DESIGNING WATER-BORNE ACRYLIC PRESSURE-SENSITIVE ADHESIVES FOR COMPLIANCE WITH EUROPEAN UNION FOOD CONTACT MIGRATION TESTING

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Abstract

Labels for food contact applications are often manufactured with acrylic polymer-based pressure sensitive adhesives (PSAs). In many cases, these PSAs are applied as water-borne emulsions formulated with stabilizers, thickeners, biocides, and other additives.

In the United States, PSAs for food contact are regulated under 21 CFR 175.105 (indirect food contact) and 21 CFR 175.125 (direct food contact). In the European Union (EU), Framework Regulation (EC) No. 1935/2004 defines the basic rules for all materials in contact with food, including adhesives. In addition to complying with Regulation 1935/2004, manufacturers of PSA labels are seeking to improve food safety by adopting regulations for food contact plastics (EU 10/2011 Plastics Regulation) in the absence of a specific regulation on adhesives. The Plastics Regulation includes a positive list of authorized substances, requirements on migration testing (overall and specific to certain components), risk assessment for not intentionally added substances (NIAS), and provisions to use substances not included in the Regulation positive list. No damage to food taste and odor and use of Good Manufacturing Practices (GMP) are also requirements of Framework Regulation 1935/2004.

Evaluating acrylic PSAs in label constructions for EU 10/2011 compliance can be challenging. Innovations in polymer design have resulted in food-contact compliant adhesives with excellent performance and safety profiles. This paper reviews the aspects of EU 10/2011 relevant to label PSAs, in particular migration testing procedures. Factors influencing the design of water-borne acrylic adhesives for migration performance will also be discussed.

Introduction

PSAs frequently come into contact with food, such as when they are applied as labels and closures on foodstuffs and food packaging. Various regulatory agencies, including those of the EU have created requirements for such food contact materials, including PSAs, to avoid endangering health or damaging food. The EU Framework Regulation (EC) No 1935/2004, Article 3, provides several overall objectives for ensuring safe food contact materials, mandating that food contact materials should "be manufactured in compliance with good manufacturing practice so that under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health, bring about an unacceptable change in the composition of the food, or bring about a deterioration in the organoleptic characteristics." [1] As envisioned by this regulation, food contact materials such as PSAs serve to protect and beautify food while remaining inert and leaving the food itself unchanged. Nonetheless, given the complexity of food contact materials and their applications, these are challenging goals which require more specific regulations for implementation.

In this respect, the European regulatory landscape for food contact materials is a patchwork comprised of European harmonized regulations such as EU directives and regulations as well as national legislations. Not all materials are regulated in the same way in the EU, as shown in Figure 1. Food contact materials are subject to Framework Regulation (EC) 1935/2004[1] as well as the GMP Regulation 2023/2006. [2] Various classes of materials such as plastics, ceramics, cellulose films, and active & intelligent (A & I) materials are subject to specific regulations. National legislation applies to certain classes of materials as well, including adhesives. Nonetheless, there is no harmonized EU food contact regulation for adhesives.

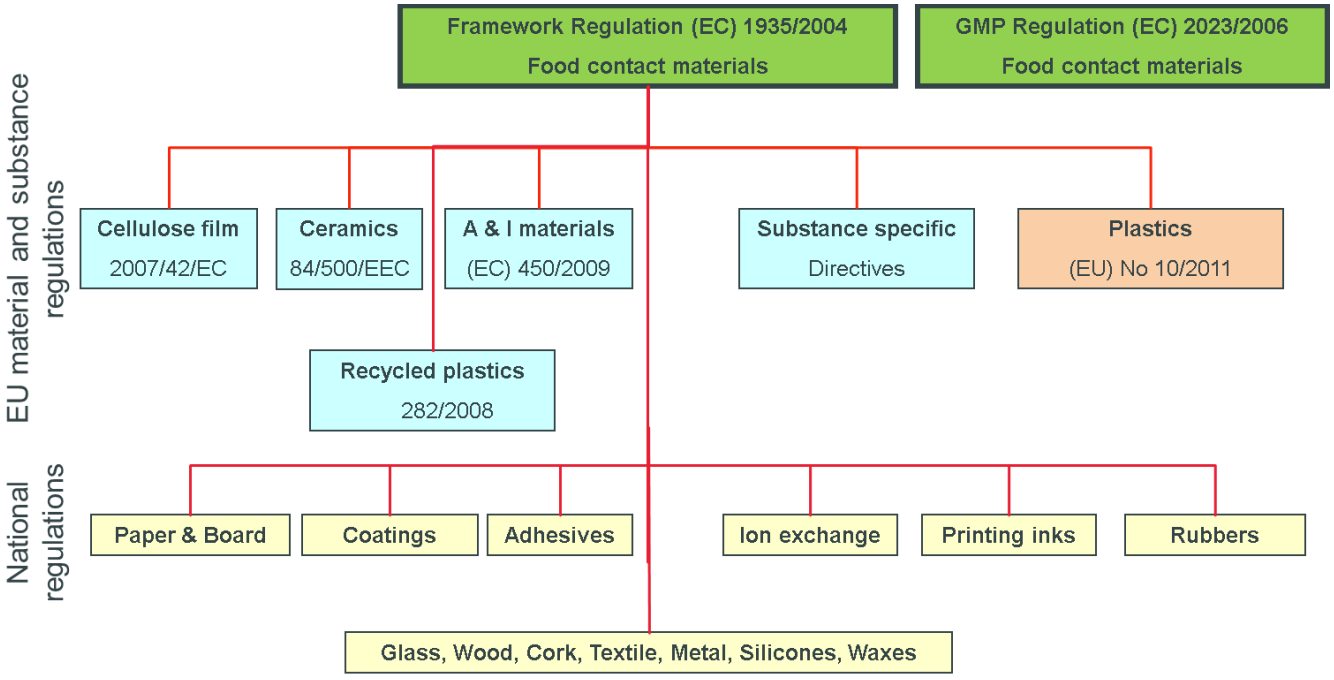

Figure 1. EU and National Food Contact Material Regulations

In the absence of harmonized EU regulations for adhesives, the Plastics Regulation EU 10/2011 is being adopted as an industry standard.[3] This regulation includes five main provisions that food contact materials be

- Manufactured with positively listed substances
- Compliant with overall migration limits as an inertness test (10 mg/dm² contact area)
- Compliant with restrictions or specific migration limits for listed substances as a toxicity test
- Tested for migration under use conditions with specified food types (non-fatty, acidic, dairy, fatty, etc.)
- Subject to risk assessment for NIAS [4]

The Plastics Regulation includes a list of authorized monomers, starting materials, additives, polymer production aids, and other substances which are allowed for use in the manufacture of food contact materials. Often, adhesives customers request that manufacturers certify that their products contain only substances included in this list. However, the Regulation does allow for use of substances not on the positive list if they are not mutagens, carcinogens, reproductive toxins, or nanomaterials and if they are used in accord with provisions including use behind a functional barrier and a migration level less than 0.01 mg/kg.[3]

Migration testing, a foundational requirement of the Plastics Regulation, comprises measurement of the quantity and identity of substances which may migrate from the food contact article into food in the end use application. In the migration test, a specified surface area of the food contact article is exposed to a food simulant for a specified time and temperature to simulate its most severe expected conditions of use. Because it would not be practical to test migration on actual food mixtures, the Plastics Regulation provides for several food simulants which are intended to mimic different classes of food (

Figure 2). Because the Plastics Regulation is not written for PSAs, not all of the tests described in this regulation are suitable for PSAs. Typically, PSAs are tested by coating the adhesive on a facestock at a coat weight of 20 g/m² and exposing the coated construction to food simulant for 24 h at 40°C. Food simulant D2 for fatty food tends to be the most challenging, because the hydrophobic food simulant may dissolve the PSA or adsorb upon the facestock.

After exposure of the food contact article to the food simulant, the facestock is removed along with any adhesive film still adhering to it, and the food simulant is tested for migratory substances. Two types of migration are tested: overall and specific. Overall migration, with a limit of 10 mg/dm^2 (except for materials for food for infants and young children), is a gravimetric test for all non-volatile materials according to the principle that excessive migration of any substance could harm the quality of food. In the case of a volatile food simulant such as 95% ethanol, overall migration is measured as the residual weight following evaporation of the ethanolic solution exposed to the adhesive film on facestock. Measurement of migration in vegetable oil works according to similar principles but is more complex. Because 1 dm^2 of adhesive film coated at 20 g/m^2 contains 200 mg of adhesive dry weight, the 10 mg/dm^2 migration limit implies that no more than 5% of the adhesive dry weight may migrate into the food simulant.

Food simulant	Abbreviation		Food description
Ethanol 10 % (v/v)	Food simulant A		Hydrophilic, pH>4.5 (aqueous food)
Acetic acid 3 % (w/v)	Food simulant B		Hydrophilic; pH<4.5 (acidic food)
Ethanol 20 % (v/v)	Food simulant C		Alcoholic foods with alcohol content up to 20 %
Ethanol 50 % (v/v)	Food simulant D1		Foods with lipophilic character able to extract lipophilic substances or alcohol content of above 20 % or oil in water emulsions (milk products)
Vegetable oil (substitutes:95% ethanol or isooctane)	Food simulant D2		Lipophilic foods or foods which contain free fats at the surface (fatty food)
poly(2,6-diphenyl-p-phenylene oxide), particle size 60-80 mesh, pore size 200 nm	Food simulant E		Testing specific migration into dry foods

Figure 2. Migration testing food simulants

On the other hand, specific migration is a test for the quantity of a listed substance with a specific migration limit which migrates into the food simulant. For instance, most common acrylate esters and acrylic acid are subject to a total limit of 6 mg/kg, where the specific migration limit is expressed as a weight ratio intended to reflect the real surface to volume ratio in actual use of the food contact material. Because the precise use of a PSA film may not be known in advance, the Plastics Regulation provides that a generic ratio of 6 dm^2/kg food may be used (except for materials for food for infants and young children). [3] Accordingly, the limit mentioned above for total acrylate esters and acrylic acid is equivalent to 1 mg/dm^2 of adhesive film. Standard methods for both overall migration [5] and specific migration exist. [6]

Since the advent of the overall and specific migration tests in EU regulations, several studies have examined migratory species in acrylic polymers generally and acrylic adhesives specifically. Franz and Brandsch investigated the diffusion properties of monomers such as *n*-butyl acrylate (BA) and methyl methacrylate (MMA) and their respective homopolymers in contact with food simulants. [7] Nerín and coworkers screened a variety of acrylic, vinyl, and hotmelt adhesives in food packaging laminates for migratory species, investigated their diffusion behavior, and compared their migration to specific migration limits.[8, 9, 10] However, these studies emphasized laminating adhesives and focused on specific migration of individual compounds rather than the overall migration performance of the acrylic adhesive. Accordingly, the aim of this work was to elucidate the composition and process factors which affect the overall migration of water-borne acrylic PSAs in 95% ethanol as a fatty food simulant to enable the design of low-migration PSAs.

Experimental

Preparation of Pressure Sensitive Adhesive Dispersions

The pressure sensitive adhesive dispersions were prepared by a typical semi-continuous emulsion polymerization process according to the compositions in Table 1. For two runs, the monomer compositions were changed, and other variables were kept the same. For twelve runs, the monomer composition was kept the same, and persulfate initiator amount, polymerization feed type, chain transfer agent amount (CTA), crosslinker amount, and chase process were varied systematically. Reagent amounts are given as weight % (wt%) relative to the total monomer charge.

Table 1. Pressure Sensitive Adhesive Dispersion Compositions and Overall Migration Results

EHA (wt%)	MMA (wt%)	Sty (wt%)	BA (wt%)	AA (wt%)	Initiator (wt%)	Feed type	CTA (wt%)	Cross-linker (wt%)	Chase type	OM (mg/dm^2)
0	3.2	2.5	93.7	0.6	1.2	B	–	–	A	305
81.5	15.4	2.5	–	0.6	1.2	B	–	–	A	65
82.4	16.6	–	–	1.0	0.4	A	–	–	A	9.4
82.4	16.6	–	–	1.0	0.4	A	–	–	B	11.9
82.4	16.6	–	–	1.0	0.4	A	–	0.5	A	8.6
82.4	16.6	–	–	1.0	0.4	B	0.5	0.5	A	18.6
82.4	16.6	–	–	1.0	0.4	A	0.25	0.5	B	20.5
82.4	16.6	–	–	1.0	0.4	B	–	–	A	10.5
82.4	16.6	–	–	1.0	0.8	A	–	0.5	B	66
82.4	16.6	–	–	1.0	0.4	B	0.5	–	B	34.7
82.4	16.6	–	–	1.0	0.8	A	–	–	A	25.5
82.4	16.6	–	–	1.0	0.8	B	0.5	–	A	124.2
82.4	16.6	–	–	1.0	0.8	B	0.5	0.5	B	30.5
82.4	16.6	–	–	1.0	0.8	B	0.5	–	B	106.2

*EHA = 2-ethylhexyl acrylate, Sty = styrene, AA = acrylic acid, OM = overall migration

Preparation of Pressure Sensitive Adhesive Films

The prepared aqueous acrylic dispersions were directly coated onto facestock (e.g., biaxially oriented polypropylene, polyethylene terephthalate, aluminum foil, etc.) at a target coating weight of 20 g/m^2 and dried for 5 minutes in an oven at 80°C. Each film is then covered with a silicone release liner.

Overall Migration Testing Method

The release liner was removed from the film, and then the film was exposed to the appropriate food simulant for 24 hours at 40°C by total immersion in a beaker with a volume to surface ratio of 100 mL/dm^2. The food simulant was 95% ethanol in water (volume/volume). After exposure the sample was removed from the food simulant. The simulant was slowly evaporated to dryness, and the beaker with residue was conditioned at 105°C until constant mass was obtained. The weight of the residue was determined as weight difference (weight beaker with residue minus weight empty beaker). Overall

migration was calculated by dividing the residue weight by the area of film originally exposed. The tests were carried out in triplicate with the average reported.

Statistical Analysis

Overall migration responses for the twelve process variation runs were modeled using linear models with coded main effects and two-factor interactions. Because runs were executed by two different chemists, the runs were separated into two blocks, and block was modeled as a random effect using restricted maximum likelihood methods. Fit models were reduced to include only terms with p-values $\leq$ 0.05 or those included in significant interaction terms.

Results and Discussion

Effect of Bulk Monomer Composition on Migration of Water-Borne Acrylic PSAs

BA and EHA are the two most common bulk monomers used to make low (approx. -40°C) Tg acrylic copolymer PSAs. As an initial test, acrylic copolymer PSAs based on each of these two monomers were prepared by emulsion polymerization, with the Tg of the EHA-copolymer adjusted upward with a greater share of MMA (Table 1). The overall migration of the BA-based PSA was very high; in fact nearly all of the film transferred into the 95% ethanol food simulant. The migration value is higher than the theoretical maximum of 200 mg/dm^2 for a coat weight of 20 g/m^2 because the actual adhesive coat weight was higher than 20 g/m^2. Overall migration for the EHA-based PSA was much lower than that of the BA-based PSA, with most of the adhesive material remaining in the film on the facestock, even though its overall migration is much higher than the limit of 10 mg/dm^2. One possible reason for the lower migration of the EHA-based PSA is that the ethanolic food simulant is relatively polar when compared to both acrylic PSAs tested. Poly(BA) is more polar and hence more similar to 95% ethanol than poly(EHA), so it tends to migrate into this food simulant to a greater extent.

Effect of Composition and Process Factors on Water-Borne EHA-Based PSAs

The overall migration of the EHA-based PSA studied above was still very high (65 mg/dm^2), showing the difficulty of obtaining excellent fatty food migration performance for acrylic PSA dispersions. In order to further improve this performance, several common composition and process factors were varied systematically for an EHA-based PSA, and overall migration was tested for the resulting PSA variants (Table 1). The composition factors included amounts of chain transfer agent and crosslinker, which were expected to modulate the molecular weight of the EHA copolymer, and amount of persulfate initiator, which was expected to change both the polymer molecular weight and polarity. The process was also varied by employing two different feed profiles during the polymerization and two different methods of chasing residual monomer to low levels following the polymerization. Among the twelve PSA variants, overall migration ranged from very high extraction (>100 mg/dm^2) for entries with high initiator and chain transfer agent without crosslinker to very low migration (<10 mg/dm^2) for entries with low initiator and no chain transfer agent.

Table 2. Significant Effects and Parameter Estimates for Overall Migration Process Study

Response	Effect	Prob>|t|	Parameter Estimate
OM (mg/dm^2)	Initiator (wt%)	0.01	19
	CTA (wt%)	0.11	11
	Crosslinker (wt%)	0.10	-10
	CTA * Crosslinker	0.02	-18

Statistical analysis of the results indicated that neither polymerization feed profile nor chasing method had a significant effect on the overall migration (Table 2). In contrast, the level of initiator had a very strong impact on overall migration, with higher initiator leading to higher migration. Increased initiator in this EHA-based water-borne PSA is likely to both decrease the molecular weight of the polymer and increase the polymer polarity through persulfate end groups, both of which would tend to make the PSA more likely to migrate into the polar ethanolic food simulant. Similarly, crosslinker and chain transfer agent amount also had significant effects on overall migration with an interaction term in the model, likely due to how their influence on molecular weight and gel fraction affect the solubility of the EHA-based PSA in the food simulant. Increasing chain transfer agent in the absence of crosslinker increased overall migration, while increasing crosslinker in the absence of chain transfer agent decreased overall migration. With both chain transfer agent and crosslinker present, the effect of crosslinker tended to overwhelm the effect of the chain transfer agent to keep migration low (18–31 mg/dm^2 for entries with both present), as reflected by the interaction term.

Despite the challenges of reaching low overall migration with acrylic PSA dispersions, this study found several examples of PSAs with fatty food overall migration below the 10 mg/dm^2 limit when the initiator level was less than 0.4 wt %. It also indicated a range of crosslinker and chain transfer agent amounts which can be used while keeping migration relatively low. Moreover, it revealed that the PSA manufacturing process may be varied without adversely affecting migration. Together, these results demonstrate that fatty food overall migration performance may be achieved within a range of water-borne PSA compositions and process.

Conclusions

PSAs in food packaging and labels act as food contact materials and should be designed to preserve health and food quality. Although there is no harmonized EU food contact regulation for adhesives, many in the PSA industry are adopting the Plastics Regulation EU 10/2011 as a standard. The overall migration requirements within this regulation are challenging for water-borne acrylic PSAs, particularly for fatty food contact. However, judicious design of PSA composition can enable excellent migration performance. For fatty food contact overall migration tested in 95% ethanol, this study revealed that an EHA-based PSA had lower migration than a BA-based PSA, likely due to the lower polarity of the poly(EHA) composition relative to the ethanolic food simulant. Moreover, for a given EHA-based PSA dispersion composition, decreasing initiator and chain transfer agent level and increasing the crosslinker level led to lower migration, likely due to the effects of these components on polarity and molecular weight.

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