, but for the present work, we have developed our own model formulations of acrylic latices. The

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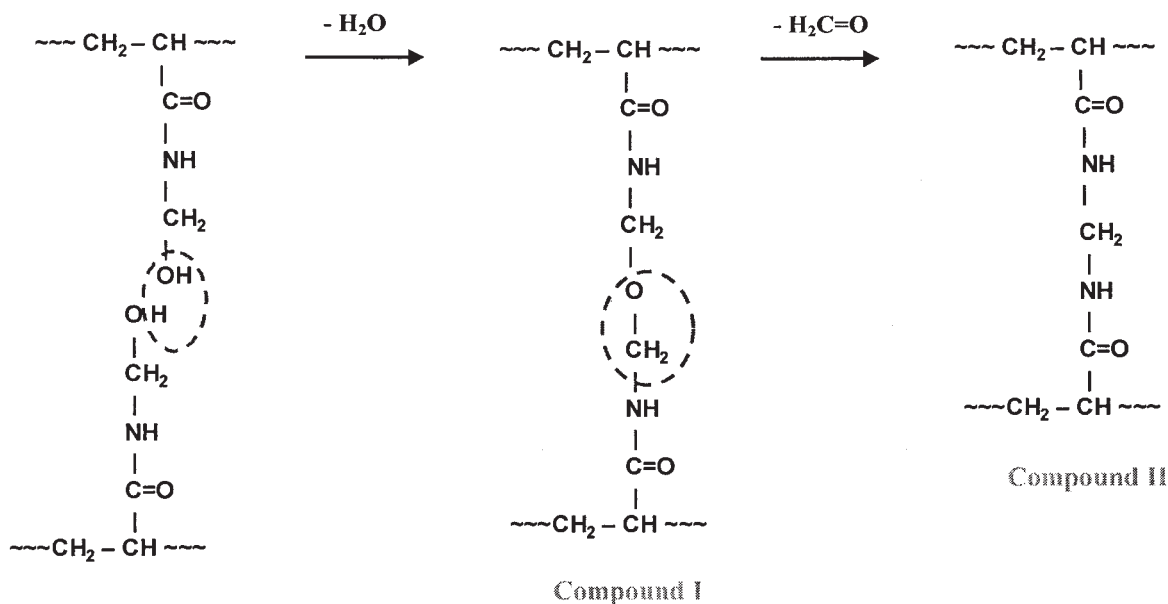


Figure 1 Self-condensation mechanism of methyloxy functions.

purpose here is to better understand the latex crosslinking mechanisms obtained by copolymerization of methyl methacrylate (MMA) with butyl acrylate (BA) and including some amounts of NMA or NMMA (*N*-methyloxy methacrylamide). NMMA is a functional monomer having the same crosslinking function as NMA, but is more hydrophobic. We will examine more particularly the influence of these crosslinking agents on the viscoelastic properties of the latex films obtained from the latex dispersions. Concurrently, crosslinking reaction will be investigated using a novel procedure by thermogravimetric analysis (TGA).¹⁵ Finally, tensile tests will be used to complete this study and should enable us to establish correlations between the mechanical properties of films and their structure.

EXPERIMENTAL

Materials

Synthesis of chemical binders

Anionic latices based on MMA and BA were synthesized via a semicontinuous reaction scheme. The synthesis was carried out in a 500-mL glass reactor vessel

equipped with a condenser, a nitrogen inlet, an inlet for the introduction of reactants, and a high torque stirrer. The stirring rate was 250 rpm under a nitrogen flow. In the following, the values are given as percentage weights with respect to the total weight of the monomers. Monomer quantities (MMA and BA) were determined using Fox's law¹⁶ to obtain a T_g of -20°C , and the dry solid content has been set at 40%. The quantity of NMA or NMMA used as crosslinking agents amounts to 3.5%. Stabilization of the latex is provided by an ionic surfactant, sodium dodecyl sulfate (SDS) introduced at 3%. The reaction is initiated by 0.2% sodium persulphate. Sodium bicarbonate (0.45%) helps to maintain the ionic force and the pH constant during the reaction. The initiator, sodium bicarbonate, 5% of SDS, 10% of monomers, and 2/3 of water were placed in the reactor at a temperature of 70°C , under nitrogen for 30 min. A mixture composed of 90% of monomers, the NMA, 1/3 of water, and 95% of SDS was prepared and was fed to the reactor gradually during polymerization (6 h). When monomer addition was complete, the latex was gradually cooled to ambient temperature.¹⁷

The liquid form of the latex obtained has a milky white aspect and transparent, soft and slightly tacky films can be obtained from it by drying at room tem-

TABLE I
Characteristics of Chemical Binders

Latex	Crosslinking agent	pH	Zeta potential ^a (mv)	Dry content (%)	T_g ($^\circ\text{C}$)
SC NMA	NMA	8.4	-34.0 ± 1.0	41	-12.6 ± 0.2
SC NMMA	NMMA	8.1	-31.3 ± 0.9	41	-19.3 ± 0.5

^a Average on 5 tests.

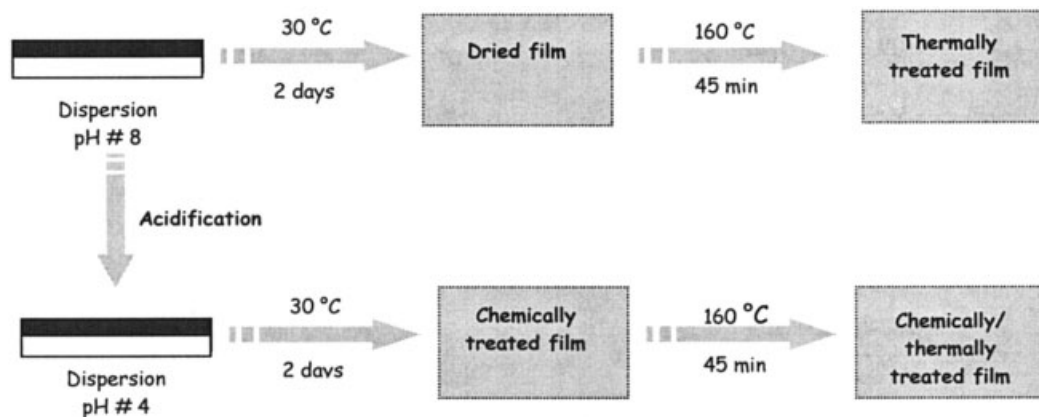


Figure 2 Preparation of various latex films.

perature. The values of T_g have been checked by differential scanning calorimetry. Experiments were carried out under helium flow (50 mL/min) on a TA Instrument DSC-2920 from -70 to 200°C and at a heating rate of $20^\circ\text{C}/\text{min}$. The test is done on the latex film coalesced at room temperature and then treated at 160°C for 45 min. The Zeta potential gives a measure of the stability of the latex particles: this property was measured on a Zetasizer 3000 apparatus. If the Zeta potential is >20 mV in absolute value, the emulsions can be considered to be stable electrostatically, which is the case of both latices. The latex characteristics obtained are given in Table I.

Film preparation

As mentioned in the introduction, the crosslinking of our latex films is catalyzed in acid medium. However, the pH of the synthesized latices is very slightly basic (~ 8), so that the pH of the latex solution obtained had to be adjusted to 4 by addition of a hydrochloric acid solution (1M).

Four sets of latex films have thus been prepared and analyzed: they are designated as dried, thermally treated, chemically treated, and chemically/thermally treated (Fig. 2). They are prepared as follows: the liquid latex has been spread out on a Teflon recipient and left to dry at room temperature for 2 days. The solid film obtained constitutes the dried film. Thermally treated films are obtained from this dried film after a curing cycle of 45 min at 160°C in an oven. For chemically treated films, the pH of the synthesized dispersion has been adjusted to 4, before film preparation. Chemically/thermally treated films result from these dried films after a curing cycle of 45 min at 160°C in an oven.

Film characterization

Tensile testing

Tensile measurement is carried out on dried and treated films on an MTS DY/2M dynamometer, using

a 10 N load cell at a crosshead speed of 100 mm/min. Typical film dimensions are equal to $4.2 \times 1 \times 20$ mm³. A pretension of 0.1 N is applied to the sample before each test.

Rheological study

An ARES rheometer from Rheometric Scientific has been used. This strain-controlled rheometer has a special device for testing solid films in rectangular torsion. The film is held between two fixtures (Fig. 3): the lower fixture oscillates at a given strain and frequency and a transducer mounted on the upper fixture measures the resulting torque on the sample. The strain limits are strongly dependent on sample dimensions, which are here approximately equal to $4.4 \times 1 \times 16$ mm³. A slight tension (~ 0.01 N) has been systematically applied to the film before beginning each test, especially at high temperatures, because the film softens and becomes slack. Corrections in the sample dimensions were made accordingly.

Different types of tests have been performed on the films: strain sweep at different frequencies to determine the linear viscoelastic region, frequency sweeps, and transient tests.

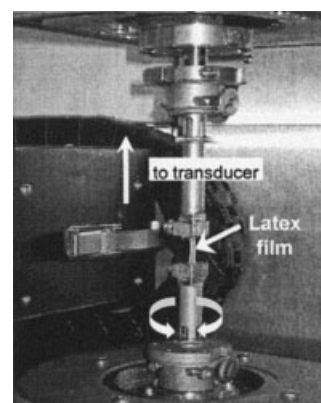


Figure 3 Set-up of film sample on rheometer.

TABLE II
Mechanical Characteristics Obtained in Uniaxial
Tension on Latex Films

	SC NMA	SC NMMA
Stress at break (MPa)		
Dried	2.5 ± 0.3	2.8 ± 0.3
Thermal	3.0 ± 0.4	3.4 ± 0.5
Chemical	3.5 ± 0.3	4.7 ± 0.2
Chemical/thermal	5.0 ± 0.4	5.9 ± 0.7
Elongation at break (%)		
Dried	661 ± 59	600 ± 55
Thermal	578 ± 55	358 ± 73
Chemical	656 ± 53	395 ± 23
Chemical/thermal	291 ± 43	233 ± 35
Elastic modulus (MPa)		
Dried	0.71 ± 0.08	0.94 ± 0.06
Thermal	1.02 ± 0.12	1.37 ± 0.41
Chemical	1.66 ± 0.31	2.20 ± 0.13
Chemical/thermal	2.43 ± 0.11	4.52 ± 0.44

Thermogravimetric analysis

TGA is performed on dried and treated latex films, using a TA 2950 Instruments Thermobalance at 10°C/min from 25 to 200°C under air flow (40 mL/min). Samples (about 10 mg) were placed in open platinum pans. The sensitivity of the apparatus makes it possible to detect and measure very small losses or profits of weight (<1 µg); the precision of the balance is ±0.1%. Precision of temperature measurements is ±0.5°C.

RESULTS AND DISCUSSION

Force–elongation curves

The mechanical characteristics of latex films according to the nature of the crosslinking agent or to the treatment are given in Table II.

Comparison between heating effect/pH effect

The results reveal the significant influence of the pH of filmication on the mechanical properties of the films. For chemically treated films (acid pH), the elastic modulus values are higher than those obtained on dried films (increase of 134% for latex functionalized by NMA and for latex functionalized by NMMA). This phenomenon also leads to a reduction in elongation at break and an increase in stress at break. Furthermore, the results show that chemically treated films have better mechanical properties than thermally treated ones.

This suggests that acidification of the liquid latex favors the onset of the condensation reaction between the methylol groups (CH₂—OH), which are sufficiently close. Indeed, during filmication, the localized functional groups on the surface of the particles are in

intimate contact with each other, and the presence of chemical species of acid nature is enough to catalyze the crosslinking reaction.¹⁰

Nevertheless, it is the combination of chemical treatment and thermal treatment that leads to the optimum crosslinking, confirmed by the highest values of elastic modulus and lowest values of elongation at break. For the latex functionalized by NMA, the increase in modulus is of 242% and the reduction in elongation at break is about 56% (compared to those of dried films). For latex functionalized by NMMA, the increase in modulus is of 381% and the reduction in elongation is about 61% (compared to those of dried films).

A study based on the characterization of polymer particles obtained by copolymerisation of BA with either styrene or MMA and including a few NMA percents showed that the pH at which the film has been formed is an important parameter in determining all the mechanical properties of films: low pH resulted in an increase in the elastic modulus values and stresses, while higher temperatures were necessary to cause significant crosslinking of the polymer.⁶

Influence of the polarity of the functional monomer

The results observed on dried films and treated films (chemically or thermally or both) highlight an improvement of the mechanical properties in favor of latex films functionalized by the NMMA, a monomer that is less hydrophilic than the NMA: the elastic modulus and breaking stresses of films functionalized by NMMA are higher than those of films functionalized by NMA, while the elongations are lower. We can thus assume that the polarity of the functional monomer is a determining factor on the structure of films, playing a significant role during the filmication and the various treatments of films.

Bonardi¹⁰ proposed to increase the incorporation of the methylol groups in the particles for styrene/BA latex to decrease the hydrophilic character of the functional monomer. Thus, the film resulting from latex had a honeycomb-like network, leading to better mechanical properties.¹⁸

Hidalgo et al.¹⁹ studied the influence of the hydrophily of the functional monomer on the kinetics of polymerization in emulsion of styrene and the *n*-butylacrylate. They noted that the increase in the hydrophoby of the functional monomer lead to a better homogeneity in copolymer and that the most hydrophilic monomer homopolymerized in a separate phase.

All these studies suggest that if the functional monomer is more lipophilic, it will be incorporated more easily and homogeneously in the particles. This provides an explanation for the better mechanical properties of latex films functionalized by NMMA

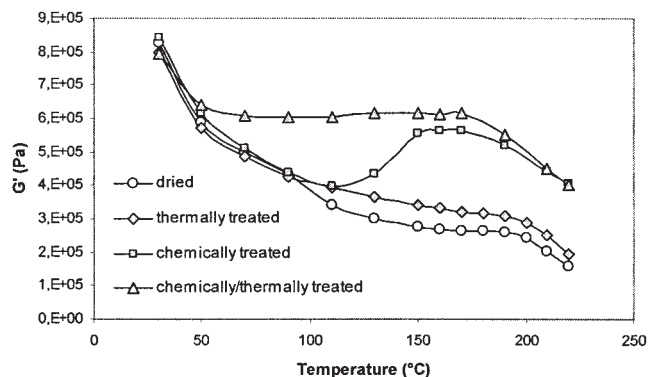


Figure 4 Variation of G' with temperature for dried and treated SC NMA latex films.

compared with those of NMA, before and after treatment (chemical and/or thermal).

Rheology

The dried and cured film samples have been submitted to strain sweeps at different frequencies and temperatures. These preliminary tests have allowed us to determine the optimum strain and frequency to use throughout the rest of the study to ensure linear viscoelasticity. These conditions are: frequency = 10 rad/s and strain = 1.5% and have been employed in the remaining tests.

To follow the crosslinking process, a test sequence has been performed on the film samples. This test consists of a series of isothermal tests at different temperatures ranging from 30 to 200°C. The duration of each isotherm is about 5 min. The sample is allowed to reach thermal equilibrium between each temperature step before starting the test. We have then calculated $G'(T)$, the average value of all the experimental points of G' at a given temperature T . $G'(T)$ is then plotted against temperature.

Figure 4 presents the results obtained for latex SC NMA: the films have undergone various treatments (dried, chemically, and chemically/thermally treated).

For the dried and thermally treated films, G' decreases when temperature increases from 50 to 110°C, and a plateau region is obtained in the 110–190°C temperature range. Beyond 190°C, a rapid fall in G' is observed, probably, as a result of sample degradation. For the chemically/thermally treated film, the plateau region is obtained instead in the 50–170°C temperature range. It can be noted that at a given temperature, the chemically/thermally treated film has a higher modulus than the dried and thermally treated films. The results are different for the chemically treated film: G' decreases when temperature increases from 50 to 110°C, and then increases in the temperature range of 110 up to 170°C. We can, therefore, attribute this

increase in modulus to the crosslinking phenomenon: crosslinking brings an increase in mechanical properties due to the formation of a three-dimensional network.

The rheological curves can be interpreted in terms of the different transition states of the films. For the dried and thermally treated films of SC NMA latex, the first temperature range corresponds to the glass transition: we observe here only the end of this transition. To observe the whole transition, we have to move below the glass transition temperature of this latex, which is around -13°C . The second region corresponds to the rubber plateau: G' does not vary with temperature. In the third and last region, the rapid fall of G' observed can be attributed to material degradation.

The behavior of latex SC NMMA (Fig. 5) is quite different. Up to 130°C, a decrease of G' is observed with the thermally and chemically/thermally treated films, followed by a plateau modulus. For the dried and chemically treated films, G' decreases when temperature increases, and then increases in the temperature range of 150–200°C for the dried film and in the temperature range of 110–130°C for chemically treated film.

First, we can note that the G' values of SC NMMA latices are higher than those obtained with the SC NMA latices. These results confirm those already obtained during the study of tensile behavior of the films: the polarity of the functional monomer has an influence on the latex structure (see section "Influence of the polarity of the functional monomer").

With the SC NMA latex, the increase in G' , attributed to crosslinking, is observable only on chemically treated film, but in the case of SC NMMA latex, this behavior is observed for both chemically treated and dried films. The acidification treatment leads to a lowering in the crosslinking temperature (110°C for chemically treated film against 150°C for dried film). These results, thus, confirm that the crosslinking of the two latices is catalyzed in acid medium.

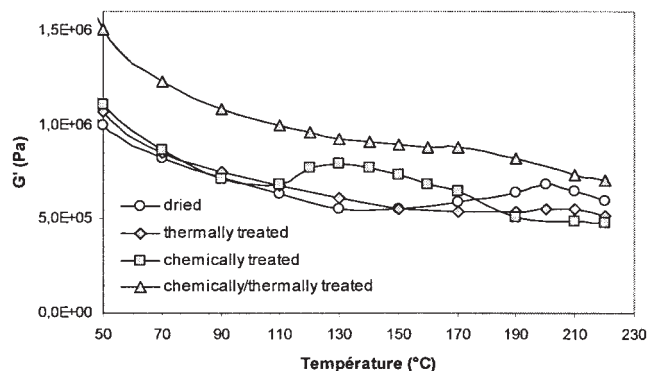


Figure 5 Variation of G' with temperature for dried and treated SC NMMA latex films.

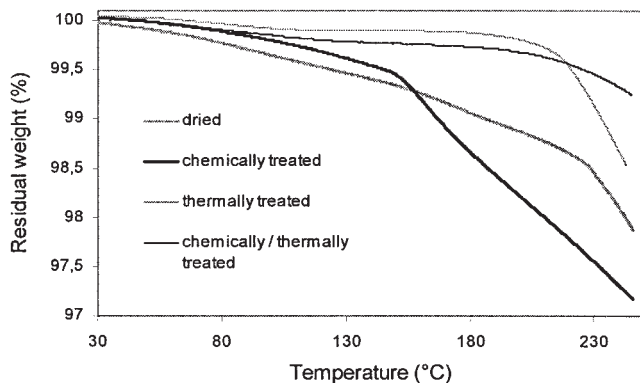


Figure 6 Residual percentage weight in TGA (SC NMA latex).

Moreover, we also notice that the zone of crosslinking for the chemically treated film of SC NMMA latex is smaller than that of chemically treated film of SC NMA latex (20 against 60°C). It would thus seem that the kinetics of crosslinking is faster with the NMMA used as crosslinking agent. We may assume that the methylol functions coming from NMMA within the latex macromolecular chains are more accessible than those introduced by NMA, thus facilitating the self-condensation reactions of the methylol functions during the thermal treatment. This assumption was also reported in other studies.^{10,20,21} They highlight an incorporation of the functional monomer in the particles, which is all the more facilitated and homogeneous when this monomer is hydrophobic.

Thermogravimetric analysis

Thermogravimetry can be used to investigate the crosslinking reaction of polymers. For example, Miles and Cowie²² used this technique to investigate itaconate copolymers, which during crosslinking gave rise to volatile materials and could, thus, be studied by measuring the residual weight fraction during cure. In the case of acrylic latices functionalized by NMA or NMMA, self-crosslinking occurs by the formation of ether or methylene bonds, and water and formaldehyde are released during this polycondensation reaction (Fig. 1). There is, hence, a weight loss, which can be quantified by TGA.

The results obtained with SC NMA latex are depicted in Figure 6: the residual percentage weight is represented against temperature. A weight loss is observed up to 100°C for the four samples, but the dried and the chemically treated films present the highest loss (1.1 and 1.8%, respectively). This corresponds to water evaporation from the films: the dried and the chemically treated films have the highest water content, as could be expected, since the thermally and the chemically/thermally samples have both already lost

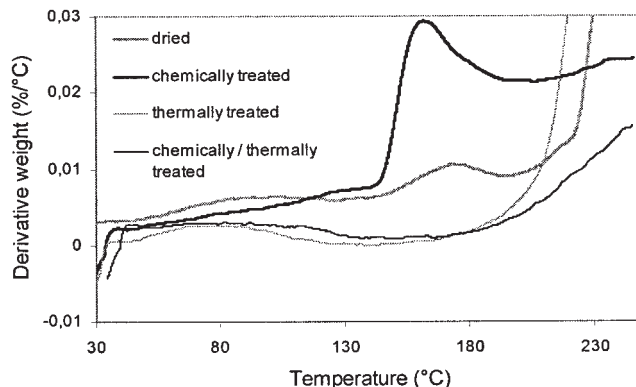


Figure 7 Derivative weight loss against temperature (SC NMA latex).

practically all their water content during their respective thermal treatments. The same results are obtained with the SC NMMA latex.

The weight loss due to drying and self-crosslinking phenomenon is more pronounced on the derivative weight curve where peaks are significant and easily observable (Figs. 7 and 8).

For the dried films, we note the presence of two peaks on the TGA curves. The first peak, very broad, lies from 60 to 130°C for SC NMA latex and from 70 to 150°C SC NMMA latex. This first peak corresponds to the evaporation of the residual water present in the sample. This peak is, however, more significant with the latex functionalized by NMMA. The appearance of the second peak is much more marked: it lies from 150 to 200°C for SC NMA latex and from 170 to 220°C for SC NMMA latex. For the SC NMMA latex, this peak can be attributed without ambiguity to the crosslinking phenomenon. This observation confirms the rheological results where an increase in G' is observed in the same temperature range. For the SC NMA latex, the transition of G' is not observed in the temperature range where this second peak appears on the TGA

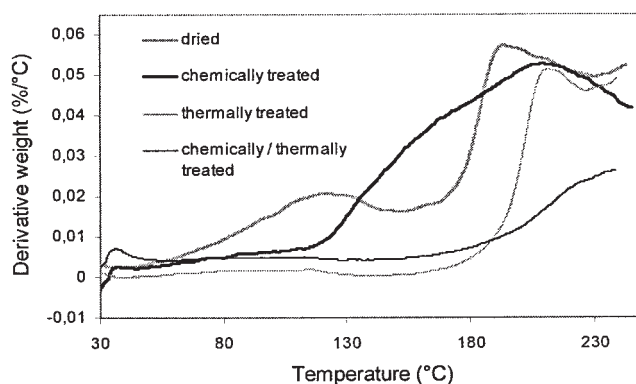


Figure 8 Derivative weight loss against temperature (SC NMMA latex).

curve. It thus seems that thermogravimetry is more sensitive than rheology to characterize the modifications due to the crosslinking of materials.

For thermally treated films, no peak appears on the TGA curve for SC NMA latex. We can thus assume that on this film, crosslinking is complete. The results obtained in rheology are thus confirmed by the TGA results. On the other hand, for SC NMMA latex, a peak appears in the high temperature range and lies from 180 to 230°C. It would thus seem that on this film, crosslinking was incomplete. TGA once again seems to be more sensitive than rheology to characterize this type of phenomenon. Indeed, no transition of G' was observed in this temperature range.

For chemically treated films, we observe only one peak on the TGA curves, spreading out from 140 to 200°C for SC NMA and from 115 to 250°C for SC NMMA. If we compare the appearance of this peak with the evolution of G' , it appears clearly that the latter can be attributed to the crosslinking of latex insofar as the increase in G' occurs very close in this temperature range. The different experimental conditions between the TGA and rheology (heating speed of 10°C/min for the TGA and isothermal stages in rheology) explain the shifts in temperature of the phenomena observed between the two techniques.

For chemically and thermally treated films, the TGA curves do not show any peak, whatever the latex considered. For these films, we can thus say that crosslinking is completed. This observation confirms the rheological results.

CONCLUSIONS

The study of crosslinking of acrylic latices through several techniques of characterization gave various information on this process.

Tensile behavior of the different latex films prepared reveals the significant influence of pH of filmification on the mechanical properties of films. This study confirms that crosslinking is catalyzed in acid medium.

The two techniques—rheology and thermogravimetry—employed in this work to investigate the crosslinking process give complementary and agreeing results and the temperature range in which crosslinking occurs can be determined by both methods. The results showed that NMMA-functionalized acrylic latices crosslinked at lower temperatures com-

pared with those of NMA-functionalized ones, and that acid catalysis makes it possible to lower their crosslinking temperature. The hydrophilic nature of the crosslinking agent and the pH of the dispersions give clues to explain the mechanical and rheological properties of the latex films. For these acrylic latices, the pH of the dispersion seems to be a more determining factor for crosslinking than the thermal treatment used to activate the process, but it is the combination of acidification/thermal treatment which provides the optimum crosslinking.

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