

Characterization of resol resins modified by the addition of PVC plastisols

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Abstract: Plastisols, which are a blend of poly(vinyl chloride) resin and a plasticizer (DEHP), were used as a toughening agent of a resol resin in order to improve the mechanical properties. It was not possible to formulate resol blends by adding more than 10 % of plastisol owing to a lack of apparent homogeneity in the systems, which also showed many air bubbles. The relationship between dynamic mechanical, mechanical and thermal properties and the amount of plastisol added was studied. It was determined from the infrared spectroscopy and dynamic mechanical results that the resol–plastisol blends seem to be formed by a reaction between the phenol and PVC giving a higher crosslinked structure. An improvement in the thermal resistance of the blends at lower temperatures was observed with an increase in the percentage of plastisol. Flexural analysis showed the elastic behaviour of the systems. However, it was not possible to observe the effect of the plasticizer (DEHP) owing to the low quantity of plastisol that was added to the resol.

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Keywords: PVC plastisol; resol resin; blends; dynamic mechanical properties; thermal behaviour

INTRODUCTION

Phenolic resins are among the most commonly used thermosetting resins. This is an irreplaceable material for selective high-technology applications, offering high reliability under severe conditions. They have been widely used in the manufacture of wood products, coatings, structural adhesives, moulding compounds, composites and thermal-insulation materials. Most of these applications are due to their excellent thermal and chemical resistance and good dimensional stability.^{1,2}

However, one of the main drawbacks of phenolic resins is their high fragility, which is due to their high crosslinking density. This disadvantage limits their use in applications requiring high impact resistance. Over the last few years there have thus been many research efforts to improve the toughness of thermoset resins.^{3–5} Phenolic resins have been modified with flexible elastomers,⁶ and thermoplastics have also been suggested in order to improve their toughness.^{6–10} Recently, Choi *et al*¹¹ have used flexible diacids to improve the brittleness of a resol-type phenolic resin. Plastisols, which are a blend of poly(vinyl chloride) (PVC) resin and a plasticizer, are characterized by their high flexibility and impact properties. Therefore, they are a promising material to blend with brittle

thermosets in order to reduce their fragility. For instance, plastisols have been used as a toughening agent to improve some properties of an epoxy resin. López *et al*¹² studied the relationship between mechanical, thermal and electrical properties of epoxy–plastisol systems. They found that it is possible to toughen the epoxy resin when a plastisol at a concentration higher than 60 % is blended with the resin. However, there was no information about the behaviour and properties of phenolic–plastisol systems. Robila *et al*¹³ proposed a reaction between phenol and PVC, where the chlorine atom of the PVC structure was substituted by the *para* position of the phenolic ring.

The aim of this work was to study the behaviour of a phenolic–plastisol system in order to obtain materials with improved mechanical properties. The relationship between dynamic mechanical, mechanical and thermal properties and the amount of plastisol added were studied.

EXPERIMENTAL

Materials

A resol-type phenolic resin was prepared with a formaldehyde-to-phenol molar ratio (F/Ph) of 1.3.

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Samples of phenol and a formaldehyde aqueous solution (37 % w/w) (Cicarelli) were placed in a 1500 ml stainless steel reactor with a low-velocity stirrer, thermometer and reflux condenser. The pH was kept at 9.0 with a solution of 40 % (w/w) NaOH and the mixture was permitted to react for 2 h at 90 °C. The mixture was then neutralized with a solution of boric acid until the pH reached a 6.8–7.0. The dehydration of the resol was performed inside the same reactor in a vacuum at 75–80 °C pending the total extraction of water. The resol was stored at –10 °C until the moment it was used.

A PVC resin, Vestolit B-7021 (HULS, Germany), was mixed with a plasticizer, Vestinol AH (HULS) [di-ethylhexyl phthalate (DEHP)], and a phenolic antioxidant, Irganox 1076 (Ciba-Geigy, Switzerland) to prepare the plastisols. These components were mixed in a 100/70/2 ratio of PVC/DEHP/stabilizer in a Brabender P-600 mixer for 20 min at 23 ± 2 °C. The paste obtained was then put in a vacuum dryer (pressure 7×10^2 Pa) for 5 min to eliminate air bubbles and the samples were then considered to be ready for blending.

Resol-plastisol blends were prepared at various plastisol percentages: 2, 5 and 10 %. The resol was catalyzed with a 3 % sulfuric acid solution (25 % v/v) prior to mixing with the plastisol. Blends were cured in an oven for 150 min at 90 °C.

Methods

The determination of the dynamic mechanical properties of the blends was carried out with a Perkin-Elmer DMA-7 at a fixed frequency of 1 Hz and a heating rate of 5 °C min⁻¹ in a three-point bending mode. Flexural testing was performed at room temperature using an Instron 4467 instrument according to the ASTM D790M-93 standard. The specimens used for these tests were cut from plaques of 2 mm thickness, obtained by curing the blends between two glass plates previously treated with a silicone release agent supplied by Siliar SA (Argentina).

Fourier-transform infrared (FTIR) spectra (drift mode) were acquired with a Bruker IFS 45 spectrometer. The acquisition conditions were as follows: spectral width of 400 to 4000 cm⁻¹, 32 accumulations, 2 cm⁻¹ resolution. Samples were obtained from the cured plaques and finely ground in order to obtain a well-homogenized mixture, which was then placed on a sample cell. For comparison purposes, spectra were normalized by using the intensity of the band at 1610 cm⁻¹. This band was assigned to C=C stretching of the benzene ring and its intensity was expected to remain constant for all samples.¹⁴

Dynamic degradation measurements were carried out using a Mettler-Toledo 851e-TGA-SDTA system coupled to STAR-E software. Tests were performed in a dynamic mode in order to cover a wide range of thermal conditions in a nitrogen environment (flow rate 200 ml min⁻¹). Temperature programmes were

run from 30 to 800 °C at a 10 °C min⁻¹ heating rate. Thermogravimetric analysis (TGA) tests were performed in 5.9 × 4.7 mm alumina crucibles in which samples were placed without any prior treatment and experiments were run immediately. The sample weight in all tests was approximately 10 mg.

RESULTS AND DISCUSSION

It has been shown previously that it is possible to cure resol resins by temperature or by adding a catalyst.¹⁵ In previous work¹⁶ we found that it was not possible to get a complete cure of the resol without the use of a catalyst if temperatures were below 190 °C. A slow heating cycle was used in order to allow the elimination of volatile products such as water and formaldehyde. When the resol and plastisol under this curing cycle were blended, it was not possible to obtain a homogeneous system because of the quick plastisol gelation, which reduced the cure of the resol and resulted in inadequate blending. It was therefore necessary to use a catalyst for curing the resol. In previous work¹⁷ it was indicated that the addition of sulfuric acid leads to an acceleration of the curing reactions. So, in the present study it was possible to obtain suitable mixtures for characterization by heating them at 90 °C during 150 min after the addition of sulfuric acid. However, in this work it was not possible to prepare blends containing plastisol percentages higher than 10 % because of a lack of apparent homogeneity in the blends, which also showed many air bubbles.

In order to determine whether the resol really reacted with the plastisol, the blends were analyzed by infrared spectroscopy. Figure 1 shows the FTIR spectra of resol and its blends with 2, 5 and 10 % plastisol. Slight differences in the height of some of the characteristic bands were observed. Those at

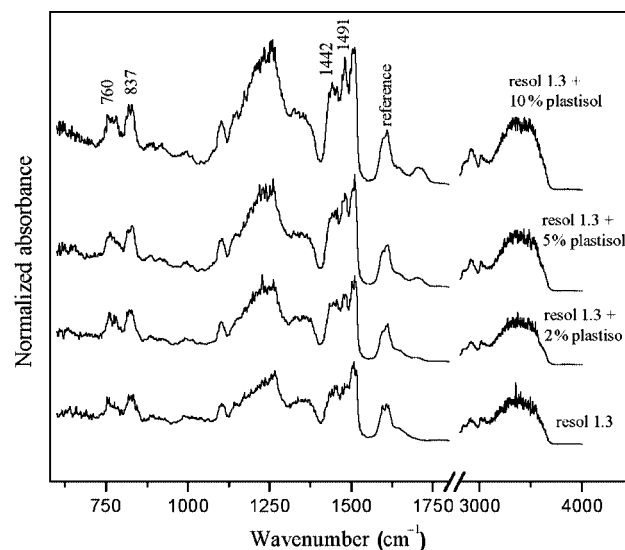


Figure 1. FTIR spectra of resol and its blends with 2, 5 and 10 % PVC/DEHP plastisol.

1442 and 1491 cm^{-1} are characteristic of the *para-para* and *ortho-para* methylene bridges in the resol, respectively.¹⁸ The heights of the bands at 1442 and 1491 cm^{-1} were similar in the spectrum of the resol but the band at 1491 cm^{-1} became higher with increasing plastisol amounts. Therefore, there was a higher quantity of *ortho-para* methylene bridges in the resol when blended with plastisol, showing some interaction in the blends. Another significant difference appeared in the relative height of the bands at 760 and 837 cm^{-1} , which correspond to substituted benzene rings.¹⁴ The band at 760 cm^{-1} is characteristic of 1,2-disubstituted and 1,2,6-trisubstituted benzene rings, and that at 837 cm^{-1} is characteristic of 1,4-disubstituted and 1,2,4-trisubstituted benzene rings. The band at 837 cm^{-1} became more intense with increasing plastisol content, indicating an increased proportion of benzene substituted at the *para* position. The results obtained by FTIR were in accordance with the reaction between phenol and PVC proposed by Robila *et al*¹³—that the chlorine atoms in the PVC macromolecule are substituted by the phenolic ring in the *para* position. The FTIR analysis showed that the addition of plastisol favoured the *para* substitution of the benzene ring and that there was an increase of the *ortho-para* methylene bridges in the resol because the *para* position was already occupied by the PVC chain.

Dynamic mechanical analysis of the resol–plastisol blends was performed in order to determine the viscoelastic properties of the systems. Figure 2 shows the curves of storage modulus (E'), loss modulus (E'') and $\tan \delta$ as a function of temperature for the blend of resol with 2 % PVC/DEHP plastisol. The variation of the glass transition temperature T_g , determined as the temperature of the maximum of the $\tan \delta$ curve, and the height of the $\tan \delta$ curve were measured as a function of the percentage of plastisol added (Figs 3 and 4). It was observed that there was an increase in the T_g and a decrease in the height of $\tan \delta$ which is related to the polymeric chains dampening, with the addition of plastisol. These results indicate that the addition of plastisol increased crosslinking density of the system. It is well known that the main reaction of PVC at temperatures up to 300 °C

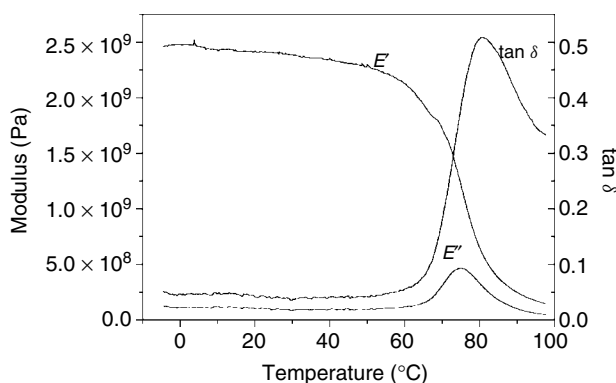


Figure 2. Dynamic mechanical analysis of the blend of resol with 2 % PVC/DEHP plastisol.

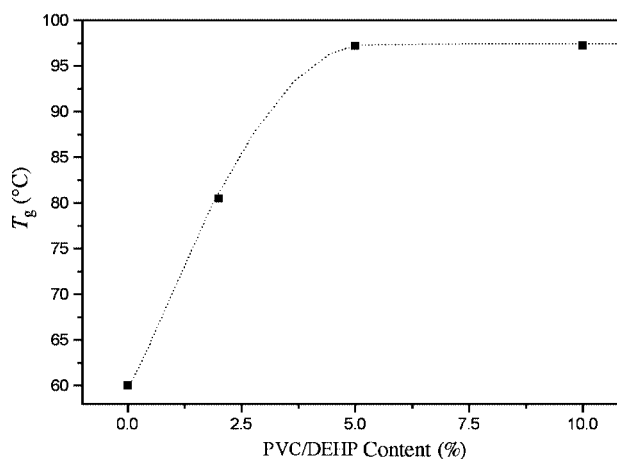


Figure 3. Glass transition temperature as a function of the percentage of PVC/DEHP plastisol added to the resol resin.

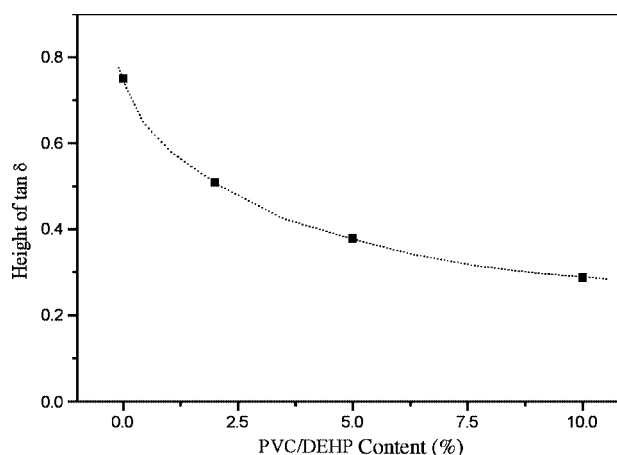


Figure 4. Height of $\tan \delta$ as a function of the percentage of PVC/DEHP plastisol added to the resol resin.

is dehydrochlorination, resulting in the evolution of HCl as the main volatile product and the formation of C=C bonds in macromolecules.¹⁹ Therefore, it is possible that the high crosslinking density of the resol–plastisol system was due to the high quantity of acid catalyst (HCl) in the medium that accelerated the curing reaction of the resol.

Figure 5 shows the load *versus* deformation curves of the cured blends obtained by flexural analysis. It can be seen that there was no plasticization in the blends and that they seemed to be as rigid as the resol. This was due to the low quantity of plastisol that was added to the resol. If it were possible to add higher quantities of plastisol, different behaviour would be expected. Previous work based on the study of epoxy–plastisol blends¹² showed that by adding more than 60 % plastisol to the epoxy resin a difference in mechanical properties was observed. This was due more to the addition of a plasticizer (DEHP) than to the effect of the mixture of PVC resin with an epoxy. Similar behaviour would be expected for resol–plastisol blends.

The flexural modulus of the blends at room temperature decreased with increasing PVC/DEHP

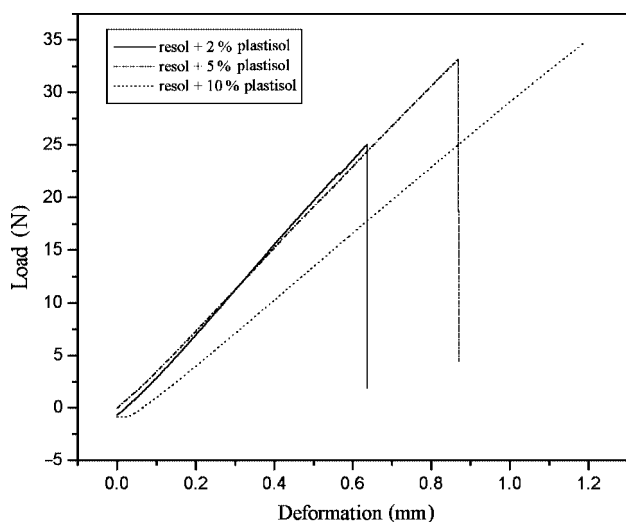


Figure 5. Flexural load versus deformation of the cured blends of resol and PVC/DEHP plastisol.

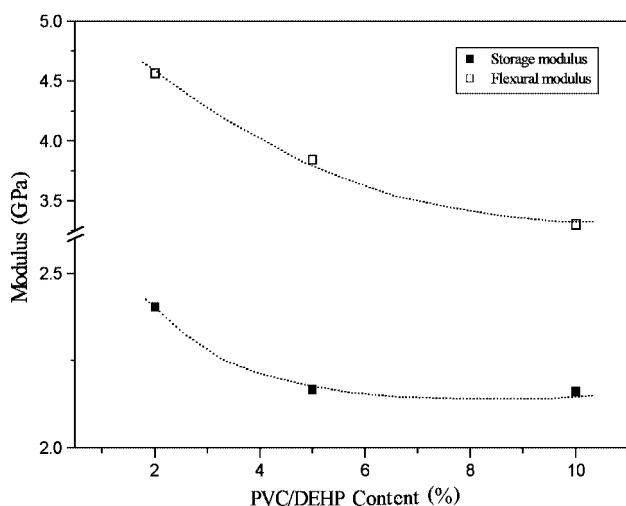


Figure 6. Flexural and storage modulus at room temperature as a function of the percentage of PVC/DEHP plastisol added to the resol resin.

content (Fig 6), and an increase in the deformation and the load at break was observed (Fig 5). This could be due to the presence of voids in the cured blends, which were observed by scanning electronic microscopy (SEM). As an example, Fig 7 shows a micrograph of the blend of resol and 10 % PVC/DEHP plastisol. It could be expected that the addition of PVC/DEHP plastisol increases the void content in the blend due to the higher quantity of solvents present. As mentioned earlier, the higher acid content used for the preparation of the blends results in an increase in the crosslinking density, hindering the evaporation of the solvents of the plastisol, as well as water and formaldehyde because of the condensation of the resol. In the study of thermal degradation of plastisols it was observed that the concentration of voids in such materials increased after treatment with acids at degradation temperatures.²⁰ The storage modulus

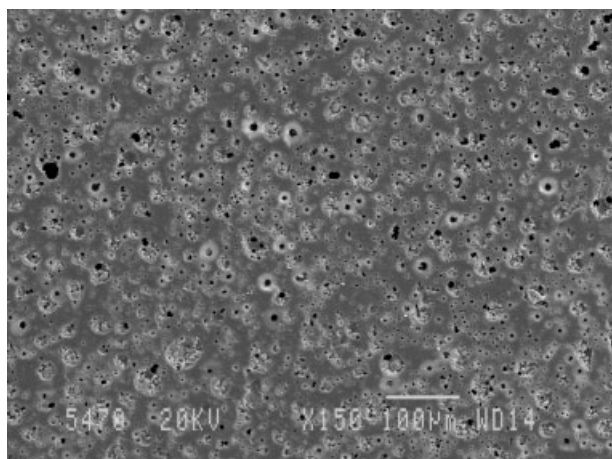


Figure 7. SEM micrograph of the blend of resol and 10 % PVC/DEHP plastisol.

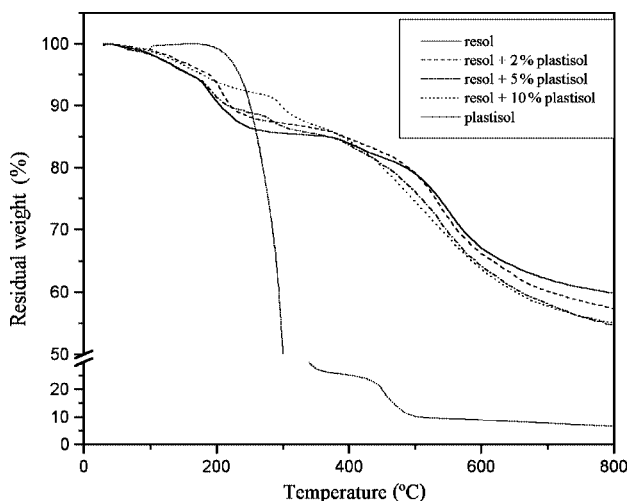


Figure 8. TGA curves of resol, the PVC/DEHP plastisol and their blends.

(E') in the glass state determined by means of dynamic mechanical analysis at room temperature decreases with increasing PVC/DEHP plastisol content (Fig 6), as was also observed in the modulus determined by flexural analysis.

The thermal degradation behaviour of resol, plastisol and their blends was studied by TGA (Fig 8). The loss of weight at low temperatures, up to approximately 400 °C, was faster for the resol than for the plastisol. However, for temperatures higher than 400 °C, the resol was more thermally resistant and had a higher char yield at 800 °C. The increase in the thermal resistance of the blends at lower temperatures was consistent with the increase in the crosslinking density with the addition of plastisol to the resol, as discussed earlier. The curves for the blends with plastisol content of 5 and 10 % showed a slight weight loss at around 300 °C, corresponding to the plastisol fraction. This result indicated that the thermal behaviour of these blends could be considered as the superposition of both components.

CONCLUSIONS

Blends of resol with up to 10 % PVC/DEHP plastisol were formulated and characterized. The main process responsible of the formation of such blends seems to be a reaction between the resol and PVC, resulting in more crosslinked structure. This conclusion was based on the FTIR and DMA results. The FTIR spectra showed that the *para* substitution of the benzene ring was favoured by the addition of plastisol, and that there was an increase of the *ortho-para* methylene bridges in the resol. DMA showed an increase in the T_g value and a decrease in the height of $\tan \delta$ with the addition of plastisol to the blends. TGA indicated an increase in the thermal resistance at lower temperatures with plastisol content. Flexural analysis showed a decrease in the modulus and an increase in the deformation and the load at break when the percentage of plastisol added to the resol increased. However, the systems showed an elastic behaviour. Therefore, it was not possible to observe the effect of the DEHP plasticizer owing to the low quantity of plastisol that could be added to the resol.

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