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Adhesion and flammability properties of nanoclays rubber based PSA adhesives

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Pressure sensitive adhesives (PSA) are polymeric adhesives used mainly in tapes and labels, showing strong and permanent tack at room temperature and can be applied with very low pressure. The present investigation was aimed to verify the influence on adhesion and flammability properties of modified nanoclays in a natural rubber based PSA compared to a reference adhesive using ground $CaCO_3$ on compound formulation. The adhesive compounds were prepared using a laboratory scale banbury HAAKE Rheocord 90 and a Sigma Blade mixer. The adhesives were characterized by their properties of cohesion (bond test), adhesion to steel (peel test), tack and flammability, as well as physico-chemical analyses. Significant improvements on PSA adhesion and flame retardancy properties were found for all the nanoclays adhesives compared to the control compound.

1. Introduction

There are 3 types of Pressure sensitive adhesives (PSA): solvent based, water based and hot melt. Solvent based presents few limitations on manufacture, like flammability and toxicity, but are still often used, due to good adhesion to polar substrates, good bonding to some plastics and durability (Benedek, 1996). Natural rubber is still widely used with tackifiers to provide the required balance among adhesive properties, such as peel adhesion, tack and shear resistance. These properties depend strongly on the viscoelastic behaviour of the PSA. Mineral fillers, as clays and ground $CaCO_3$, are generally used in the polymer industry as fillers lowering the high cost per unit volume of the polymeric systems (Wypich, 1999). However, inert or non-reinforcing fillers could decrease mechanical properties of the material, cost reduction would be achieved at expense of performance. Adhesion, for instance, could be affected by the choice of filler. Clay minerals such as kaolinite and montmorillonite are widely used as fillers for rubber and plastics. The efficiency of fillers as reinforcing agents to improve the physical-mechanical properties of the polymer is determined by the quality of its dispersion in the polymeric matrix being influenced, in turn, by the particle size and interactions with the matrix. Nowadays, polymeric/nanoparticles compounds, as modified clay nanocomposites, are novel materials of huge interest due to their improved thermal resistance, flame retardancy and mechanical properties, as a result great advantages on several applications can be achieved (Varguese et al., 2003; Teh et al., 2004; López-Manchado et al., 2004; Arroyo et al., 2003). However, up to know, nanoclays have not been studied for rubber adhesives compounds. Therefore, the present investigation was aimed to verify the influence on adhesion and flammability properties of modified nanoclays in a natural rubber based PSA compared to a reference adhesive using ground $CaCO_3$ on compound formulation.

2. Methodology

Natural rubber was supplied by Cargill, type RSS 1. The phenolic resin used (18 phr) was BC1054 (Reichhold). The tackifying agent (51 phr) was terpene Sylvares TR B115 (Arizona Chemical). The fillers used were: ground calcium carbonate (58 phr) and organically modified nanoclays Cloisite® (Southern Clay Products). These nanometer scale additives are layered magnesium aluminum silicate platelets, derived from natural montmorillonite. Two grades were used: Cloisite® 20A and Cloisite® 25A, both are surface modified with ammonium quaternary salts, but different organic modifier agent. A Design of Experiment was used to study two compounding factors: concentration, 3 phr and 6 phr, and grades of the organophilic clays: Cloisite 20A and 25A. The adhesive compounds were prepared using a HAAKE Rheocord 90 (80 rpm and 70^{o}C) and a Sigma Blade mixers (external heating and 1,200 rpm). Hand spread film samples where prepared with the adhesives (coating weight controlled, without solvent) using PVC and polyester films substrates for characterization of adhesion properties.

Shear or adhesion to steel (peel test) was measured using a KRATOS universal machine, at a speed of 300 mm/s and angle of 180^o, according to NBR 5057/82. Tack (rolling ball) was measured following "Test #6" of *Pressure Sensitive Tape Council Test* angle of 45^o and 5 g sphere. Bond test, cohesion of the adhesive, was done using a weight of 10 N and an area of 1 in^2. Flammability tests (NBR 5057/83 standard) were done with the adhesives tapes, using a substrate of flexible PVC flame retardant tape. Dynamic Mechanical Thermal Analysis were carried out on PSA samples, tensile mode, from -80^{o}C to +80 ^{o}C, at 5^{o}C/min (Rheometrics Scientific), as well as X-Ray Diffraction analyses, CuKα radiation, at 0.02° step size and scan at 2 θ/min=5 (Philips X´Pert). The spectra were measured from 2° to 20^o (2θ angle). Thermogravimetric and FTIR analyses were also done but not presented here.

3. Results and Discussion

Table I presents the results of adhesion tests: shear or adhesion to steel, bond or cohesion of the adhesive and tack (rolling ball). The factorial statistical analysis for shear (adhesion to steel) did not show significant effect for the single factors, but it was found significant factors interaction (90% of confidence): "type of nanoclay + quantity of nanoclay". The increase on the amount of the Cloisite 20A increases slightly the adhesion values of the compound adhesives (samples 6-20A), while Cloisite 25A shows opposite behavior (samples 3-25A). Compared to the control or reference compounds (samples with $CaCO_3$) no significant differences on shear results were observed for these nanoclay samples.

The results for cohesion of the adhesives, bond test, showed statistical influence (90% of confidence) for the quantity of nanoclay and for the factors interaction "type + quantity". The compounds with the higher amount of Cloisite 20A (samples 6-20A) showed a significant increase on cohesion (see Table I), while compounds with Cloisite 25A did not show significant changes. Control samples or reference adhesive compounds showed very low cohesion, which indicates that the amount of $CaCO_3$ used has a negative effect on this property. The statistical analysis for tack results (rolling ball) showed significant effects for both single factors and interaction (90% of confidence). In the case of Cloisite 20A samples, the increase on its quantity means a decrease on the tack property, measured by the longer stretch of the rolling ball (Table I), while with Cloisite 25A samples this effect was not observed. The control samples (reference adhesive) showed similar tack behavior as Cloisite 25A samples, but Cloisite 20A samples showed lower tack.

Table I: Tests results for the ten PSA adhesives tapes (n: samples, II: replicate).

Sample phr/grade	*Bond - min (n=3)*	*Adhesion N/cm (n=6)*	*Rolling Ball - cm (n=3)*	*Flammability-cm (n=3)*
3/20A	133.67 ± 7,0	2,82 ± 0,1	5,63 ± 0,4	1,37 ± 0,2
3/20A II	109,67 ± 13,0	2,60 ± 0,4	4,83 ± 0,3	0,87 ± 0,1
6/20A	214,33 ± 14,6	3,04 ± 0,3	6,40 ± 0,5	1,07 ± 0,3
6/20A II	308,33 ± 38,8	2,93 ± 0,2	7,10 ± 0,1	1,20 ± 0,1
3/25A	136,33 ± 7,4	3,03 ± 0,2	4,80 ± 0,3	0,97 ± 0,1
3/25A II	114,33 ± 11,0	2,82 ± 0,2	5,03 ± 0,2	0,83 ± 0,3
6/25A	165,00 ± 20,4	2,79 ± 0,2	5,23 ± 0,6	1,13 ± 0,1
6/25A II	115,67 ± 11,9	2,87 ± 0,1	4,76 ± 0,5	0,93 ± 0,1
Ref.	33,33 ± 11,9	3,10 ± 0,2	4,60 ± 0,4	1,67 ± 0,3
Ref.II	29,33 ± 3,0	3,09 ± 0,1	4,90 ± 0,2	1,73 ± 0,2

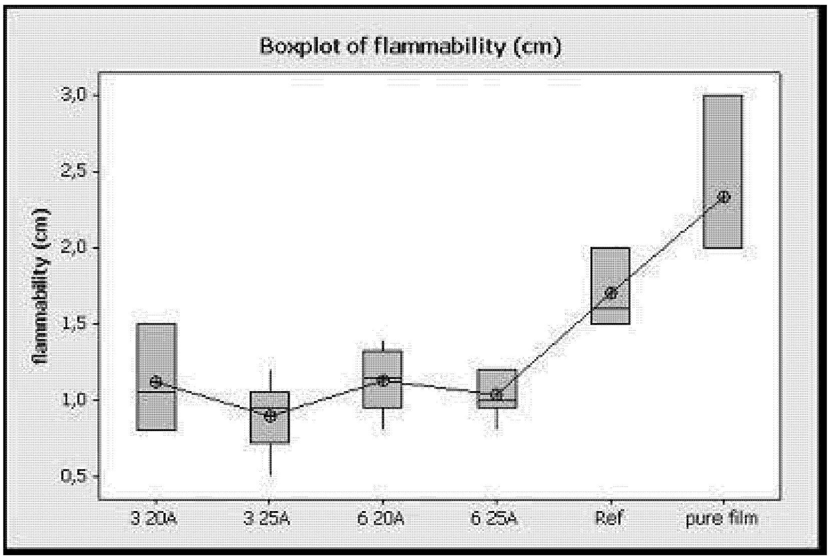

Figure 1: Boxplot of flammability tests (cm of burned length) for PSA tapes with nanoclays, $CaCO_3$ (reference) and PVC (pure film).

The flammability test was done using PVC flexible flame retardant tapes as substrate for all PSA adhesives. The measurement was done considering the length of the burned area. The results (Figure 1) for nanoclays PSA tapes did not show any statistical significance for clay concentration (3 or 6 phr) or type (20A or 25A). But the adhesive tape with $CaCO_3$ (58 phr) presented results a little bit higher on burned length and the PVC tape alone (pure film) showed the large burned length, twice than the nanoclays PSA tapes. The time for flame extinguishion was around 2 seconds for all PSA samples.

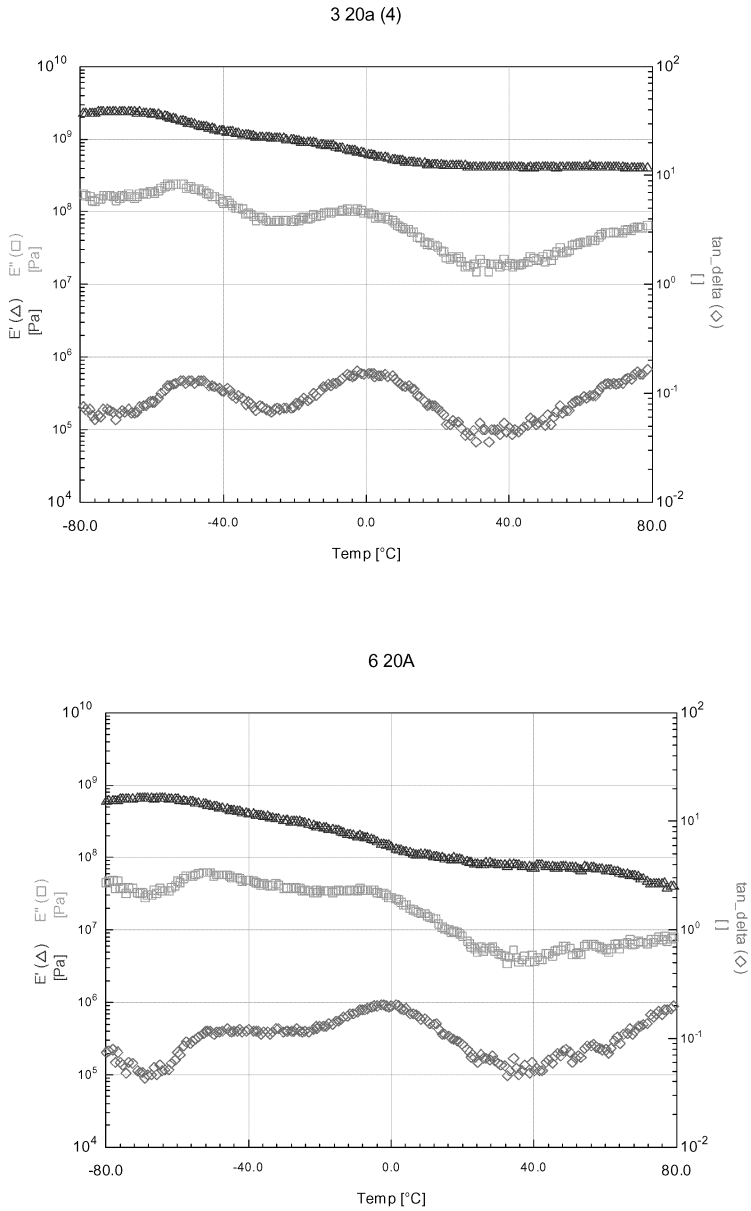

Figure 2: DMTA analyses for PSA with Cloisite 20A (upper curve is for E' modulus, lower curve for Tan delta). Upper graph is for sample with 3 phr and bottom for 6 phr.

DMTA analyses showed that nanoclay PSAs could present two Tg (tan δ at 1 Hz): around 0°C for all samples (also the reference) and from -50°C to -40°C for nanoclay samples, Cloisite 20A and 25A respectively, at any concentration used. Figure 2 shows the results for Cloisite 20A. The higher Tg could be due to the terpene resin effect. The lower Tg could be related to the natural rubber matrix. Some effects on the Tg could be also due to the structure of the organic modifier agents of nanoclays: Cloisite 20A has two long tails of hydrogenated tallow (~65% C18; ~30% C16; ~5% C14) on the quaternary ammonium salt, and Cloisite 25A has one dehydrogenated tallow and one 2-ethylhexyl on the quaternary ammonium. The PSA storage modulus (E') varies almost one order of mangnitude as a function of nanoclay concentration (Figure 2). The adhesives compounds with lower nanoclay concentration, 3 phr, presented higher modulus. The adhesives with nanoclay 20 A showed lower modulus reduction as a function of temperature increase. It could mean that at ambient temperature the PSA with nanoclay 20A should be less flexible than with the 25A.

XRD analyses, Figure 3, did not show any significant diffraction peaks for the PSA adhesives at 2θ ~ 4°, using Cloisite 20A and 25A. But it was not possible to confirm if this was a desired exfoliation or a dillution of clay (very low concentration). Nanoclays interplanar distance were d_{001}=18.2 Å (Cloisite 20A) and d_{001}=25.0 Å (Cloisite 25A).

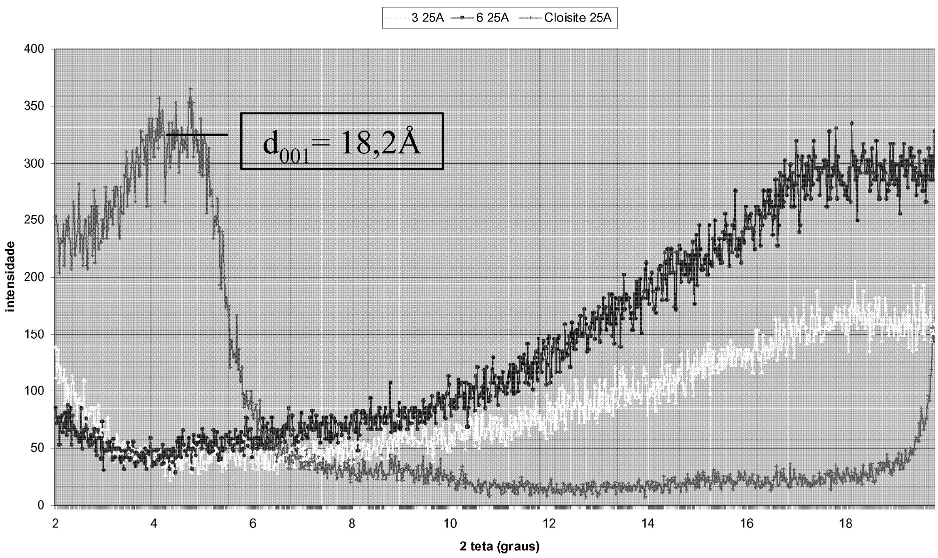

Figure 3: Lower righthand XRD spectrum is for Cloisite 20A, middle and upper righthand spectra are for PSA with 3 and 6 phr of Cloisite 20A, respectively.

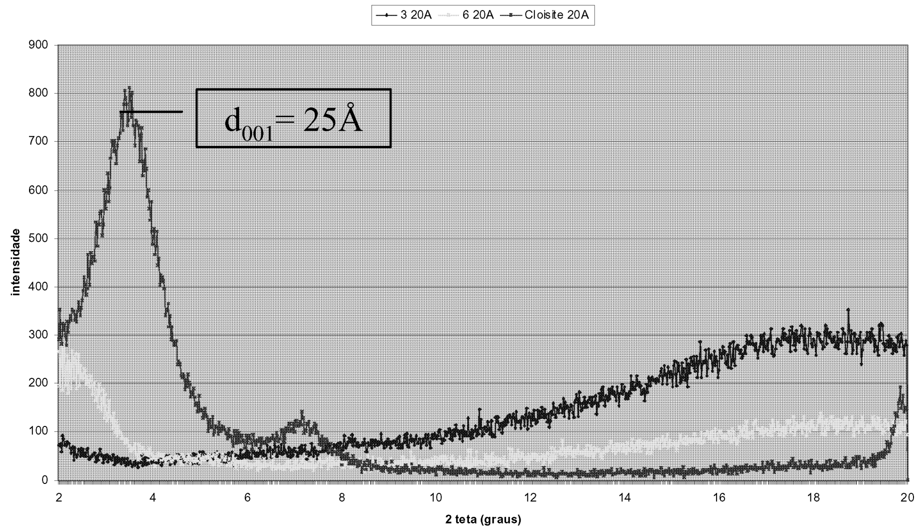

Figure 4: Lower righthand XRD spectrum is for Cloisite 25A, upper and middle righthand spectra are for PSA with 3 and 6 phr of Cloisite 25A, respectively.

4. Conclusions

The nanoclays PSA adhesives showed significant improvements on specific properties of cohesion (shear) and adhesion at 90% confidence., but the most important contribution observed was the achievement of antagonist properties, like cohesion and shear with one kind of modified clay. Flame retardant properties are other significant results in this investigation. It was not possible to be more accurate to know if an exfoliation of the nanoclays was achived in the adhesive systems, but the flame retardant properties were very promising taking account the small amount of clay used.

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