A variety of ketone-based resins has been synthesized and cyanoethylated in good yields using excess acrylonitrile as solvent and aqueous sodium hydroxide as catalyst. The rheological parameters controlling the processing, the storage stability and the application of these products have been determined. It was proved that, generally, the modified resins exhibit superior properties as compared to the starting products, being suitable for use in the preparation of adhesives and coatings for the improvement of the processing characteristics and the solid content of such systems.

**INTRODUCTION**

The development of synthetic resins has become an important pathway in producing sustainable materials for industrial use. In this context, it is worth mentioning the employment of ketone-formaldehyde-based resins as additives in various commodity applications.1-3 To impart new functions to the ketone/aldehyde resins, they were subjected to different chemical modifications, either via their hydroxyl and carbonyl groups, or through condensation with several modifiers. Significant examples of such changes are the catalytic hydrogenation of the carbonyl groups to secondary alcohols to obtain weather and environment resistant materials,4,5 the synthesis of water-soluble sulfonated resins by reaction of ketones and formaldehyde in the presence of sodium bisulfite,7,10 or the modification of the resins through their reaction with carboxylic anhydrides, phenols, melamine, aniline, p-amino benzoic acid and other compounds.11-22 Most of the manufactured products are used as additives in modifying the properties of high molecular weight film makers, or are encountered in components of pigments for pasta, flexography and printing inks, PVC and nitrocellulose polishing lacquers, varnishes for wood and paper, toner, cosmetics, enamels or nail polishes. Virtually, these resins appear as irreplaceable when seeking to obtain high quality materials.

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As hydroxyl compounds, ketone resins can be also modified by cyanoethylation to impart new functions to the starting material. The aim of this study was to obtain and investigate the rheological features of cyanoethylated ketone resins, a key component in the development of coatings and adhesives.

RESULTS AND DISCUSSION

The preparative aspects involved the application of the conventional cyanoethylation procedure, using excess acrylonitrile to ensure a good homogenization and dissolution. The reaction between the resins and acrylonitrile is presented below (ketone fragment):

\[
\begin{align*}
\text{~ C - CH}_2 - \text{CH}_2 - \text{OH} \quad + \quad \text{CH}_2 = \text{CH} - \text{CN} \quad \xrightarrow{\text{NaOH}} \quad \text{~ C - CH}_2 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CN}
\end{align*}
\]

Usually, this reaction yields a brick, elastic and sticky product, whose consistency depends on the employed resin type.

Five types of resins were synthesized: acetone-formaldehyde (AF), cyclohexanone-formaldehyde (CHF), acetophenone-formaldehyde (APhF), 4-nitro acetophenone-formaldehyde (NAPhF), 4-methoxy acetophenone-formaldehyde (MeAPhF), in alkaline conditions, following the procedures previously described.\textsuperscript{23-24} The obtained resins were cyanoethylated with acrylonitrile and further designated as AF-AN, CHF-AN, APhF-AN, NAPhF-AN, MeAPhF-AN, respectively. It should be mentioned that the AF resin was prepared starting from one part acetone and three parts formaldehyde.

Structural changes occurring by cyanoethylation were evidenced by the FT-IR spectra which revealed the presence of a new absorption band at 2248 cm\(^{-1}\), attributed to the stretching vibration of –CN group, in addition to those characteristic for the starting resins (1700 cm\(^{-1}\) for >C=O group, 840–850 cm\(^{-1}\) for substituted aromatic rings or 1100–1115 cm\(^{-1}\) for stretching vibrations of -C-O- C- ether groups). It should be noted that the higher the degree of cyanoethylation, the lower the intensity of the bands assigned to –OH groups. At the same time, the absorption bands of the modified resins based on aliphatic ketones appear sharper and more intense than those of the cycloaliphatic or aliphatic-aromatic ketone resins.

The thermal behavior was studied up to 600°C in nitrogen atmosphere, three steps of degradation being evidenced for all resins. Table 1 summarizes the thermal characteristics for the main decomposition stage and it seems that the cyanoethylated materials have higher initial, maximum and final process temperatures, and that the residues are somewhat higher for these products. It can be thus supposed that the cyanoethylation favors the obtaining of materials with higher thermal stability, probably due to the presence of –CN groups in their structure.

Rheological characterization. Three types of oscillatory and rotational rheological tests were performed, for both unmodified and modified resins: a) amplitude sweep (strain test), b) frequency sweep, and c) flow tests at temperatures equivalent to the melting point.\textsuperscript{25-26}

a) Amplitude sweep (Fig. 1) is used to determine the limits of the linear viscoelastic domain (LVE), where no irreversible deformation of internal structure of the material appears. Even if this test allows the evaluation of the limiting values of strain or shear stress, it also gives valuable information on the mechanical stability of the analyzed samples.\textsuperscript{27}

<p>| Table 1 |
|------------------|--------------------|----------------|----------------|----------------------|----------------------|
| <strong>Thermal characteristics of unmodified and modified aliphatic, cycloaliphatic and aliphatic-aromatic resins</strong> |</p>
<table>
<thead>
<tr>
<th>Resin</th>
<th>Thermal properties</th>
<th>( T_i ) (^\circ)C</th>
<th>( T_m ) (^\circ)C</th>
<th>( T_f ) (^\circ)C</th>
<th>Weight losses, %</th>
<th>Residue, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>158.0</td>
<td>192.0</td>
<td>214.0</td>
<td>63.11</td>
<td>16.01</td>
<td></td>
</tr>
<tr>
<td>AF-AN</td>
<td>181.8</td>
<td>197.6</td>
<td>228.6</td>
<td>37.15</td>
<td>21.19</td>
<td></td>
</tr>
<tr>
<td>CHF</td>
<td>336.6</td>
<td>353.4</td>
<td>444.1</td>
<td>68.48</td>
<td>6.70</td>
<td></td>
</tr>
<tr>
<td>CHF-AN</td>
<td>350.0</td>
<td>371.7</td>
<td>492.7</td>
<td>44.13</td>
<td>20.21</td>
<td></td>
</tr>
<tr>
<td>APhF</td>
<td>285.0</td>
<td>367.3</td>
<td>404.4</td>
<td>74.22</td>
<td>14.82</td>
<td></td>
</tr>
</tbody>
</table>
Table 1 (continued)

<table>
<thead>
<tr>
<th>Resin</th>
<th>$G'$</th>
<th>$G''$</th>
<th>$G'$</th>
<th>$G''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>APhF-AN</td>
<td>309.5</td>
<td>347.0</td>
<td>401.5</td>
<td>75.38</td>
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<tr>
<td>NAPhF</td>
<td>256.5</td>
<td>285.2</td>
<td>305.8</td>
<td>17.68</td>
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<tr>
<td>NAPhF-AN</td>
<td>273.9</td>
<td>323.6</td>
<td>343.6</td>
<td>38.75</td>
</tr>
<tr>
<td>MeAPhF</td>
<td>270.9</td>
<td>301.7</td>
<td>320.7</td>
<td>25.63</td>
</tr>
<tr>
<td>MeAPhF-AN</td>
<td>297.2</td>
<td>328.7</td>
<td>484.8</td>
<td>61.07</td>
</tr>
</tbody>
</table>

Fig. 1 – Amplitude sweep for: (a) AF and AF-AN resins; (b) CHF and CHF-AN resins; (c) APhF and APhF-AN resins; (d) NAPhF and NAPhF-AN resins; (e) MeAPhF and MeAPhF-AN resins.
The measurements for AF and AF-AN resins were performed at 60°C and revealed, for both products, a dominant viscous behavior having the loss modulus higher than the storage modulus (Fig. 1a) for the entire experimental domain. Consequently, one may suppose a stable liquid-like structure with an extended LVE. The parallel dynamic moduli are an indication that a type of liquid-like stable network is characteristic for both unmodified and modified resins. The cyanoethylated product is more flexible and has a higher mechanical stability than the unmodified resin.

Amplitude sweep tests for the unmodified and the modified CH-based resins were performed at 110°C and, as in the previous case, both products were shown to present a dominantly viscous character (Figure 1b). Nevertheless, for these resins significant differences may be observed between the initial product and the modified resin. Only the cyanoethylated product develops a stable network of forces for the whole experimental domain. The higher values for both G′ and G″ suggest that the products situated in this category are stiffer than the AF products, the unmodified resin being less stable.

The unmodified and modified APhF-based resins were tested at 100°C (Fig. 1c). The recorded data show that the unmodified resin presents a gel-like structure for small deformations (G′ > G″), for γ > 0.6225% the intermolecular crosslinks being destroyed, this suggesting their physical nature. The APhF resin is the only compound exhibiting solid-like behavior for small deformations. The transition from viscous gel behavior to that specific for solutions is marked by the intersection of G′ and G″ curves. This crossover point, not recorded for other resins, also known as threshold of tension, marks the irreversible transition from viscous to solid phase. The corresponding cyanoethylated product has a stable liquid-like structure for the entire measured domain. On the other hand, the APF resin presents the highest loss and storage moduli, greater rigidity and a predominantly elastic character at low deformations.

A particular behavior was observed for MeAPF product, its loss modulus G″ being four orders of magnitude higher than the storage modulus G′, this indicating a strong sticky character. The amplitude sweep diagrams of the modified resins confirm their viscous behavior (Fig. 1e). The highest values of linear viscoelastic range were registered for NAPhF-AN and MeAPF-AN resins, which can be translated into high rigidity and low decantation possibilities. These data show that the highest stability and linear viscoelastic domain pertain to MeAPF resin and the lowest ones to NAPhF.

b) Frequency sweep (mechanical spectra). These tests are usually used to determine the nature of inter- and intramolecular forces in a material. In this test, a sinusoidal strain with constant amplitude (depending on the LVE range limits of each sample) was applied and the oscillation frequency was varied (between 10¹ and 10² rad/s). The oscillatory tests with frequency sweep were indicative of the preponderantly liquid-like behavior of the samples with G″ > G′ over the entire applied frequency domain. Taking into consideration the potential applications of the analyzed samples in coatings and adhesives, the frequency sweep is the desirable test to evaluate the consistency at rest, long-term behavior and separation behavior of the samples (sedimentation, settling, flotation or syneresis). The G′ value at low angular frequency (ω ≤ 0.1 rad/s) gives information on the “at rest” (G′₀) behavior. By applying the Carreau-Yasuda model, the zero-shear viscosity (η₀) can be determined and correlated with the application characteristics of the samples.

For both unmodified and modified AF-based samples (Fig. 2a), as well as for the unmodified and modified CHF-based samples (Fig. 2b), the loss modulus (G″) dominates the storage modulus (G′) over the entire measurement domain. This is an indication of the liquid-like (viscous) character of the systems. The dynamic moduli are parallel, but clearly frequency dependent, therefore being understandable that the structure is stabilized through a physical network of forces. Obviously, no frequency-dependent crossover point of the dynamic moduli appears in the considered frequency range. The complex viscosity is slightly dependent on frequency, this dependency almost disappearing for the modified resins. A similar behavior is also characteristic for MeAPF-based samples (Fig. 2e). As expected, the samples based on APF (Fig. 2c) and NAPhF (Fig. 2d) have a slightly different behavior. The unmodified APF resin exhibits a gel character for low frequencies and dynamic moduli three orders of magnitude higher than the rest of the synthesized samples. The cyanoethylolation significantly reduces the rigidity of the system and improves the stability of the liquid-like network, favoring the development of physical crosslinks among the macromolecular chains. Almost all samples have a shear-thinning behavior more evident for the unmodified APF and the modified NAPhF resins. For all samples, theoretical curves overlap very well over the experimental ones and enable the determination of zero shear viscosity. The highest η₀ value corresponds to the unmodified APF resin in
The obtained data suggest that the AF-AN sample is more stable in time and the decanting of active ingredients from the mixtures of these resins will be more difficult than from those of the AF resin. Low viscosities on the entire experimental domain, a good overlap of the experimental data with the theoretical curve are characteristic for the CHF-AN sample and higher values for zero shear viscosity for the CHF resin. As for the NAPhF and the MeAPhF resins, the values of the complex viscosity are slightly affected by the frequency and the zero shear viscosities still remain very low as compared to those recorded for the APhF resin. The viscosity of APhF-AN and NAPhF-AN samples depends on the oscillation frequency, while that of MeAPhF-AN is independent of this parameter.

Fig. 2 – Frequency sweep for: (a) AF and AF-AN resins; (b) CHF and CHF-AN resins; (c) APhF and APhF-AN resins; (d) NAPhF and NAPhF-AN resins; (e) MeAPhF and MeAPhF-AN resins.
c) Flow curves. The oscillatory tests results are confirmed by the rotational tests. Rotational measurements used to describe the dependence of viscosity and shear stress on the shear rate (Fig. 3) are carried out for a better understanding of the rheological behavior of the analyzed samples. The flow curves were recorded in terms of both shear stress ($\tau$) and viscosity ($\eta$). Almost all samples exhibit non-Newtonian behavior for nearly the whole measurement domain, with a viscosity depending on the shear rate. The first Newtonian domain is obvious, as well as the beginning of the shear-thinning behavior. A Newtonian behavior was noticed for AF and MeAPhF unmodified resins, but in all cases the shear-thinning behavior is strengthened by cyanoethylation. The
experimental results were fitted with the Carreau–Yasuda model and the experimental data proved to be in agreement with the theoretical model. The tests point out the lower time stability of the AF resin, more exposed to phase separation in the mixtures than the modified material (also confirmed by the frequency sweep tests). On the other hand, the cyanoethylated product can faster recover after being subjected to an instant strain such as pumping, mixing, filling the forms, etc.

The high zero shear viscosities of APhF and NAPhF-based samples suggest high materials stability. Moreover, for almost all samples the modification of the resins improves their stability. It is worth mentioning that the data from these tests are perfectly consistent with the results obtained from the frequency sweep measurements.

EXPERIMENTAL PART

a) Materials and methods

The materials used in this study – cyclohexanone (CH), acetoephone (APh), 4-nitro-acetoephone (NAPh), 4-methoxy-acetoephone (MeAPh) and formaldehyde (F) (37% solution) – were purchased from Fluka AG, while acrylonitrile (AN), acetonitrile (AAc), acetic acid and sodium hydroxide came from Merck, Darmstadt, Germany. All chemicals were analytically pure and were used as received for the synthesis and modification of the corresponding ketone resins. Five resins were synthesized – acetone-formaldehyde (AF), cyclohexanone-formaldehyde (CHF), acetoephone-formaldehyde (APhF), 4-nitro-acetoephone-formaldehyde (NAPhF), 4-methoxy-acetoephone-formaldehyde (MeAPhF) – in alkaline conditions, following the procedures described in the literature.\(^\text{23, 24}\) The obtained resins were cyanoethylated with acrylonitrile and designated as AF-AN, CHF-AN, APhF-AN, NAPhF-AN, MeAPhF-AN, respectively. The AF resin was prepared starting from one part acetone and three parts formaldehyde.

Usually, the cyanoethylation is accomplished by the reaction of the resin with acrylonitrile in the presence of a small amount of caustic alkali as catalyst. Typically, 5g of resin and 50 mL of AN were placed in a water-cooled (heated) round-bottom three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. While the temperature of the flask was raised to 40°C, 10 mL of 12.5% NaOH solution were added gradually drop wise to the flask under vigorous stirring. In a few minutes the color of the mixture turned dark yellow to brown, after 90 minutes at 50°C the reaction being completed. The content was poured into a large amount of water acidified with acetic acid to isolate the modified product. The precipitate was then dissolved in a large amount of acetonitrile and the solution was mixed with a large amount of water to separate the cyanoethylated resin. This procedure was repeated several times and finally the precipitate was dried in vacuum at 40°C for 72 h.

b) Measurements

The IR spectra of the modified resins were registered on a FT-IR Perkin Elmer Spectrometer. The thermal behavior was analyzed on a Mettler Toledo TGA-SDTA 851e type equipment in N\(_2\) atmosphere with 20 mL/min flow rate and 10 K/min as heating rate. The rheological investigations were carried out on a Physica MCR 501 (Anton Paar, Austria) modular rheometer provided with a Peltier device for the temperature control. Parallel plate geometry with serrated plates to avoid slippage was used. The upper plate, made from stainless still, was of 50 mm diameter. A solvent trap was used in all rheological tests to diminish solvent evaporation.\(^\text{28}\) Various rheological parameters were calculated using the Rheoplus software.

CONCLUSIONS

Ketone-formaldehyde resins are used as additives in many industrial applications. To open new areas of application, ketone resins have been subjected to various modifications using their functional groups. In this study, five different resins based on aliphatic, cycloalyphatic and aliphatic-aromatic ketones were synthesized and then modified by cyanoethylation. Simple and oscillatory rheological tests offered valuable information on resins structure and stability. The rheological tests underlined that the modified products exhibit improved properties, allowing them to be used in coatings industry. The modification of the initial resins strengthened the non-Newtonian character of the samples, a type of stable liquid-like network being formed due to the contribution of weak physical interactions. The experimental results indicated that the modified resins may lead to stable mixtures with different active ingredients, can promote the adhesive strength of the coatings and are easier to process. Therefore, the knowledge of the viscoelastic parameters of such resins can be used to predict the future performances of different materials and their possible use in specific applications.

Acknowledgements: This paper was realized with the support of EURODOC “Doctoral Scholarships for research performance at European level” (ID-59410) project, financed by the European Social Found and the Roumanian Government. The rheological and thermogravimetric tests were performed in the Rheology Laboratory of the Interdisciplinary Training and Research Platform “High performance multifunctional polymeric materials for medicine, pharmacy, microelectronics, energy/information storage, environmental protection” of the Natural and Synthetic Polymers Department, “Gheorghe Asachi” Technical University of Iași, Roumania.

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