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Design of Pressure-Sensitive Adhesives by Free-Radical Emulsion Copolymerization of Methyl Methacrylate and 2-Ethylhexyl Acrylate. 1. Kinetic Study and Tack Properties

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Pressure-sensitive adhesives must develop simultaneously two conflicting properties: adhesion and cohesion. To fulfill these requirements, it is imaginable to synthesize suitable materials by free-radical emulsion copolymerization of complementary monomers: methyl methacrylate (MMA) and 2-ethylhexyl acrylate (EHA). The copolymerization kinetics of various MMA/EHA mixtures is studied using a "batch" process. In all cases, the reaction proceeds at a steady-state rate and the copolymer composition (evaluated by ¹H NMR analysis) is quite proportional to the conversion degree. The tack properties of films obtained by coalescence of the latexes are evaluated using a "mechano-optical tack tester", which allows one to determine the tack strength (F_{tack}), the tack energy (G_{tack}), and the actual contact area (A) as functions of time. These tack properties are correlated with the copolymers and adhesive film structures.

Introduction

The tack properties of pressure-sensitive adhesives (PSA) result from the association of two conflicting behaviors: instantaneous adhesion and cohesion. Instantaneous adhesion of the adhesive film is expected in the sticking step, whereas cohesion gets involved in the release step, when the adhesive film splits off completely (without any stuck mark) from the surface of the substrate. In the sticking step, quite instantaneous wetting of the substrate surface and spreading under weak shearing stress are required from the adhesive film, which implies high flow ability. On the contrary, because the adhesive film dissipates the deformation energy in the release step, viscoelastic properties are involved, implying convenient bulk cohesion. The bulk properties depend on such characteristics of the adhesive material as glass transition temperature T_g , average molar mass \bar{M} and \bar{M}_e (between entanglements), molar mass distribution and structure, or morphology of its polymeric base.^{1–5}

Formulation, by mixing polymeric bases with additives (plasticizers, tackifiers, and fillers), is very often used to achieve suitable PSA. The specific synthesis of

polymers able to behave as PSA is also possible.^{6,7} Within this framework, we propose to synthesize high molar mass (in order to get sufficient cohesion) copolymers, by free-radical emulsion copolymerization of methyl methacrylate (MMA) and 2-ethylhexyl acrylate (EHA). Because the corresponding homopolymers are not compatible with each other, suitable separations between hard (PMMA) and soft (PEHA) phases can be expected, provided convenient structuring of the copolymer particles can be achieved.

A first part of this paper deals with the kinetic study of batch emulsion copolymerization of MMA and EHA in various molar ratios. As described for other comonomer systems,^{8–12} the batch process affords controlled particle structures, depending on the diffusion coefficient of the monomers in water and on their respective reactivity ratios (r_1 and r_2). The second part of the paper deals with the characterization of adhesive films obtained by coalescence of the latexes. Their tack properties have been evaluated using a mechanical-optical tack tester (MOTT, from GRL departments of ATOFINA), which allows accurate determinations of the tack strength

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(F_{tack}), tack energy (G_{tack}), and actual contact area (A).^{13,14} In the end, the discussion of the experimental data leads to correlation of the tack properties with the structure of the copolymers.

Experimental Techniques

Chemicals. MMA (99% purity, stabilized by 10–100 ppm methyl hydroquinone) and EHA (98% purity, stabilized by 10 ppm methyl hydroquinone) were purchased from Aldrich. Before use, the monomers were distilled and stored at 0–5 °C. Initiator (potassium persulfate, KPS), emulsifier (sodium dodecyl sulfate, SDS), and buffer (disodic phosphate, Na_2HPO_4) were purchased from PROLABO and were used without further purification.

Elaboration of Adhesive Materials. *Process.* The syntheses were carried out in a 250 mL glass reactor implemented with a mechanical stirrer, a flux condenser, a nitrogen inlet, and a septum intended to take samples for kinetic studies. Reaction mixtures were heated at 80 °C and stirred at 400 rpm, under nitrogen flow. In a typical experiment, a mixture of 100 mL of distilled water, 0.06 g of Na_2HPO_4 , and 0.4 g of SDS was stirred and heated at 80 °C, for about 10 min. Then, a solution of 0.1 g of KPS in 20 mL of distilled water was added, and the copolymerization was started by pouring 40 g of a comonomer mixture into the reactor. Various reaction conditions have been studied with molar ratios in MMA/EHA units ranging from 100/0 to 0/100.

Kinetic Study. Aliquot samples were taken from the reaction mixture at different polymerization times. They were poured into aluminum foil dishes, and the polymers were precipitated by methanol, in the presence of small amounts of hydroquinone (to prevent any further polymerization). The copolymers were dried to constant weight under reduced pressure in an oven at 100 °C. From the copolymers and aliquot sample weights, the monomer conversion was calculated and recorded as a function of time.

Composition of the Copolymers. ^1H NMR analyses, in CDCl_3 , using an AC 250 MHz Bruker spectrometer, allowed one to determine the composition of the copolymer samples, by integration of the characteristic signals of EHA and MMA units at respectively 3.90 and 3.60 ppm.

PSA Samples. Films (200 μm thickness) were prepared by coating aluminum sheets with the final latexes (100% conversion), drying in an oven under reduced pressure, and cutting off rectangular 20 mm \times 30 mm pieces.

Characterization of PSA Films. *Differential Scanning Calorimetry.* T_g values of the materials were determined using a Mettler Toledo DSC 30 system (implemented with a low-temperature cell and TC10/TC15 units), with 30–40 mg samples being scanned from –100 to +160 °C at a 10 °C/min heating rate.

*Tack Measurement with the MOTT.*¹³ Tack measurements were achieved at controlled temperature, using the MOTT (Figure 1). As shown on a typical curve (Figure 2), the tack strength (F_{tack}) is the maximum force (F) measured during the pulling up of a quartz probe, after contact with the adhesive film for a determined contact time (t_c), under a controlled contact stress (P_c). The tack energy (G_{tack}) is given by

$$G_{\text{tack}} = \frac{r}{A} \int_{t_i}^{t_f} F(t) dt \quad (A, \text{m}^2; r, \text{m/min}; t, \text{min})$$

with r the pulling controlled rate ($r = 0.5 \text{ mm/s}$) and A the actually wet probe area.

The main originality of the apparatus is its ability to measure, at any time, the prism area actually wet by the adhesive. For this purpose, the quartz prism is designed to transmit the light beam of a photodiode quite completely when

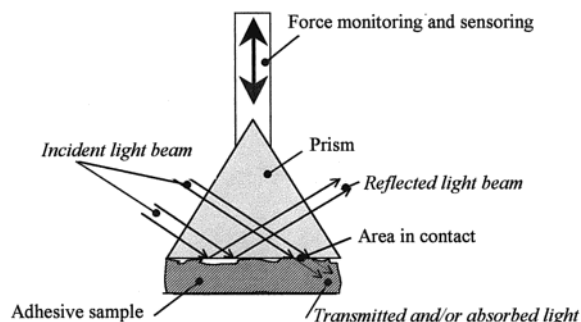


Figure 1. MOTT: Principle of the simultaneous measurement of the tack force and of the wet area.

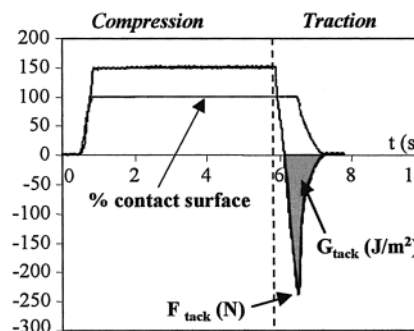


Figure 2. Typical "tack" curve: contact strength $F_c = 150 \text{ N}$ and contact time $t_c = 5 \text{ s}$.

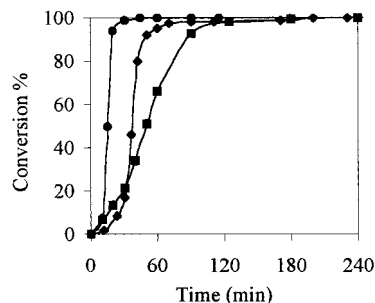


Figure 3. Kinetic study: typical weight conversion vs time (●, PMMA [100/0]; ♦, 50/50; ■, PEHA [0/100]); steady-state interval between 15 and 20% and 80–90% conversion.

the prism is not at all in contact with the adhesive sample and to transmit a part of the light beam, proportional to the free area, when the prism is in contact with the PSA.

Results and Discussion

Composition of the Copolymers. The evolution of the weight conversion versus time has been studied for a tenth MMA/EHA feeds (initial composition ranging from 100/0 to 0/100 MMA/EHA molar ratios). Figure 3 gives the conversion vs time curves for typical 100/0, 50/50, and 0/100 MMA/EHA feeds. The whole curves range between 100/0 and 0/100 limits. They are S-shaped whatever the initial composition, with a steady-state interval (linear conversion vs time evolution, i.e., constant polymerization rate) between 15 and 20% and 70–80% conversion. As shown by Figure 4, the steady-state polymerization rate (R_p) is strongly dependent on the amount of MMA units incorporated in the adhesive material. It increases markedly beyond a threshold corresponding to 50% MMA units.

As concerns the instantaneous composition of the latexes, Figure 5 (corresponding to a typical 50/50 MMA/

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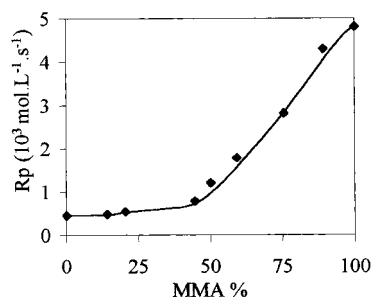


Figure 4. Dependence of the copolymerization rate R_p (as measured in Figure 3 type curves) on the percentage of MMA units in the initial feed.

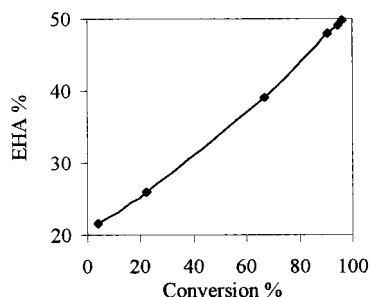


Figure 5. Composition of polymers versus overall monomer conversion for a 50/50 molar feed.

EHA feed) indicates that the EHA molar ratio (F_{EHA}) is proportional to the overall comonomer conversion. The polymers seem to incorporate EHA units progressively. The experimental results are in fair accordance with both the reactivity ratios ($r_1 = 2.00$ for MMA radicals and $r_2 = 0.13$ for EHA radicals)¹⁵ and the solubility of monomers in water (16 g/L for MMA versus 0.8 g/L for EHA). EHA units are logically incorporated in the latex particles slower than MMA units. However, the question arises as to whether the latex particles are only constituted of mixtures of PMMA and PEHA homopolymers or contain MMA/EHA copolymers.

The comparison of the ^1H NMR spectra of the materials, on the one hand, and of the homopolymers (synthesized in the same experimental conditions), on the other hand, can give an answer. The spectra of the materials show a splitting of the characteristic peaks of MMA (a) and EHA (b) units (Figure 6). The signal corresponding to the carboxymethyl groups of MMA units is divided into two signals: (a_1) at 3.58 ppm which is also found in the NMR spectrum of PMMA and (a_2) at 3.64 ppm. Signal a_1 can be assigned to MMA units linked to each other in homopolymeric PMMA sequences, whereas signal a_2 can be assigned to MMA units linked to EHA units in copolymeric sequences. The same trend is observed for the EHA signal, divided into two signals at 3.94 and 3.91 ppm, allowing one to conclude that chain segments containing both monomers (i.e., copolymers) are actually formed in addition to homopolymeric segments.

Because the ratio of copolymer/homo-PMMA sequences increases with the conversion, a heterogeneous structure is expected for the copolymers: MMA-rich sequences are formed in the early stages of the reaction, with the macromolecules growing progressively richer

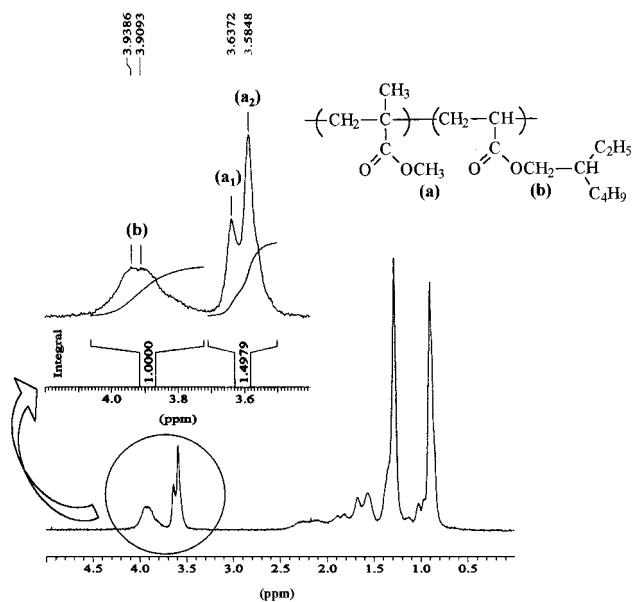


Figure 6. Typical NMR spectrum of the polymeric material.

and richer in EHA units, which leads to a large diversity of the chain compositions.

Particles Structure. In some examples,¹⁶ it is assumed that, as the polymerization proceeds, the first formed macromolecules may be encapsulated by the latest formed ones. Large polymeric radicals diffuse very slowly in the particles, and their terminal SO_4^- function (issuing from the water-soluble initiator) stays at the particle–water interface. So, the polymer chains remain close to the particle surface until they are pulled away from the surface to the inside by new growing chains.

If a second monomer is introduced in the reactor after consumption of the first one, core–shell particles can be obtained. When the comonomers are allowed to react simultaneously (i.e., in batch processes), homogeneous particles are expected, unless the reactivities and diffusion rates of the monomers are different or unless the monomers are unable to solvate the copolymer. Then, encapsulated type particles are likely to be formed.

Because MMA/EHA systems fulfill both conditions, we assume that a composition gradient is achieved at the latex particle level: each particle grows richer and richer in EHA sequences from the core, mainly composed of MMA-rich (about 75% MMA) sequences, to the shell, mainly composed of EHA-rich sequences.

Adhesive Films Structure. The broad glass transition domains (onset–offset ΔT_g up to 80 °C) in the DSC analyses of the films evidence an overall structural homogeneity, associated with a marked submicron-scale heterogeneity. Depending on the composition, tendencies to phase separations (two different T_g domains, as shown in Table 1) can be detected with MMA-rich microdomains in a copolymer continuous phase (for MMA-rich compositions) or copolymer microdomains in an EHA-rich continuous phase (for EHA-rich compositions).

Tack Properties. *Methodology.* Setting evaluations have been made for a 40/60 MMA/EHA composition, in

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Table 1. Glass Transition Temperatures of the Adhesive Films

MMA/EHA molar ratio	T_g (°C)		
	EHA-rich copolymer	statistical copolymer	MMA-rich copolymer
100/0			+127
90/10		-14	+101
75/25		-15	+69
60/40		+1	
50/50		-5	
45/55		-10	
40/60	-46	-2	
30/70	-53	-12	
15/85	-53	-15	
0/100	-64		

Table 2. Tack Parameters of the Film Obtained from a 45/55 MMA/EHA Composition

measurement conditions	25 N and 5 s	25 N and 60 s	150 N and 5 s	150 N and 60 s
tack strength (N) \pm 15 N	136	175	219	257
tack energy (J/m ²) \pm 40 J/m ²	284	337	418	537
A (%) \pm 10%	64	74	95	100

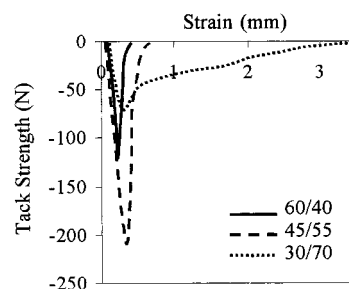
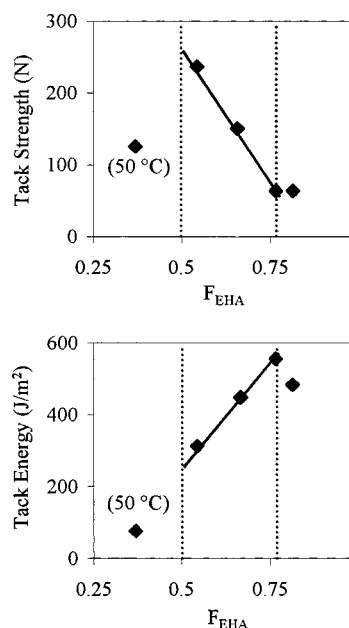
various experimental conditions: short (5 s) or long (60 s) t_c ; low (25 N) or high (150 N) F_c . They were intended to analyze the influence of these experimental features on the measured tack parameters and to state the actual meaning of the tack parameters: F_{tack} (N), G_{tack} (J/m²), and A (%).

As shown in Table 2, F_{tack} and A behave in the same way: strong dependence on F_c and weaker dependence on t_c . Both parameters express the ability of the adhesive film to wet the MOTT probe, with F_{tack} measuring also the adhesion strength. Because either F_{tack} or A seem to be independent of t_c at 150 N F_c , this contacting load will be preferred for all further experiments. Contrary to F_{tack} , G_{tack} depends strongly on t_c . It can be assumed that, within 5 s, the film may not relax the contacting deformation, which implies that G_{tack} is close to the actual adhesion energy. Within 60 s, the film may relax the squeeze flow deformation in its own bulk and behave as a viscoelastic material, allowing G_{tack} to express not only the adhesion energy but also the cohesion energy of the film. Then, more accurate G_{tack} values are likely to be obtained in 5 s t_c experiments.

Influence of the Copolymer Composition. Different behaviors have been observed, depending on the MMA units/EHA units ratio in the polymeric material.

From 100/0 to about 50/50 composition, the film cohesion is so high that no tack can appear: $G_{\text{tack}} = 0$ J/m². Typically, the 60/40 material does not have any tack at room temperature, in agreement with its too high $T_g = +1$ °C, when suitable values are 3–5 tenths or so degrees below room temperature.^{2,3} At 50 °C, some tack properties arise, but A %, F_{tack} , and G_{tack} stay quite low.

Between 50/50 and 25/75 compositions, tack properties are effective (as shown in Figure 7), with a clear evolution from a rather elastic behavior (high F_{tack} , low A %, and low G_{tack}) to a rather viscoelastic behavior (low F_{tack} , high A %, and high G_{tack}). In the latter cases, fibrillation phenomena occur during the release step, involving high film deformation and energy dissipation. Within the tack domain, F_{tack} decreases when F_{EHA}

**Figure 7.** Tack curves for 60/40 (at 50 °C), 45/55, and 30/70 MMA/EHA films (150 N and 5 s).**Figure 8.** Tack properties of adhesive films versus composition (150 N and 5 s).

increases, because of loss of cohesion, while G_{tack} increases, because of the enhancement of the viscoelastic dissipation of energy (Figure 8).

From 25/75 to 0/100 compositions, cohesive failure of the bonded joints occurs, leaving adhesive residues onto the MOTT probe. The adhesive films have no more tack but only pegosity (instantaneous adhesion without cohesion), and neither F_{tack} nor G_{tack} is still meaningful.

Conclusion

The free-radical emulsion copolymerization of complementary monomers, cohesion-favorable MMA, and adhesion-favorable EHA has been studied in terms of the dependence of kinetics and copolymer composition on the reaction conditions. Because of the different reactivities and diffusion rates of the monomers, heterogeneous copolymers are formed, composed of more or less MMA- or EHA-rich sequences. Because of the insolubility of the copolymers in the monomers, encapsulated-type latex particles are obtained, with MMA-rich cores, EHA richer and richer layers, and a EHA-rich shell.

Coalescence of the latexes gives films whose structure and properties can be related to the particle structure. The overall homogeneity of the films hides a submicron-scale heterogeneity, with more or less MMA-rich microdomains dispersed in less or more EHA-rich continuous phases.

Films issuing from MMA-rich compositions (100/0 to 50/50 MMA/EHA) do not have tack properties, because of their excess of cohesion. Conversely, films issuing from EHA-rich compositions (25/75 to 0/100 MMA/EHA) do adhere to many substrates but are not cohesive enough to allow further neat (without any stuck residue) separations. Intermediary compositions (50/50 to 25/75 MMA/EHA) give suitable PSA films, whose behavior ranges from rather elastic to rather viscoelastic. The former should be used as multiple stick and release, "post-it" type, PSA when the later should be used as permanent, peel-resistant, PSA.

Finally, we have shown that suitable PSA may be obtained directly by free-radical emulsion copolymerization and that their tack properties may be monitored by the reaction conditions.

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