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NEW MATERIALS FROM LIGNIN

Lignin is a natural amorphous polymer, which, together with cellulose and hemicellulose, is one of the main constituents of wood. It is generally obtained, as a by-product in the paper production, through the separation from the cellulose fibers. Although its industrial attractives, rarely lignin has been used to obtain new materials; in fact only in the last years some trials have been made to use it as a thermoplastic.

Lignin structure depends of the kind of process used for delignification [1]. Due to its phenolic nature, many chemical modifications have been studied. For example, it has been used as a main chain on which other synthetic polymer chains can be grafted [2]. Moreover, due to the presence of the phenolic groups it is expected that it can increase the oxidation, thermal and light stability of polymeric materials. It is a low-density, low abrasive and low-cost material, features that could be interesting in its use as filler instead of inorganic fillers [3]. With certain polymers, in suitable formulations, it can give partially or completely biodegradable composites [4]. All these features are attractive from the industrial point of view, nevertheless rarely lignin has been used to obtain new materials; in fact only in the last years some trials have been made to use it as a thermoplastic.

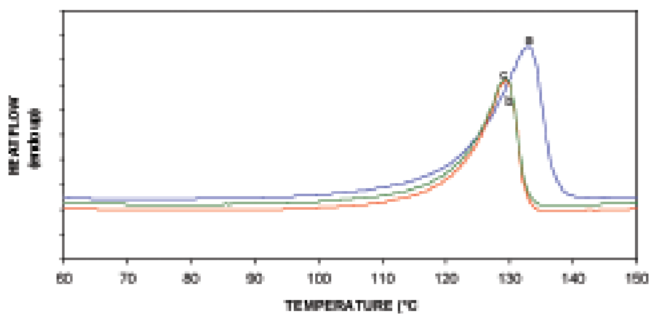

Fig. 1 - DSC scan from 60 °C to 150 °C at 20 °C/min. for Lupolen (a), blend with 10% lignin (b), blend with 20% lignin (c)

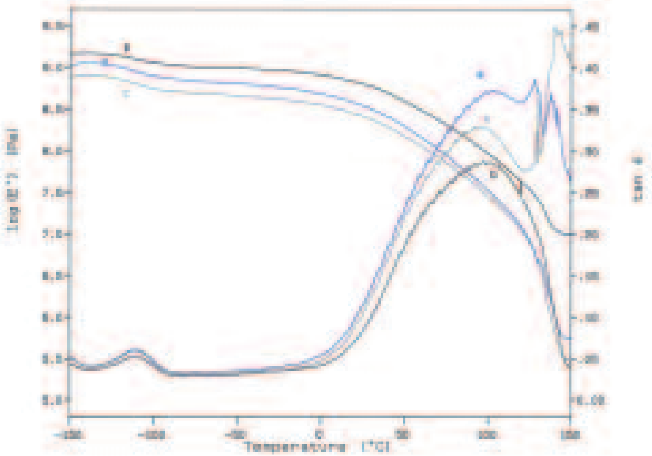

Fig. 2 - Storage component of the modulus (logE') and loss factor (tanδ) as a function of temperature for Lupolen (a), blend with 10 % lignin (b), blend with 20% lignin (c) evaluated by DMTA

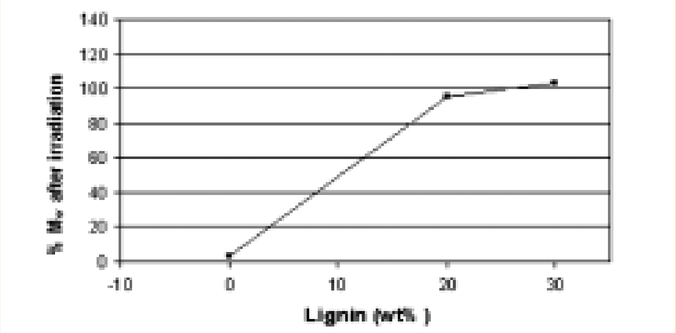

Fig. 3 - Percent of the weight average molecular weight hold after irradiation of blends lignin-polystyrene with a 15 W UV lamp for 48 hours

Results and Discussion

Blends [5]

The thermal properties of blends have been evaluated by Differential Scanning Calorimetry (DSC). The transition temperatures are scarcely influenced by the presence of lignin, while the lower normalized heats of transition point are due to the formation of less perfect crystals (Fig. 1).

The dynamic-mechanical tests reveal in all cases a general increase of the module upon the addition of lignin (Fig. 2).

The samples have been tested for the UV stability determination of the effect of lignin presence and content. The addition of lignin to PSD, Flexirene and Riblene causes an increase in the average molecular weight after irradiation, on increasing the content of lignin, thus suggesting a protecting action against photooxidation exerted by the filler (Fig. 3). In contrast, the addition of lignin causes a neat degradation of Lupolen.

The obtained blends are processable with the techniques in use for thermoplastics. Lignin stabilizes polystyrene and low-density polyethylene against the UV radiation. As far as the mechanical properties are concerned, the addition of lignin increases the modulus of blends, with respect to the neat polymers. Nevertheless, the presence of lignin decreases the tensile strength and the elongation at breaking. These results have been related with the poor compatibility between lignin and the synthetic apolar polymers and to the non uniform distribution and poor adhesion of the lignin particles to the matrix (Fig. 4). These problems may be overcome by using more efficient mixing techniques and a compatibilizing agent.

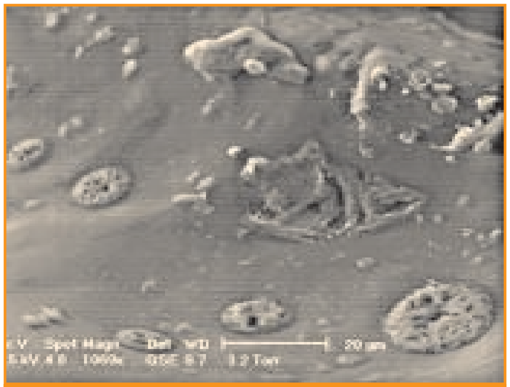

Fig. 4 - ESEM micrograph of the fracture surface of LF10

Polyurethanes and polyesters [6]

Polyurethanes were obtained treating steam exploded lignin from straw with 4,4'-methylenebis(phenylisocyanate), 4,4'-methylenebis (phenylisocyanate)-ethandiol, and poly(1,4-butandiol) tolylene-2,4-diisocyanate terminated. The obtained materials were characterized by using gel permeation chromatography (Fig. 5), infrared spectroscopy (Fig.6) and scanning electron microscopy.

Differential scanning calorimetry analysis showed a T_g at -6 °C, assigned to the glass transition of the poly(1,4-butandiol) chains. The presence of ethylene glycol reduced the yields of the polyurethanes. The use of the prepolymer gave the best results in polyurethanes formation. Steam exploded lignin was used as starting material in the synthesis of polyesters. Lignin was treated with dodecanoyl dichloride. The products were characterized by using gel permeation chro-

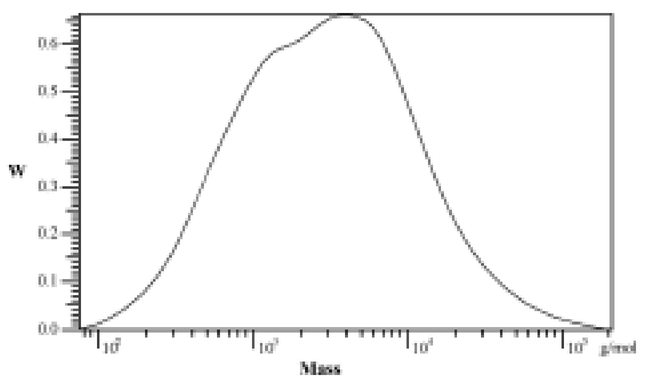

Fig. 5 - Gel permeation chromatogram of polyurethane from poly(1,4-butandiol)tolylene-2,4-diisocyanate terminated and lignin

ABSTRACT

Nuovi materiali dalla lignina

La lignina è un polimero naturale amorfo che, insieme a cellulosa ed emicellulosa, è uno dei principali costituenti del legno. Viene generalmente ottenuta, come by-product nella produzione della carta, mediante separazione dalle fibre di cellulosa. La sua struttura dipende dal tipo di processo utilizzato per la delignificazione. A causa della sua natura fenolica, sono state studiate molte modificazioni chimiche. La lignina costituisce un materiale a bassa densità, bassa abrasività e basso costo, caratteristiche che potrebbero risultare interessanti nel suo utilizzo come carica al posto di cariche inorganiche. Con alcuni polimeri, in adatte formulazioni, può dare compositi parzialmente o completamente biodegradabili. Nonostante tutte queste caratteristiche siano attrattive dal punto di vista industriale, la lignina è stata raramente utilizzata per ottenere nuovi materiali, infatti solo negli ultimi anni sono stati effettuati dei tentativi per utilizzarlo come termoplastico.

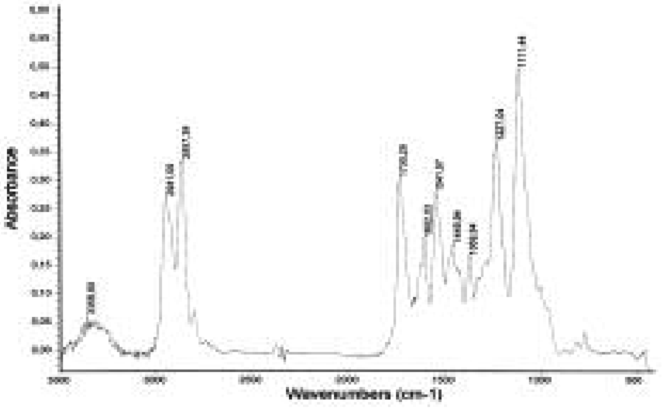

Fig. 6 - FTIR of polyurethane from poly(1,4-butandiol)tolylene-2,4-diisocyanate terminated and lignin

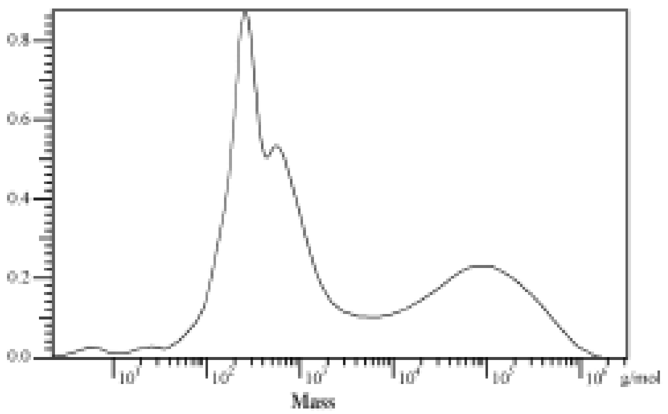

Fig. 7 - GPC of copolymer lignin-methyl acrylate

matography, infrared spectroscopy, ^{13}C and ^{1}H nuclear magnetic resonance spectrometry, and scanning electron microscopy.

Copolymers [7, 8]

FTIR of copolymers showed absorptions due to the presence of both lignin and alkenes. GPC analysis showed the presence of fractions with high molecular weights (Fig. 7): the M_z of lignin from pine was 3,729 while the copolymer with methyl acrylate showed M_z = 383,790.

Differential calorimetry showed the presence of glass transitions in

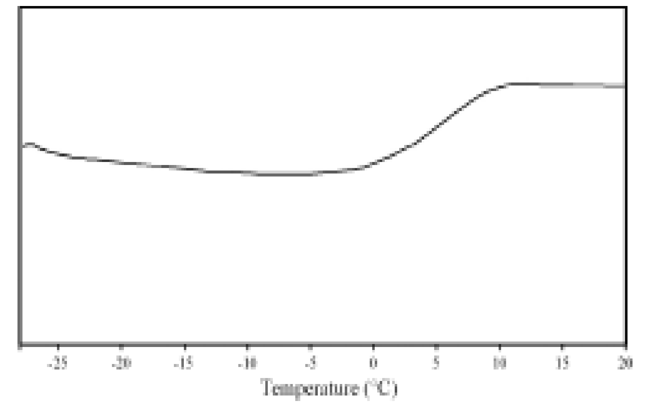

Fig. 8 - DSC of copolymer lignin-methyl acrylate

the range of -9 to 4.5 °C due to the presence of grafted polyalkene chains (Figure 8). When acrylonitrile was used as starting material DSC analysis of the product showed a glass transition at 119 °C, which can be attributed to grafted polyaacrylonitrile chain.

Lignin from pine gave better results than that from straw. These results can be explained on the basis of the structural properties of used lignins.

Conclusions

The aim of this work is to demonstrate that lignin can be a useful precursor of new materials. Many techniques can be used to obtain new materials from lignin. Isocyanates are commonly used in the preparation of wood adhesives. In this case heat is able to form polyurethanes after adsorption on wood. We described our results on the interaction between a lignin from steam explosion and diisocyanates to give polyurethanes. The aim of this study is to verify the possible use of lignin as an additive with UV protective properties in this type of adhesive. In fact, we showed that lignin has an UV protective action on polyethylene and polystyrene blends. Furthermore, polyesters can be used in the formulation of polyurethane coatings. The applicability of this procedure with lignin from straw obtained by using steam explosion is reported in this study: the formation of polyesters can broaden the possible uses of steam-exploded lignins.

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