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Tack Properties of Methyl Methacrylate and 2-Ethylhexyl Acrylate Emulsion Copolymers: Influence of the Polymerisation Process

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SUMMARY: With the aim of designing inherently tacky macromolecular structures, emulsion free-radical copolymerisations of methyl methacrylate and 2-ethylhexyl acrylate were achieved. Indeed, such comonomers should give materials cohesive and adhesive enough to behave as suitable Pressure Sensitive Adhesives. Kinetic studies of the comonomers consumption and evaluations of cohesion and tack allowed to study the influence of the process on the composition of the dispersed particles on the one hand and on the properties of the coalesced latexes on the other. With regard to the tack properties, the release mechanisms ranged from outright to progressive fibrillationwise failure.

Introduction

The tack properties[1-4)] of Pressure-Sensitive Adhesives (PSA) depend on two conflicting characteristics, adhesion and cohesion, whose association is generally obtained by mixing polymeric bases with such additives as plasticizers, tackifiers and microcrystalline waxes. To check the actual influence of macromolecular structures and morphologies onto the tack properties, suitable copolymers must be synthesised. Because the polymerisation procedure can exert a strong influence on the structure of the latexes that are eventually obtained,

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emulsion copolymerisation is a quite convenient route to obtain good controlled PSA. The behaviour of films obtained from various emulsion copolymers was studied using a specifically designed device. Then the correlation between the copolymerisation process and the tack properties was established.

Emulsion copolymerisation process

From methyl methacrylate MMA (cohesive homopolymer) and 2-ethylhexyl acrylate EHA (sticky homopolymer) as comonomers, various syntheses were carried out from 70/30 (volume ratio) water/comonomers (50/50 molar ratio) feeds, with sodium dodecyl sulphate (SDS) as the emulsifier. Three different copolymerisation processes were applied:

- seeded emulsion copolymerisation, in two steps (MMA as the seed and EHA as the subsequent feed); in accordance with the incompatibility of polyMMA and polyEHA, phase segregations were observed in the resulting materials, which were turned out to be unusable as PSA,
- batch copolymerisation (**"B"**),
- continuous feed copolymerisation (**"C"**), in which the monomers and the initiator were slowly added into the reactor previously filled with water, SDS and a buffer.

Both batch and continuous feed processes yielded quite complete conversion of the monomers. In both cases, the kinetics of the overall consumption of the monomers was evaluated by means of mass measurements of precipitated samples, whose average composition was determined from ^1H NMR analyses. As the main result, it was observed that the batch process is characterised by a progressive enrichment (almost linear) of the copolymer in EHA units, with the degree of conversion. As well the reactivity ratios ($r_{MMA} = 2$ and $r_{EHA} = 0.5$, as calculated from the *Q-e* Alfrey-Price system), the solubilities in water (16 g/l for MMA versus 0.8 g/l for EHA) account for the slower incorporation of EHA in the latex particles. Contrary to the batch process, the instantaneous composition was almost constant in the continuous feed process (Fig 1). Thus the overall composition of the latex particles was homogeneous in this case, when it was heterogeneous in the case of the batch process, as generally observed[5-9).

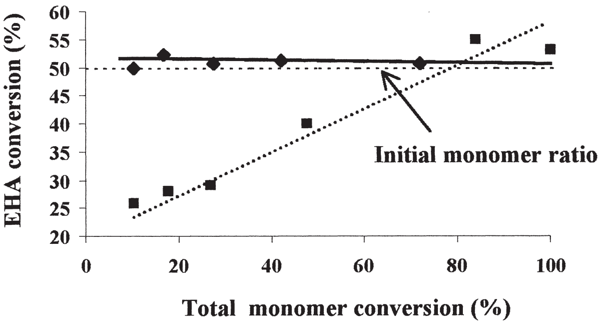

Fig. 1: EHA instantaneous conversion (calculated from the comparative integration of ^{1}H NMR signals) as a function of total monomer conversion
◆: **"C"** process, ■: **"B"** process

The differences between the overall particle compositions were confirmed by Differential Scanning Calorimetry (DSC) studies of films (100-200 µm) obtained by coating (unadhering surface) and drying (at 40°C) the **"B"** and **"C"** latexes. Both film types present a glass transition domain, about - 30°C, but the domain is much broader for **"B"** type films (up to 100°C wide) than for **"C"** ones (less than 40°C wide).

Tack properties

Owing to the heterogeneity of the latex particle structure, the films are likely to behave as physically cross-linked elastomers. Actually, tensile stress-strain analyses (room temperature; NFT 51-034 type probes; 500 mm/min stress rate) enabled observation of typical PSA behaviour: elastic modulus from 10^5 Pa (**"C"**) to 7.10^5 Pa (**"B"**), ultimate force from 4 N (**"C"**) to 20 N (**"B"**) and ultimate strain from 500% (**"B"**) to 1000% (**"C"**), the better homogeneity of **"C"** type latexes accounting for the differences between the film performances.

As concerns the tack properties, the "Mechano-Optical Tack Tester" MOTT (an original device developed by GRL Departments of ELF-ATOCHEM) allows accurate determination of the tack strength (*F*), the tack energy (*G*) and the actual contact area (*A*), for tests at controlled contact force (*Fc*), contact time (*tc*) and release rate (*r*)$^{10,11)}$. *F* (N) is the maximum strength measured during the release phase. *G* (J/m^2) is given by:

$$G = \frac{r}{A}\int_{t_i}^{t_j} F(t)dt \qquad (A : m^2\ ;\ r : m/min\ ;\ t : min)$$

Typical tack measurement curves are given in Fig. 2 (**"B"** films) and Fig. 3 (**"C"** films).

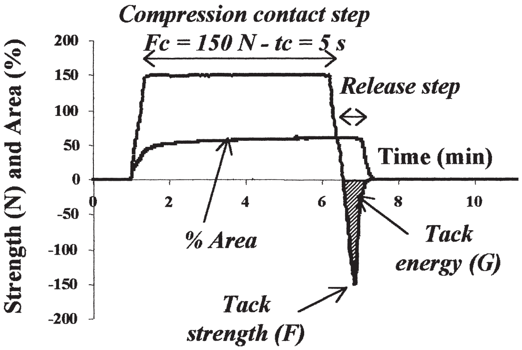

Fig. 2: Typical **"B"** films Strength/%Area = f(t) curves

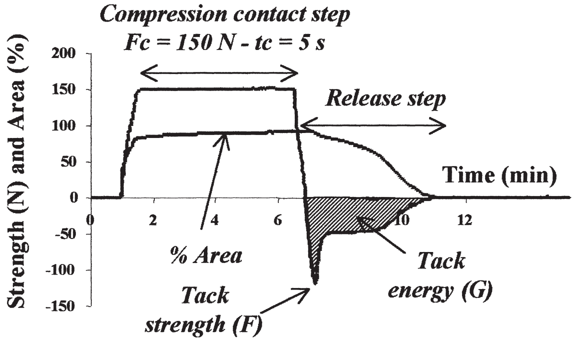

Fig. 3: Typical **"C"** films Strength/%Area = f(t) curves

The experimental studies were achieved in different conditions: *Fc* = 25N and 150N; *tc* = 5s and 60s. The results, reported in Fig. 4, show that the tack strength is higher for **"B"** type films than for **"C"** ones, whereas the opposite trend is evident for the tack energy. Outright failures are observed in the case of **"B"** type adhesives, when progressive releases (with a fibrillation phenomenon in connection with the "shoulder" of the curves) occur in the case of **"C"** type adhesives. These behaviours can be correlated with the heterogeneous character and rather high cohesion of the **"B"** type PSA and with the homogeneous character and rather low cohesion of the **"C"** type PSA.

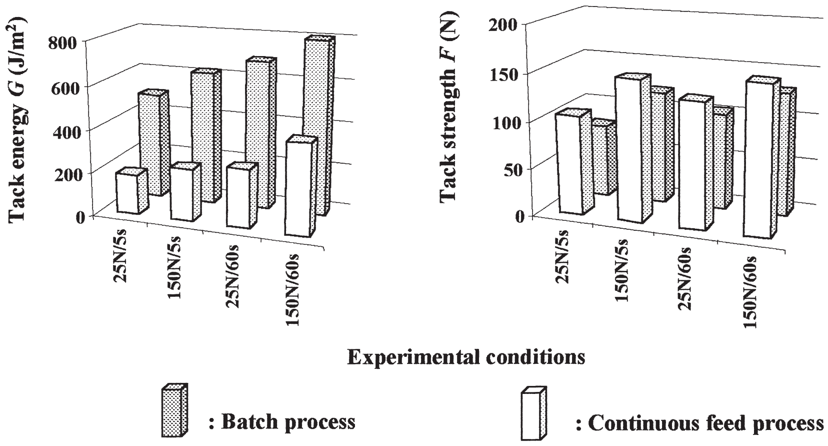

Fig. 4: Tack energy (*G*) and tack strength (*F*) of films obtained from batch and continuous feed processes

It is worth noting that both film types are influenced by experimental conditions in the same way:

- The tack strength increases with the contact force *Fc* and with the contact time *tc* (i.e. with the actual contact area). This shows that the tack strength relates to the capacity of the film surface to establish strong interactions (optimal wetting) with the glass probe of the MOTT.
- The tack energy also increases with *Fc* and *tc*. Moreover, the effects of high *Fc*-short *tc* and of low *Fc*-long *tc* are almost the same. A possible explanation is that the tack energy is representative of the viscoelastic bulk properties of PSA, i.e. of their ability to relax strains during the contact compression step on the one hand and to dissipate energy (fibrillating if need be, as the **"C"** PSA does) during the release step. Energy dissipation by fibrillation, which is linked to the homogeneous composition of the initial latexes, explains why the tack energy of the **"C"** PSA is markedly higher than that of the **"B"** PSA, when their tack strength is likely to be a little lower.

Conclusions

This study points out the strong influence of the emulsion copolymerisation process on the characteristics of the "synthesised" adhesives. For the same overall composition, the batch process gives high modulus, suitable tack strength and low tack energy adhesives, when the continuous feed process gives lower modulus, scarcely lower tack strength but much higher tack energy adhesives. As the former can behave as repositionnable "post-it" type PSAs and the later as long-lasting PSAs, the association of both process types is likely to enable design of tailor-made, inherently tacky, PSAs.

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