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(54) Benævnelse: **ANVENDELSE AF EN LIGNIN TIL DEN MEKANISKE FORSTÆRKNING AF EN ELASTOMER, OG ELASTOMER SÅLEDES FORSTÆRKET**

(56) Fremdragne publikationer:
US-A- 3 223 697
US-A- 3 699 091
US-A- 3 984 362
C.H. GILES AND S.N. NAKHWA: "Studies in adsorption. XVI. The measurement of specific surface areas of finely divided solids by solution asdorption", JOURNAL OF APPLIED CHEMISTRY, juin 1962 (1962-06), pages 266-273, XP002696653, Glasgow
None

USE OF A LIGNIN FOR THE MECHANICAL REINFORCEMENT OF AN ELASTOMER, AND ELASTOMER THUS REINFORCED

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a novel use of a pure and non-degraded biopolymer of natural polyphenol type represented by a particular lignin – hereinafter, lignin – for the mechanical reinforcement in elastomer-type polymeric structures.

The present invention also relates to an elastomer prepared by implementation of the use according to the invention.

The novel use according to the present invention resides in the implementation of a particular lignin coming from a vegetable raw material, in particular wheat straw, and which is composed of linear oligomers with a low molecular weight behaving like oligomers and homologous phenolic polymers.

The novel use of the present invention has been made possible, because the pure and non-degraded lignin (hereinafter called "Biolignine™" or also "Lignine CIMV") is prepared by a method – hereinafter the "CIMV method" – completely understood and described in particular in patent document EP-B1-1.180.171.

The notion of purity and the native character of "Biolignine™" can in particular be summarised by the following points: residual polysaccharide ratio, raw material ratio, average molecular mass and distribution, reactive function ratio (in particular, hydroxyls), all these characteristics being obtained without particular treatment.

Characterisation works conducted, in particular by Michel Delmas and Bouchra Mlayah Benjelloun, have in addition enabled to establish the structure and the functionality of Lignine CIMV thus prepared, of which the results of the works have been published in the following documents:

A "Functionality of Wheat Straw Lignin Extracted in Organic Acid", "Media Journal of Applied Polymer Science" in Vol. 121 491-501(2011);

B "Structural Elucidation of the Wheat Straw Lignin Polymer..." in Journal of the Mass Spectrometry 2003; 38: 900-903;

C "Elucidation of the Complex Molecular Structure of Wheat Straw Lignin Polymer..." in Rapid Communications in Mass Spectrometry 2007; 21: 2867-2888.

In particular, a certain functionality and/or specific physicochemical properties of this Biolignine™ or Lignine CIMV highlighted during these studies have confirmed the potential of this lignin in commercial applications in manufacturing non-toxic polymers, in particular in the field of glues for stratified, plywood particle panels and/or green plastic processing, in particular phenolic resins, epoxy resins.

More surprisingly, the specific physicochemical properties of this lignin have confirmed the potential of this lignin as an excellent substitute for carbon black for the mechanical reinforcement in elastomer-type polymeric structures.

It is this latest discovery which is the basis of the present invention.

STATE OF THE ART

The use of a lignin to replace carbon black as reinforcing element in producing elastomer-type compounds is known from document, “Lignin for Reinforcing Rubber” (J. J. Klein and Arthur Pollack – West Virginia Pulp and Paper Company, Charleston – published more than 60 years ago in “Industrial and Engineering Chemistry” Vol. 39, No. 4.

Further to the fact that the structure of the lignin described in this document is not defined, its physicochemical properties, for example in terms of specific surface area, and its functionality are fundamentally different from those of the lignin prepared and non-degraded according to the use, according to the invention.

More recent patent documents, for example EP-A1-2.223.928, relate to the use of a so-called “functionalised” lignin, which all make reference to the chemically modified lignin in rubber-based compositions.

In document US-A-3.223.697, for the use as a reinforcing element in a composition of a rubber (column 2, line 31 et seq.), reference is made to lignins obtained by coprecipitation, i.e. chemically modified lignins. In addition, it is indicated that the results obtained after reducing powder were not satisfactory. Thus, despite the efforts to increase the specific surface area and decrease the particle size, the replacement of carbon black with the lignin was not satisfactory.

Then (column 3, line 5 et seq.), this document indicates an attempt to decrease the diameter of the particles to obtain a specific surface area comprised between 3 and 5m^2/g. On the one hand, this modification has not been satisfactory from the standpoint of the results obtained and, on the other hand, it is still located in attempts to use chemically modified lignins. Then, as regards the invention which is the subject matter of this document, from column 3, line 17 et seq., a method for heating and chemically modifying the lignin is stated, in view of obtaining the powder lignin having a specific surface area of at least $20m^2/g$.

Document US-A-3.984.362 relates to the chemically modified lignin and in particular to examples 1 and 2 (see in particular, added products for preparing powder lignin). In this document, a preparation of the lignin by washing and reprecipitation with acid pH before its use in the mixture with rubber is first claimed, i.e. a preparation before use.

The lignin according to the use, according to the invention is distinguished from this in that it is not chemically modified and in that its functional groups are “available”.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention aims for a use, for the mechanical reinforcement of elastomer-type polymers, of a lignin which is not chemically modified to the available functional groups which has a specific surface area comprised between $0.5m^2/g$ and $5m^2/g$, and preferably comprised between $1m^2/g$ and $2.5m^2/g$.

According to other characteristics of the invention:

- said lignin has a low molecular mass and the Mw of which is comprised between 700g/mol and 2000g/mol;

- said lignin has a polydispersity index equal to about 1.3;

- said lignin comprises available functional groups chosen from the group consisting of aliphatic hydroxyls, phenolic hydroxyls and carboxylic acids;

- aliphatic hydroxyls are present in an amount of 1.5mmol/g to 3.0mmol/g, preferably in an amount of 2.3mmol/g;

- phenolic hydroxyls are present in an amount of 1.1mmol/g to 2.0mmol/g, preferably in an amount of a content not less than 1.1mmol/g;

- carboxylic acids are present in an amount of 0.5mmol/g to 1.5mmol/g, preferably in an amount of a content equal to about 1.0mmol/g;

- said lignin has an average weighted particle diameter comprised between 5 microns and 100 microns, and preferably comprised between 10 microns and 15 microns. The invention also aims for an elastomer.

The invention also proposes an elastomer incorporating a lignin implemented in a use according to the embodiments of the invention.

According to another characteristic, the elastomer does not comprise carbon black.

BRIEF DESCRIPTION OF THE FIGURES

The present invention will now be described using examples of embodiments and results tables given purely illustratively and in a non-limiting manner, and in reference to the appended drawings, wherein:

- figure 1 is a graph illustrating the grain size repartition/distribution of the particles of a “standard” 500-micron Biolignine™;

- figure 2 is a graph illustrating the grain size repartition/distribution of the particles of a finely milled 15-micron Biolignine™;

- figures 3 to 6 are microscopic views by Scanning Electron Microscope of different mixtures according to the invention and/or reference products.

DETAILED DESCRIPTION OF THE INVENTION

A lignin powder has been prepared as follows from a Biolignine™ obtained according to the CIMV method:

From a wheat straw Biolignine™, a fine milling is carried out by means of a planetary ball mill, which has the following characteristics:

- Dry matter: 95%

- Specific surface area: 1.56m^2/g

- Grain size distribution: 50% of the particles have an average weighted particle diameter at 15 microns and 90% of the particles have an average weighted particle diameter of less than 100 microns.

The grain size distribution of the particles is illustrated in figure 1 of the drawings appended to the present description.

The grain size distribution of the particles of a “standard” Biolignine™ has also been represented in figure 2, which has the following characteristics:

- Dry matter: 95%
- Specific surface area: 0.077m^2/g
- Grain size distribution: 40% of the particles have an average weighted particle diameter comprises between 350 microns and 1000 microns and 90% of the particles have an average weighted particle diameter comprised between 45 microns and 1000 microns.

Dispersion tests of Biolignine™ in an elastomer, and more specifically in an EPDM (Ethylene-Propylene-Diene Monomer) which is used in all fields of the rubber industry, have been carried out.

The lignin powder has been incorporated directly in a rubber by a roller mixer.

The results of these tests have been compared with a reference mixture composed of carbon black and EPDM.

The microscopic state of these mixtures by dispersion has been evaluated by Scanning Electron Microscope (SEM) and the results are illustrated in figures 3 to 6 which are microscopic views, with a magnification of 250 times.

It is observed that, whatever the incorporation ratio of Biolignine™ in EPDM, a heterogeneity of the mixture is observed in any case.

Comparative tests have been carried out with three samples of EPDM/ Biolignine™ mixtures and an EPDM/Carbon Black reference sample, the results of which are as follows:

<u>Table 1</u>

“Standard” 500-micron Biolignine™.

500-micron Biolignine™				
EPDM mass proportion	100	100	100	100
Biolignine mass proportion		35	72	105

Carbon black mass proportion	100	0	0	0
Density g/cm^3	1.18		1.06	1.15
Hardness shA	69	55	68	HS
Breaking elongation Ar mm	270	240	165	100
drc (22h 70°)%	40			

Table 2

Finely milled 15-micron Biolignine™, specific surface area 1.56m^2/g

15-micron Biolignine™				
EPDM mass proportion	100	100	100	100
Biolignine mass proportion	0	35	72	35
Carbon black mass proportion	100	0	0	0
Density g/cm^3	1.18			
Hardness shA	69	61	62	67
Breaking resistance DaN	10 to 15	6.6	13.2	27.2
Breaking elongation Ar mm	170 to 270	139	342	270

Despite the heterogeneity of the Biolignine™/EPDM mixtures, these results show that Biolignine™ can replace carbon black in EPDM-based mixtures, with satisfactory hardness and elongation characteristics.

The increase of the specific surface area provides an improvement in the hardness and in the breaking resistance.

The increase of the incorporation ratio provides an improvement of the different characteristics.

The results relating to the Biolignine™/Carbon Black mixture in equal proportions provides results to the reference mixture without Biolignine™.

In the scope of the present description, the specific surface area has been measured according to the method called “diffraction laser” confirmed by nitrogen adsorption (method called “BET”).

See, for example:

http://www.malvern.com/LabEng/technology/laser_diffraction/gas_adsorption_bet.htm.

The molecular mass has been determined according to the method called SEC “Size Exclusion Chromatography”), THF eluant, “Refractometer” detection, three columns in series 100, 500, 1000 Angströms, in SDVB (Styrene Divinyl Benzene) at 30°C. This conventional method has been described in all “Biolignine™” or also “Lignine CIMV” publications.

See also, for example:

http://www.malvern.com/labeng/technology/size-exclusion-chromatography.htm, or

https://en.wikipedia.org/wiki/Size-exclusion_chromatography.

Patentkrav

1. Anvendelse, til den mekaniske forstærkning af polymerer af elastomertypen, af en kemisk ikke-modificeret lignin med disponible funktionelle grupper, som har en specifik overflade omfattet mellem 0,5 m2/g og 5 m2/g, og fortrinsvis omfattet mellem 1 m2/g og 2,5 m2/g.

2. Anvendelse ifølge krav 1, **kendetegnet ved, at** nævnte lignin har en lav molekylemasse, og hvis Mw er omfattet mellem 700 g/mol og 2000 g/mol.

3. Anvendelse ifølge krav 2, **kendetegnet ved, at** nævnte lignin har et polydispersitetsindeks svarende til ca. 1,3.

4. Anvendelse ifølge krav 2, **kendetegnet ved, at** nævnte lignin omfatter disponible funktionelle grupper valgt fra gruppen bestående af alifatiske hydroxyler, phenolhydroxyler og carboxylsyrer.

5. Anvendelse ifølge krav 4, **kendetegnet ved, at**:

- de alifatiske hydroxyler er til stede i en mængde på 1,5 mmol/g til 3,0 mmol/g, fortrinsvis i en mængde på 2,3 mmol/g;
- eller phenolhydroxylerne er til stede i en mængde på 1,1 mmol/g til 2,0 mmol/g, fortrinsvis i en mængde af et indhold på ikke mindre end 1,1 mmol/g;
- eller carboxylsyrerne er til stede i en mængde på 0,5 mmol/g til 1,5 mmol/g, fortrinsvis i en mængde af et indhold svarende til ca. 1,0 mmol/g.

6. Anvendelse ifølge krav 1, **kendetegnet ved, at** nævnte lignin har en vægtet gennemsnitlig partikeldiameter omfattet mellem 5 mikrometer og 100 mikrometer, og fortrinsvis omfattet mellem 10 mikrometer og 15 mikrometer.

7. Elastomer som inkorporerer en lignin implementeret i en anvendelse ifølge et hvilket som helst af de foregående krav.

8. Elastomer ifølge krav 7, **kendetegnet ved, at** den ikke omfatter carbon black.

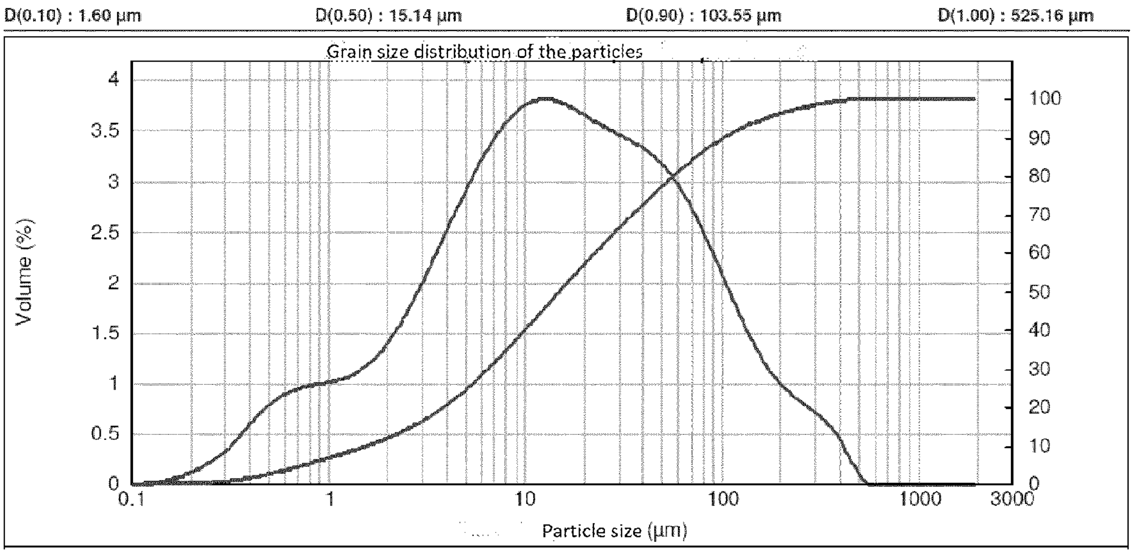

Figure 1

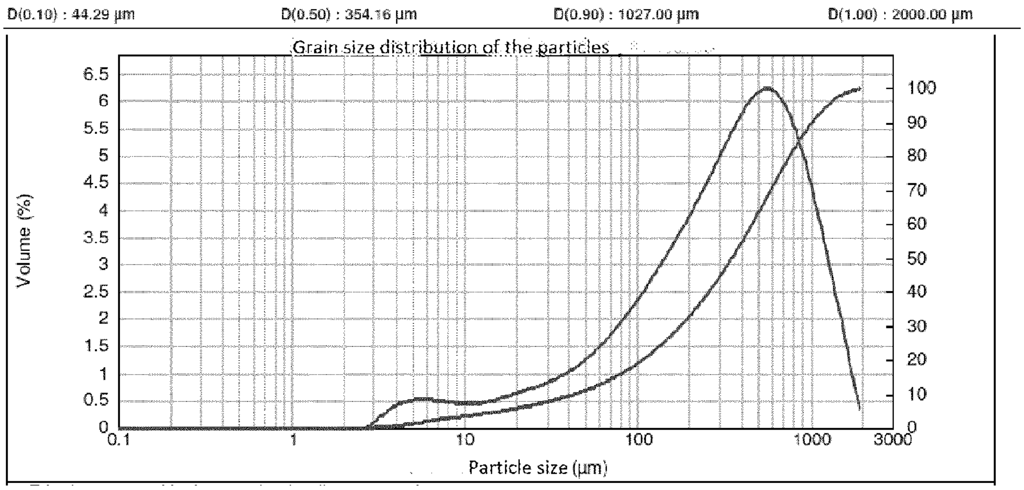

Figure 2

EPDM/CARBON BLACK : X250

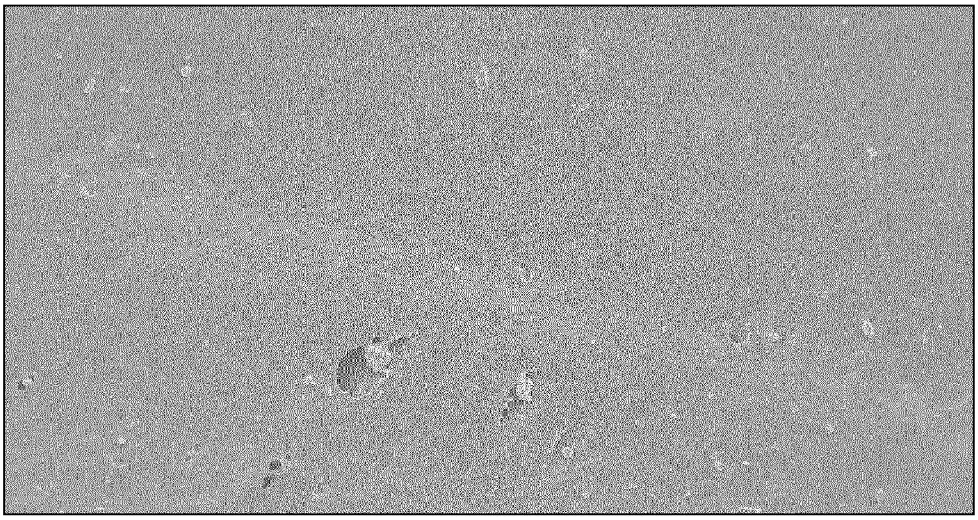

Figure 3

EPDM / Biolignine 40%: X250

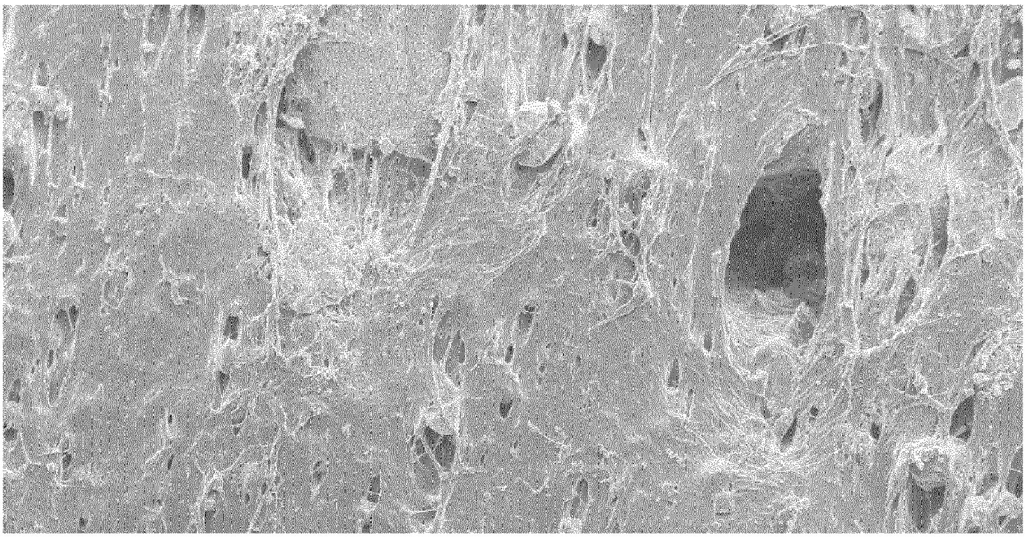

Figure 4

EPDM / Biolignine 60%: X250

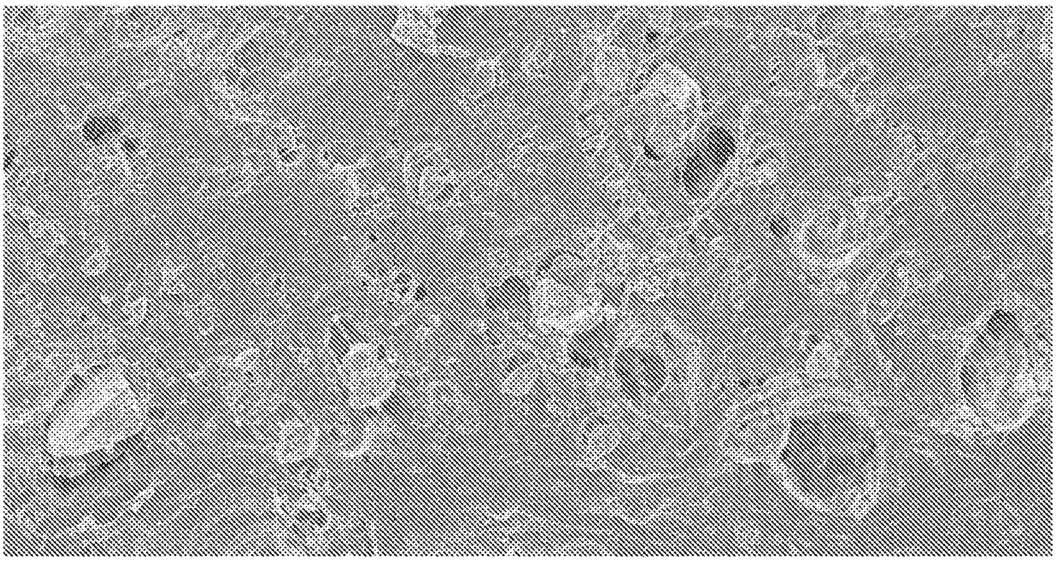

Figure 5

EPDM / Biolignine 100%: X250

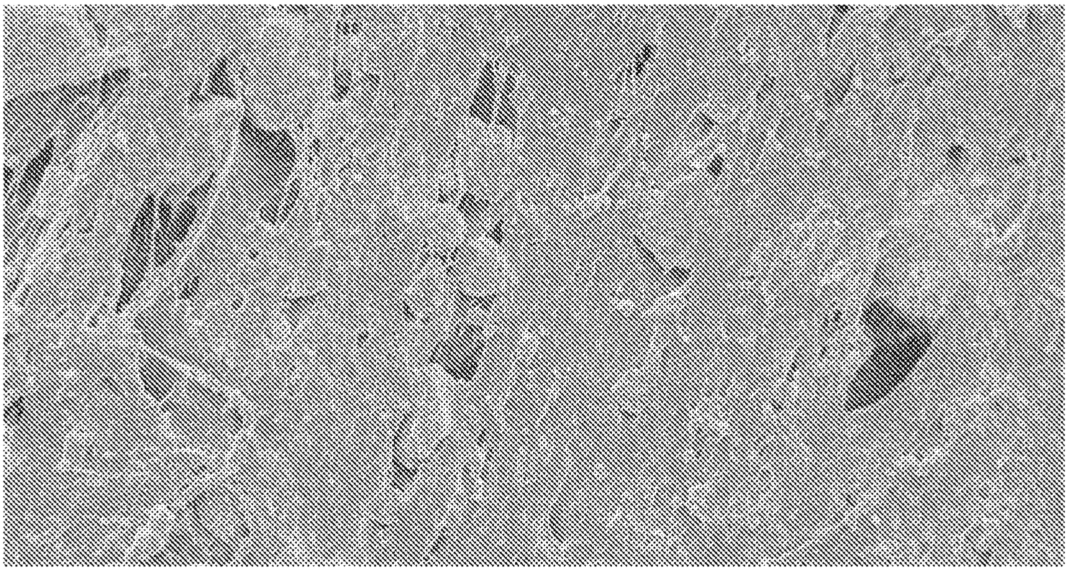

Figure 6