Abstract: The present invention provides a method for making sheet material, comprising the steps of introducing a quantity of a curable composition to a substrate and curing the composition to increase or improve the mechanical properties of the resultant sheet material compared to a sheet material formed from the substrate without the cured composition. The present invention also provides a cellulose-based product, wherein a sufficient quantity of the curable composition is introduced to a cellulose-based web to at least maintain the mechanical properties of the product through "pulp-fusion" when using lower quality cellulosic fibres as compared to a cellulose-based product having regular cellulosic fibres. In further aspects the invention provides removal of water from a web of substantially dewatered cellulosic fibres, and a substantial reduction of the energy input requirements and carbon footprint by the in situ exothermic polymerisation of the curable composition by comparison with conventional methods of producing sheet material.
METHOD FOR MANUFACTURING SHEET MATERIAL

FIELD OF THE INVENTION

The present invention relates to methods for manufacturing sheet material, and in particular paper and paperboard products. However, it will be appreciated that the invention is not limited to this particular field of use.

BACKGROUND OF THE INVENTION

The following discussion of the prior art is provided to place the invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common general knowledge in the field. Whilst the present invention has been described in several embodiments in the following discussion in relation to paper materials and paper products it will be appreciated that the present invention is not limited to such materials.

Manufacturing paper typically comprises the steps of preparing an aqueous cellulosic suspension or slurry having a consistency (percent dry weight of solids in the slurry) of less than 1%, dewatering the slurry into a web and then drying the web. Typically, the dewatered web retains about 80% water. However, the finished sheet preferably contains less than about 5% by weight of water. Accordingly, the dewatering and drying processes of papermaking are extremely important to the efficiency and cost of production. However, the drying process is especially important, since the drying sections, which may be hundreds of meters in length, are expensive to run, consume relatively large amounts of electricity, and being so physically large, requires considerable space for the production facilities. Therefore, the industry has, for many
years, sought ways to improve the efficiency of the drying process, but with limited success.

The papermaking industry, as well as other industries, has also long sought methods for enhancing the strength of products formed from fibrous materials, such as paper and board products, containing cellulose fibre or pulp as a constituent. It has also been a goal of the papermaking industry to enhance the strength of products formed from fibrous materials wherein the recycled furnish or fibre derived from wood is utilized in whole, or in part. For example, recycled cellulose fibre is typically used in the manufacture of newsprint and lightweight coated papers. These factors have dramatically increased in commercial significance in recent years, due to the increasing scarcity of suitable types of virgin timbers, and the increasing cost of such timbers if available, even in the context of premium quality papers and boards.

Various methods have been suggested in the past for improving the dry-strength and related properties of a sheet formed from fibrous materials, such as paper or board materials formed of cellulose fibre. For example, one method is to incorporate chemical additives directly to the fibre furnish prior to forming the sheet. Typical additives comprise cationic starch or melamine resins. However, these additives are ineffective in dramatically improving the mechanical properties of the paper. Another common additive is polyvinyl alcohol, the use of which is disclosed in publications such as U.S. Patent No's 2,402,469 and 4,865,691. While the use of a polymeric binder such as polyvinyl alcohol can be possible in small amounts, the use of larger amounts such as 10 percent by weight up to 20 percent by weight or more, causes processing difficulties in respect of downstream processing, e.g. calendaring or printing. Also, during drying of the web, the polymeric binder can become tacky and stick to the felts. Therefore, the potential benefits of using larger percentages of a polymeric binder in a paper-based
product have not hitherto been realised, as such products have not in the past been able to be made.

It is an object of the present invention to overcome or ameliorate one or more of the disadvantages of the prior art, or at least to provide a useful alternative.

SUMMARY OF THE INVENTION

According to a first aspect, the present invention provides a method for making a sheet material, the method comprising the steps of:

- introducing a quantity of a curable composition to a substrate and curing the curable composition, wherein a sufficient quantity of the curable composition is introduced to the substrate to increase or improve the mechanical properties of the resultant sheet material compared to a sheet material formed from the substrate without the cured composition.

In a second aspect the present invention provides a method for making a cellulose-based product, said method comprising the steps of: contacting a quantity of a curable composition with a web of dewatered cellulosic fibres and curing the curable composition, wherein a sufficient quantity of the curable composition is introduced to the web to increase or improve the mechanical properties of a cellulose-based product as compared to a corresponding cellulose-based product without the cured composition.

In a related aspect the present invention provides a method for making a cellulose-based product, the method comprising the steps of:

- contacting a quantity of a curable composition with a web of dewatered cellulosic fibres and curing the curable composition, wherein a sufficient quantity of the curable composition is introduced to the web to at least maintain the mechanical properties of the cellulose-based product when using relatively lower quality cellulosic fibres as compared to a cellulose-based product having regular cellulosic fibres.
Preferably the quantity of curable composition introduced to the web of dewatered cellulosic fibres is sufficient to increase or improve the mechanical properties of a cellulose-based product as compared to a corresponding cellulose-based product without the cured composition. Preferably a sufficient quantity of the curable composition is introduced to the web to at least maintain or preferably improve the mechanical properties of the cellulose-based product when using a mixture of relatively lower quality cellulosic fibres and regular cellulosic fibres as compared to a cellulose-based product having a mixture of relatively lower quality cellulosic fibres and regular cellulosic fibres without the cured composition.

According to third and fourth aspects, the present invention provides a sheet material or a cellulose-based product when prepared by the methods according to the first or second aspects respectively.

Preferably the sheet material of the invention is particularly adapted for use as paper or a paper product. For example, the sheet material of the invention displays many of the mechanical and physical properties of a "standard" or typical paper product, as well as the look and feel of "standard" paper products. Preferably the sheet material of the invention is adapted to be printable and displays a similar or improved flexibility and foldability to standard paper products. Preferably the sheet material of the invention displays enhanced or at least maintained printability characteristics compared with an equivalent paper product. As the skilled person will appreciate, printability is typically measured as the ability of paper to accept and hold a printed legend and resist set-off of printing when rewound into a roll after printing. The present invention preferably includes the step of printing on the sheet material, and provides printability at least equivalent to sheet material formed from said substrate without the cured composition.
In other embodiments the sheet material of the invention is adapted to be sponge-like to simulate absorbent paper towelling. In other embodiments the sheet material of the invention is adapted to be cloth-like in its look and feel. In other embodiments the sheet material of the invention has the look and feel of wood-free paper, newspaper print or magazine print.

The present invention provides significant advantages over the prior art, as discussed throughout this specification. However, one significant advantage relates to the energy requirements, and therefore the carbon footprint of the papermaking process, which may be substantially reduced. To explain, since lower quality cellulosic fibres can now be used to manufacture paper products with maintained or improved mechanical properties compared to cellulose-based product having regular cellulosic fibres, the methods of the invention significantly reduce the energy requirements to produce paper since use of lower proportions of regular cellulosic fibres means reduced transportation costs and lower consumption of less readily available timbers. The carbon footprint of the papermaking industry is a major global concern due to the combination of high energy input requirements and the consumption of forests for raw materials for pulp. For example, reductions in the carbon footprint are provided by the methods of the invention since the level of refining required to fibrillate the fibres is now reduced, and as the skilled person will appreciate the refining process is relatively energy intensive. Additional reductions in the carbon footprint may be provided since recycled fibre can be utilised. Further, and as discussed in more detail below, conventional drying processes utilise vast quantities of energy, and the present invention provides reductions in these energy requirements since the present invention assists in the dewatering of the cellulosic web. Further still, use of electron beam (EB) curing provides even further reductions in the carbon footprint since the e-beam curing process
uses relatively less power than other methods of curing, such as thermal. For example, EB uses about 20% of the power of other heat energy curing methods.

In some embodiments, the sheet material of the invention is significantly stronger in the machine and/or the cross-machine direction and may also display improved tear resistance. Preferably the dry strength of the resultant sheet material of the invention is improved, however, the wet strength may also be improved. For example, in other embodiments the sheet material is adapted to be sponge-like to simulate absorbent paper towelling. In related embodiments, the sheet material is adapted to be cloth-like in its look and feel. In other embodiments the sheet material may have the look and feel of newspaper print or magazine print (glossy on one or both sides). In preferred embodiments the sheet material of the invention approximates or simulates "standard" paper products. It will be appreciated that "standard" paper products are formed from conventional formulations to produce conventional paper-based products such as those presently in the marketplace.

In some preferred embodiments the sheet material of the invention is a speciality paper product, such as a hybrid between a standard paper product and a polymeric sheet. For example, the Applicant contemplates that in one embodiment the sheet material of the invention may be particularly useful as a bank note, which has the look and feel of traditional paper-based bank notes and yet has the strength and tear resistance of modern polymer-based bank notes. Such hybrid sheet materials could advantageously be water marked and yet also contain the security features of modern bank notes. It will be appreciated that for such speciality products the cost of the sheet material may be less of a concern than the performance or attributes of the sheet material itself.
In other preferred embodiments the sheet material of the invention is a speciality paper product, such as book printing papers which display a relatively reduced degree of surface linting compared to paper typically used for books.

In one embodiment the substrate takes the form of a supporting web, comprised substantially of a web of dewatered cellulosic fibres. In other embodiments the substrate is a web of polymeric fibres, which may be at least partially woven, such as a scrim. In further embodiments the substrate may be a web of nonwoven polymeric fibres which may be optionally needle-punched. In yet further embodiments the substrate may a combination of one or more of the above webs. In the case where the substrate is a web of nonwoven polymeric fibres the web has a thickness similar to the thickness of a web of dewatered cellulose fibres. In addition, the thickness of the polymeric fibres comprising the nonwoven polymeric web should be similar to that of the cellulose fibres when dewatered.

In some embodiments the substrate is a thin substrate, e.g. less than any one of the following thicknesses: about 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, or 0.05 mm thick. However, in other embodiments the substrate is relatively thick, i.e. 1, 1.5, 2, 2.5 or 3 mm thick.

The final cured weight of the sheet material of the invention, in one embodiment, could comprise anywhere from 20 to 450 grams/m² (gsm) depending on the intended application, for example, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150, 175, 200, 150, 300, 350, 400 or 450 gsm.

It will be appreciated that the improved properties provided by the introduction of the curable composition provides a number of advantages. For example, when the substrate is a web of cellulosic fibres, a sufficient quantity of the curable composition may be introduced thereto to at least maintain the mechanical properties of the resultant cellulose-based sheet material when using relatively lower quality cellulosic fibres as
compared to a cellulose-based sheet material having regular or virgin cellulosic fibres. It will be appreciated that the relatively lower quality cellulosic fibres could be used as either a complete or a partial replacement for the virgin fibres. It will also be appreciated that a relatively reduced amount of cellulose fibres may be used in the resultant sheet material for an equivalent strength. In other embodiments, when the substrate is a web of polymeric fibres, a significantly reduced amount of cellulose fibres are required to form the resultant sheet, which effectively simulates a standard paper sheet material.

It will be appreciated that the present invention is directed to the production of sheet material which is preferably a cellulose-based product or a simulation of a cellulose-based product, wherein relatively reduced amounts of cellulose are required in the resultant sheet material or lower quality cellulose may be utilised, and wherein the mechanical and physical properties of the resultant sheet product are at least maintained compared to "standard" products made with virgin cellulose materials. It will also be appreciated that preferably the sheet material of the invention may be manufactured at commercial productions speeds.

It will be clear to the skilled person that the curable composition should be chosen to increase or improve the mechanical properties of resultant sheet material and/or provide at least maintain mechanical properties when relatively lower quality cellulosic fibres are utilised. Whilst the cellulose-based product is preferably paper, the cellulose-based product could be paperboard, cardboard, tissue, or similar products. The sheet material may also be hybrid materials, such as bank notes, as discussed further below. However in other embodiments any reinforcing synthetic material could be used, i.e. glass fibres, nylon fibres or other polymer types. The present invention
provides a significant increase in the Machine Direction (MD) and/or Cross-machine 
Direction (CD) strengths in a wide range of fibre combinations.

The skilled person will appreciate the distinction between regular cellulosic 
fibres from those of relatively lower quality. For example, regular cellulosic fibres used 
in papermaking are typically pulped virgin fibres. The virgin fibres are typically also 
chemically treated to remove lignin, both to assist in the papermaking process and to 
bleach the fibres. For example, virgin (non-recycled) wood fibre is primarily extracted 
from hardwood (deciduous) trees and softwood (coniferous) trees. In contrast, it will be 
appreciated that fibres of a relatively lower quality are those that are relatively more 
difficult to process on standard papermaking equipment, or those that provide a 
relatively inferior paper product compared to paper made from treated virgin pulped 
fibres. For example, the characteristics of such fibres are that they may have relatively 
shorter fibre lengths, lower fibre strengths, reduced flexibility, adsorbed/absorbed 
impurities, and may have been incompletely bleached by the bleaching or pulping 
processes. Typical sources of such lower quality cellulosic fibres may be from recycled 
newsprint, office paper, or from other recycled paper materials. Other sources include 
virgin wood fibres formed from less suitable timbers, or virgin wood fibres produced 
using sub-optimal processing techniques. The use of lower quality cellulosic fibres in 
cellulose-based products, such as paper, typically results in reduced mechanical 
properties, such as tensile strength and tear resistance. In one example, "regular" or 
"long" fibre is slow-growing cold climate Boreal forest fibre, which has fibre lengths of 
about 1.5 to 3 mm. In one example, "lower quality" or "short" fibre is fast-growing 
Eucalypt, which has fibre lengths of about 0.5 to 1.2 mm. The quantity of lower quality 
fibre that can be substituted with the regular fibre will typically depend on the type of 
paper being produced and the intended application. Of course there are some paper
applications which use 100% lower quality fibre, however, typically a certain amount of
lower quality fibre is substituted with the regular fibre, for example from 5 to 30%
substitution is common. However, substitutions of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16,
18, 20, 22, 24, 26, 28, 30, 35, 40, or more are possible. Preferably the proportion of the
regular fibre is less than 30, less than 20, less than 10, less than 5 or less than 0% of the
total fibre content.

As timber supplies reduce in availability around the world, and as the cost of
virgin cellulose increases, there is a commercial as well as an environmental drive to
increase use of recycled cellulose fibres in paper products. However, as discussed
above, such recycled fibres are more difficult to process than virgin fibres and produce
relatively inferior paper products, e.g. products with reduced tensile strength or reduced
tearing resistance. For example, lower tensile strengths mean that printing speeds must
be reduced to avoid tearing, certain types of inks or printing processes must be avoided,
or both. The use of recycled fibres is also being encouraged since there is an overall
reduced requirement for bleaching, which is harmful to the environment and relatively
expensive. There is also a reduced environmental cost to make paper from waste paper
than from virgin material since recycling is more cost efficient than processing virgin
fibres. Furthermore, it will be appreciated that different species of trees provide fibres
having different characteristics, and that only some species provide fibres suitable for
papermaking. Therefore, countries or regions without a suitable supply of cellulose
fibres have little choice but to use recycled fibre.

Accordingly, the present invention provides significant advantages over the prior
art, since a cellulose-based paper product may be produced wherein the mechanical
properties of the product are at least maintained when using relatively lower quality
cellulosic fibres as compared to a cellulose-based product having only virgin cellulosic
fibres. For example, it has been found that strength improvements of 35% in the machine direction and 25% in the cross-machine direction are possible when a paper web is contacted the curable composition of the invention. From this result the Applicant contemplates that if a proportion of the virgin fibre is substituted with recycled fibre using the method of the invention the MD and CD strength can be maintained, whereas such substitution using conventional production techniques would produce a significant reduction in strength in both directions. The following improvements in strength in the MD have been found, depending on the type and content of curable composition in the resultant sheet material, namely strength improvements of the order of, or even greater than, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, and 35%. Similarly, strength improvements in the CD of the order of, or even greater than, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25% have been found. The skilled person will appreciate that these improvements are actually net improvements, since it is commonly known that EB exposure of a cellulose web generally deteriorates the strength of the web. Therefore the strength improvements may be higher than the figures cited above.

Substituting the virgin cellulosic fibres with relatively lower quality cellulosic fibres, either completely or partially, when using the method of the invention reduces the total cost of the paper product with no deleterious effect on the mechanical properties of the final paper product. The present Applicant contemplates that the cost of at least partially substituting the virgin cellulosic fibres with relatively lower quality cellulosic fibres more than offsets the cost of the curable composition introduced to the product.

In one embodiment, the web of dewatered cellulosic fibres comprises between
about 10 to about 80% water, for example 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or 75% water.

The curable composition is preferably one or more curable polymers or oligomers and/or one or more curable monomers. Curable compositions suitable for the present invention are disclosed in the prior art, for example the curable oligomers and monomers disclosed in International PCT Publication No.'s WO 00/55228, WO 82/02894 and WO 81/00569 and Australian Patent No.'s 566738 and 5391 12, which are hereby incorporated herein by reference. Whilst the curable compositions described in these publications have been developed in relation to water based inks and related printing methods (in other words, as coatings), surprisingly, they have been found to be useful in the present invention as binders to enhance strength and/or aid in dewatering a cellulose web (as discussed further below). These documents exemplify UV curing of the inks including these monomers/oligomers. However, when utilising the monomers/oligomers taught in the above-mentioned documents as binders for sheet materials as described herein, the present Applicant contemplates that UV curing may be insufficient when attempting to cure at typical papermaking line speeds, i.e. from about 600 up to 2000 m/min. Accordingly, electron beam (EB) curing is preferred since a significantly higher radical flux can be generated with EB then UV. However, it will be appreciated, that UV curing may be acceptable when operating at lower production speeds. It will be appreciated that curing may be achieved by any one or more of the following type of actinic radiation, UV, X-rays, EB and gamma rays.

The step of curing the curable composition may comprise exposing the composition introduced to the substrate to UV radiation, gamma ray radiation, electron beam radiation or X-ray radiation for sufficient time and at sufficient intensity to cure the composition.
It will be appreciated that a variety of monomers, pre-polymers, oligomers and reactive polymers could be used in the curable composition and introduced to a suitable substrate to form the sheet material of the invention. The curable composition should be polymerizable and/or cross-linkable by actinic radiation, such as UV or EB. However, alternatively, heat energy can be used to initiate polymerisation.

When using heat energy to initiate polymerisation some latent curable compositions may require additions of suitable catalysts to initiate polymerisation. Catalyst can be latent, that is those that do not facilitate polymerisation until subjected to heat energy. Upon application of heat to the catalysed monomer/oligomer, the catalyst breaks down forming free radicals which trigger the monomer/oligomer to react and polymerise. Catalysts of varying chemical structures are chosen as to the efficiency and suitability with each monomer/oligomer to effect a polymerisation at desired temperatures. Catalyst can be used as single component additions or in some cases used with synergists in duel or multi-component additions. Examples of some catalysts are (not exhaustive): Organic peroxides, ammonium persulphate, potassium persulphate, AZDN, Tertiary butyl hydroperoxide, benzoyl peroxide, and MIBK (methyl isobutyl ketone peroxide). Some dual system catalyst and synergists are: Iron III, sodium formaldehyde sulphoxylate (Rongalit C) and sodium metabisulphite. The synergists dual system is termed a "redox couple" and polymerisation can be initiated at very low temperatures e.g. 20° to 70° C. With dual systems one catalyst component may be included in the resin/pulp mix and the 2nd synergists component can be added at the point in the process where polymerisation or exothermic reaction is required. We refer the reader to International PCT Publication No.'s WO 00/55228, which is incorporated herein by reference.
As discussed previously, the composition should be chosen to improve the strength of the substrate/supporting web into which the composition is introduced. Further, the composition is preferably chosen to cure exothermically to assist in the drying process of the resultant sheet material (discussed further below).

In one embodiment the curable composition comprises: N-methylol amide ether acrylates.

In another embodiment the curable composition comprises a water soluble amine salt prepolymer formed between an oligomer having at least one or more amine groups and an unsaturated carboxylic acid. The oligomer component of the salt may be selected from a range of oligomers, including but not limited to: epoxy-amine adducts, proprietary amino based resins such as urea formaldehyde and melamine formaldehyde ether acrylate type resins, amine polyisocyanate adducts, Michael adducts of an aliphatic amine and polyacrylate or polymethacrylate compound, and glyoxal based hemi-acetyl acrylates.

In another embodiment, the curable composition comprises at least one ethylenically unsaturated radically polymerizable monomer. As used herein, "ethylenically unsaturated radically polymerizable monomer" and like terms are meant to include vinyl monomers, (meth) allylic monomers and other ethylenically unsaturated monomers that are radically polymerizable. Classes of vinyl monomers may include, but are not limited to, (meth) acrylates, vinyl aromatic monomers, vinyl halides and vinyl esters of carboxylic acids. As used herein, by "(meth) acrylate" and like terms is meant both methacrylates and acrylates.

Example of some suitable monomers are those based on hexanediol and neopentyl glycol, further glycols are polyethylene glycol, polypropylene glycol; these being in a molecular weight range of from 200 up to 2000. Additionally all may be...
modified if desired by reacting with ethylene or propylene oxide to form ethoxylated and propoxylated moieties as a basis for esterifying with carboxy acids. Esterification mole ratios can be 1:1 or 1:2. Those skilled in the art will know that a higher degree of etherification will yield a more hydrophilic base monomer desirable for water based systems. Higher molecular weight monomers are derived from trimethylol propane and pentaerythritol, either as is or further reacting to form ethoxylated or propoxylated moieties, esterificating these with one to three moles of carboxylic acid to produce desirable base monomers suitable to fulfil the aims of this patent.

A further range of monomer types are derived from at least one of alkyl (meth) acrylates having from 1 to 20 carbon atoms in the alkyl group, vinyl aromatic monomers, vinyl halides, and vinyl esters of carboxylic acids. Specific examples of alkyl (meth) acrylates having from 1 to 20 carbon atoms in the alkyl group include, but are not limited to, methyl (meth) acrylate, ethyl (meth) acrylate, 2-hydroxyethyl (meth) acrylate, propyl (meth) acrylate, 2-hydroxypropyl (meth) acrylate, isopropyl (meth) acrylate, butyl (meth) acrylate, tert-butyl (meth) acrylate, 2-ethylhexyl (meth) acrylate, lauryl (meth) acrylate, isobornyl (meth) acrylate, cyclohexyl (meth) acrylate, 3,3,5-trimethyl cyclohexyl (meth) acrylate, and isobutyl (meth) acrylate. The monomer may also be acrylated methylol amide ethers, epoxy acrylates, epoxidized vegetable oil acrylates, urethane acrylates, carboxy-salt modified urethane acrylates, polyester acrylates, carboxy-salt modified polyester acrylates, polyether acrylates, silicon acrylates, polyol multifunctional acrylates, acrylated oils, acrylated amines, acrylic acrylates, and combinations thereof. The monomer may also be a mono-(meth) acrylate with hydroxy termination. The monomer may also be oligomers of methyolated acrylates, i.e. NMA condensed with a hydroxy terminated mono-(meth) acrylate. The monomer may also be acetal of hemi-acetal formation of hydroxy terminated (meth)acrylates with glyoxal
and/or other aldehydes, urethane mono-, di-, tri-, penta- and hexa-acrylates, carboxylic salt modified urethane acrylates, ether acrylates reacted with mercaptol propionates.

A single reactive diluent or mixture of reactive diluents may also be included in the curable composition. The reactive diluent(s) may, for example, be a lower molecular weight, liquid acrylate-functional compound including the following diacrylates and mono functional acrylates: tridecyl acrylate, 1,6-hexanediol diacrylate, 1,4-butanediol diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, neopentyl glycol diacrylate, 1,4-butanediol dimethacrylate, poly(butanediol) diacrylate, tetrathylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, tetraethylene glycol diacrylate, triisopropylene glycol diacrylate, triisopropylene glycol diacrylate, ethoxylated bisphenol-A diacrylate, and isobornyl acrylate. Other examples of a reactive diluent is n-vinyl caprolactam or vinyl pyrrolidone.

The curable composition may also comprise a photoinitiator, such as, for example, a free radical photoinitiator. Suitable free radical-type photoinitiators include, for example, an acyl phosphine oxide photoinitiator, more specifically, a benzoyl diaryl phosphine oxide photoinitiator. Examples of suitable benzoyl diaryl phosphine oxide photoinitiators include: bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819 available from Ciba Additives), (2,4,6-trimethylolbenzoyl)diphenylphosphine oxide (Lucerin TPO available from BASF); bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, which is a first component (25 wt %) of Irgacure 1700 available from Ciba Additives. The second component (75 wt %) of Irgacure 1700 is 2-hydroxy-2-methyl- 1-phenylpropane- 1-one. 2-hydroxy-2-methyl- 1-phenylpropane- 1-one is also available as an individual photoinitiator named Darocur 1173. Further examples of free radical-type photoinitiators include: hydroxycyclohexylphenylketone;
hydroxymethylphenylpropanone; dimethoxyphenylacetophenone; 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one; 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one; 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one; 4-(2-hydroxyethoxy)phenyl-2(2-hydroxy-2-propyl)-ketone; diethoxyphenyl acetophenone; 2,4,6-trimethylbenzoyl diphenylphosphine: and mixtures of the foregoing. Further examples include: benzophenone with amine synergists, bi-phenyl benzophenone (i.e. Triganol 12), PBZ (4-phenyl benzophenone), ITX (2-iso-propyl-thioxanthone) and OMBB (o-methylbenzoylbenzoate).

In other embodiments, the curable composition comprises a cationically curable composition. As the skilled person will appreciate, in cationically curing systems Lewis acids are formed from initiators by irradiation, which acids then in turn initiate the crosslinking reaction. The conventional monomers known to the skilled person may be epoxy oligomers or cycloaliphatic epoxies, which may contain more than two epoxy groups in the molecule. Examples include polyalkylene glycol diglycidyl ethers, hydrogenated bisphenol A glycidyl ethers, epoxy urethane resins, glycerine triglycidyl ethers, diglycidyl hexahydrophthalate, diglycidyl esters of dimeric acids, epoxidised derivatives of (methyl) cyclohexene such as, e.g., 3,4-epoxycyclohexylmethyl (3,4-epoxycyclohexane) carboxylate or epoxidised polybutadiene. The number average molecular mass (Mn) of the polyepoxide compounds is preferably less than 10000. Reactive thinners such as, e.g., cyclohexene oxide, butene oxide, butane diol diglycidyl ether or hexane diol diglycidyl ether may also be used.

Photoinitiators for cationically curing systems are substances well known as onium salts which liberate Lewis acids photolytically under the action of radiation. Examples thereof are diazonium salts, sulfonium salts or iodonium salts. Triaryl sulfonium salts are preferred. The photoinitiators for cationically curing systems may be
used in amounts from 0.5 to 5 wt. %, based on the sum of cationically polymerisable prepolymers, reactive thinners and initiators, individually or as mixtures.

In another embodiment, the curable composition may comprise a charge transfer complex that is obtained from an unsaturated compound that has an electron donor group and an unsaturated compound that has an electron withdrawing group. The compounds include a polymerizable unsaturated moiety bonded to the electron donor group and another polymerizable unsaturated moiety bonded to the electron withdrawing group. When the complex is from two or more compounds, typically, the double bond molar ratio of the electron donating compound to the electron withdrawing compound is about 0.5 to about 2, and more typically about 0.8 to about 1.2 and preferably about 1:1.

Suitable electron withdrawing compounds may be chosen from the following:

maleic diesters represented by the formula:

\[
\begin{array}{c}
\text{O} \\
\text{OR}_1 \\
\text{OR}_2 \\
\text{O} \\
\end{array}
\]

maleic amide halfesters represented by the formula:

\[
\begin{array}{c}
\text{O} \\
\text{OR}_1 \\
\text{NHR}_2 \\
\text{O} \\
\end{array}
\]

maleic diamides represented by the formula:
maleimides represented by the formula:

maleic acid halfesters represented by the formula:

maleic acid half amides represented by the formula:

fumaric diesters represented by the formula:
fumaric acid monoester halfamides represented by the formula:

\[ R_1\text{HN}-\text{CH}=-\text{CH}OR_2 \]

fumaric diamides represented by the formula:

\[ R_1\text{HN}-\text{CH}=-\text{CH}-\text{NH}R_2 \]

fumaric acid monoester represented by the formula:

\[ R_1\text{OH}-\text{CH}=-\text{CH}OR_2 \]

fumaric acid monoamides represented by the formula:

\[ R_1\text{OH}-\text{CH}=-\text{CH}OHR_2 \]
exomethylene structures represented by the formula:

\[
R_1HN = C - OH
\]

itaconic acid derivatives represented by the formula:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

nitrile derivatives of formulae 1-13, and imide derivatives of formulae 1-13; and wherein each X and Y independently is selected from the group consisting of: ORi, OR₂, NHRi, NHR₂, NRi, and OH and wherein each Ri and R₂ in the above formulae 1-13 is independently an aliphatic group or aromatic group.

Typical aliphatic groups include alkyl groups having 1 to 22 carbon atoms and preferably 1-12 carbon atoms. Typical aromatic groups include phenyl, benzyl, biphenyl. Other examples of suitable compounds include the corresponding nitrile and imide derivatives of for instance maleic acid and fumaric acid.
Some specific electron withdrawing compounds are maleic anhydride, maleamide, N-methyl maleamide, N-ethyl maleamide, N-phenyl maleamide, dimethyl maleate, dimethyl and diethyl fumarate, adamantane fumarate, and fumaric dinitrile. Polyfunctional, that is polyunsaturated, compounds including that with two, three and four and even more unsaturated groups can likewise be employed, and in fact, are preferred. Examples include polyethylenically unsaturated polyesters, for example, polyesters from fumaric acid and maleic acid or anhydride thereof.

Suitable electron donating compounds may be chosen from the following:

- Vinyl ethers represented by the formula:
  \[
  O^\text{R}_x
  \]

- Alkenylethers represented by the formula:
  \[
  O^\text{R}_x
  \]

- Substituted cyclopentenes represented by the formula:
  \[
  O^\text{R}_x
  \]

- Substituted cyclohexenes represented by the formula:
  \[
  R_z
  \]

- Partially substituted furanes or thiophenes represented by the formula:
  \[
  Z
  \]
partially substituted pyranes or thiopyranes represented by the formula:

\[ ZR_n \]

ring substituted styrenes represented by the formula:

\[ \rightleftharpoons ZR_x(R_y) \]

wherein \( n \) in the above formulae is an integer of 1-5, the maximum depending upon the number of carbon atoms in the ring; each \( R_x \) and \( R \) is independently an aliphatic group typically containing 1 to 12 carbon atoms or aromatic group such as phenyl; each \( R_3, R_4 \) and \( R_5 \) independently is H or aliphatic, preferably alkyl having 1-12 carbon atoms such as methyl, ethyl and propyl; each \( Z \) is independently selected from the group of O and S.

With respect to the ethers, monovinyl ethers and divinyl ethers are especially preferred. Examples of monovinyl ethers include alkylvinyl ethers typically having a chain length of 1 to 22 carbon atoms and more typically 4-12 carbon atoms. Divinyl ethers include divinyl ethers of polyols having for example 2 to 6 hydroxy groups including ethylene glycol, propylene glycol, butylene glycol, 3 methyl propane triol and pentaerythritol.

Examples of some specific electron donating compounds are monobutyl 4 vinyl butoxy carbonate, monophenyl 4 vinyl butoxy carbonate, ethyl vinyl diethylene glycol, p-methoxy styrene, 3,4 dimethoxy propenyl benzene, N-vinyl carbazole, propenyl
diethylene glycol, N-propenyl carbazole, monobutyl 4-propenyl butoxy carbonate, monophenyl 4-propenyl butoxy carbonate, isoengenol, and 4-propenylanisole.

In another embodiment, the curable composition may comprise one or more unsaturated polyesters, which are condensation products of polybasic acids or of corresponding acid equivalent derivatives such as esters, anhydrides or acid chlorides and polyhydric alcohols. Polymerizable unsaturation may be introduced into the polyesters molecule by the selection of a polybasic acid or polyhydric alcohol, which contains α,β-ethylenic unsaturation. For example, a polyhydric alcohol, which contains pendant unsaturation, is glycerol monomethaclylate. In most cases, however, the unsaturation will be contained within the polybasic acid unit. Optionally, one or more additional polyacids common in the art of polycondensation may be used in addition to the unsaturated polyacid. These ethylenically unsaturated polyacids include, but are not necessarily limited to maleic, fumaric, itaconic, phenylenediacrylic, citraconic and mesaconic acid. Such unsaturated polyesters may also include reactive diluents such as styrene or methyl methacrylate, and may be cured by radiation or by free radical catalysts and promoters.

In another embodiment, the curable composition may comprise monomers adapted for the thiol-ene coupling reaction. Alternatively, the curable composition may comprise diolefins and dithiols to make sulfur-containing polymers.

In another embodiment, the curable composition may comprise monomers adapted for curing by the removal of water or alcohol, i.e. a condensation reaction. In this embodiment heat energy typically in the form of infrared energy (IR) is required to trigger the reaction driving off water. An example of such reaction is via methlolated derivatives such as used in finishing agents for fabrics, textiles "permanent press" treatments, etc.
In one embodiment the curable composition is the use of methyolated acrylamide ether acrylate combined with an IR cross-linking vinyl acrylic emulsion. The combination of these components cross-link when heated thereby converting an initially water-soluble combination insoluble once cross-linked. It must be noted, however, that in this class of reaction no exotherm occurs; heat input being required to complete the reaction.

The foregoing curable compositions may be high-solids waterborne systems, for example, with a solids content from 50 to 95 wt. %, which may be emulsified. However, the curable compositions may be 100% coating compounds which may be introduced with or without water. Alternatively, the foregoing curable compositions may be dispersions or solutions. Preferably the curable composition includes minimal water in order to minimise the addition of water which must then either be removed by the exotherm generated by the curing curable composition (see below) or by standard dewatering techniques.

Preferably the glass transition temperature (Tg) of the curable composition is within a range from about 5 to 70°C.

The process of the invention may additionally comprise the step of at least partially drying the sheet material or the cellulose-based product. The drying may comprise heating the sheet material and/or applying a partial vacuum to the sheet material and/or passing a stream of heated gas (optionally dry gas), e.g. air, over or past the sheet material of the invention.

Examples of filler materials useful in paper production include calcium carbonate, talc, mica, clay, silica powder, colloidal silica, barium sulfate, aluminum hydroxide, glass powder, alumina powder, silicon dioxide powder, glass beads, and crushed sand. These filler materials can be impregnated/coated with the curable
composition and can function as carriers for the curable composition, or alternatively, the curable compositions may function as carriers for the fillers.

Without wishing to be bound by theory, the present Applicant contemplates that the present invention, in one embodiment, provides an Interpenetrating Polymer Network (IPN) through the web of cellulosic fibres. The increase in, or maintenance of (when using lower quality fibres) the mechanical properties of the resultant paper product may be attributed to the inherent strength of the polymer comprising the IPN. However, and again without wishing to be bound by theory, in other embodiments the present Applicant contemplates that the curable composition adheres the fibres together, or forms a bridging bond between adjacent fibres, which would be absent or significantly reduced in the absence of the cured composition, thereby providing the improved mechanical properties, *(i.e. a "pulp fusion")*. It is believed that the fibres are chemically bonded together, rather than just bonded together by Van der Waals forces.

In preferred embodiments, the curable composition is substantially water-soluble.

It will be appreciated that the quantity of the curable composition introduced to the web may be any amount to achieve the desired effect. For example, a possible range of addition is between about 1 and 85% by weight of dry solids of the cellulosic fibre, however a preferable range is between about 5 and 75%. Preferably the quantity of curable composition added to the web is between about 0.2 to 1, 1 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 25, 25 to 30, 30 to 35, 35 to 40, 40 to 45, 45 to 50, 50 to 55, 55 to 60, 60 to 65, 65 to 70, 70 to 75, 75 to 80, or 80 to 85% by weight of dry solids of the cellulosic fibre. Preferably the quantity of curable composition added to the web is about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42,
Preferably, the curable composition is curable via electron beam irradiation (EB) as discussed above. However it will be appreciated that other forms of radiation will be suitable, such as UV, IR or gamma rays. One advantage with electron beam radiation is that use of photoinitiators is not required, or only reduced amounts are required in the curable compositions. Preferably the curing step uses and EB of about 0.5 Mrad, or 1 Mrad, or 1.5 Mrad, or 2 Mrad, or 2.5 Mrad, or 3.0 Mrad.

It will be appreciated that the curable composition may be introduced to the substrate of dewatered cellulosic fibres by any means. For example, in one embodiment the curable composition is coated or sprayed onto the substrate prior to drying. The curable composition may be coated onto one or both sides of the substrate, and it will be appreciated that preferably the composition completely wets or soaks through the substrate. Alternatively, the curable composition may be coated onto a suitable carrier, such as a clay particle, as is well known in the art, or even coated onto, or impregnated into the cellulose fibres. In other embodiments, the web of dewatered cellulosic fibres may be drawn through a reservoir of curable composition and then immediately cured and dried. In further embodiments, the web of cellulosic fibres is dewatered and then the curable composition is introduced thereto and then cured. In yet further embodiments, combinations of the foregoing are contemplated.

According to a fifth aspect, the invention provides a method for removing water from a substrate, the method comprising the steps of:

introducing a quantity of a curable composition to the substrate and curing the curable composition, the curable composition being adapted to reduce the water content of the substrate.
In one embodiment the curable composition cures exothermically and provides a sufficient release of heat to reduce the water content of the substrate. In another embodiment, where the curable composition is water soluble, water is expelled from the sheet material upon curing (crosslinking) of the curable composition. To explain, the curable composition is initially water soluble and upon curing is converted into a substantially water insoluble polymer. The present Applicant contemplates that this process effectively "exudes", "sweats" or "excludes" the water from the sheet material; the discharged water effectively reducing the water content of the sheet material. Preferably the cured polymer has increased hydrophobicity to enhance the discharge of water from the sheet material. The present Applicant believes that the release of heat by the polymerizing monomer, and its simultaneous conversion into a substantially hydrophobic polymer acts synergistically to expel water from the sheet. Preferably the curable composition is water soluble and cures to a substantially water insoluble composition, wherein water is expelled from said sheet material upon curing of said curable composition thereby reducing the water content of the substrate. Furthermore, and without wishing to be bound by theory, the present Applicant believes that the polymer chemically binds to the cellulose fibre, which further acts synergistically to expel water from the sheet. It will be appreciated that the curable composition may be adsorbed on the surface of the individual fibres and/or absorbed into the fibres.

Monomers/oligomers which are preferred are selected from those that are highly water soluble, hydrophilic and completely transparent solutions. An example of a suitable prepolymer is an amine salt modified epoxy acrylate having hydroxyl terminal end groups and NH groups of reaction along the prepolymer chain. Polymerization is preferably induced by radiation or heat plus free radical catalysts which induce the oligomer to polymerize. Crosslinking of the polymer causes the polymer to become
hydrophobic. Dilution water within the prepolymer bound by hydrogen bonding is forced out of the rapidly formed hydrophobic polymer and the hydrogen bonds cease to exist. Expulsion of water is assisted by the exothermic reaction heat of polymerization. A typical formulation comprises 60% of amine salt modified epoxy acrylate, 38% water and 2% Darocure 1173, with the composition being cured by UV or EB radiation or heat plus redox catalyst.

In a sixth aspect the present invention provides a method for removing water from a web of substantially dewatered cellulosic fibres, the method comprising the steps of: introducing a quantity of a curable composition to the web and curing the curable composition, the curable composition being chosen to cure exothermically and wherein the quantity of the curable composition is sufficient to provide a sufficient release of heat to reduce the water content of the substrate. Preferably the quantity of the curable composition is sufficient to provide a sufficient release of heat to substantially dry the web. It will be appreciated that the web does not need to be completely dried by the exothermic action of the curing curable composition, rather, it is sufficient that the web is somewhat dewatered by the exothermic action of the polymerization reaction. However, in preferred embodiments the web is completely dried.

In one embodiment, where the substrate is a web of dewatered cellulose fibres, the water content of the substrate will be around 80 to 85%. In other words, the substrate will include residual water from the production process for the substrate itself. In addition, the curable composition introduced to the substrate may include further water, thereby raising the total water content of the substrate. In a related embodiment, where the substrate is a web of substantially dry cellulose fibres or a dry web of synthetic polymeric fibres, the curable composition itself may be the source of water. In each of these embodiments, water is either present in the substrate prior to the
introduction of the curable composition, or is introduced to a dry substrate. The present invention assists in the removal of this water by the release of the heat of reaction (polymerization).

The skilled person will appreciate that the cost of removing water from a substrate or supporting web, such as a paper product, is substantial. This is primarily due to the relatively high heat capacity of water. The present Applicant has determined that a substantially dewatered web of cellulosic material can be dried even further, with little or no additional energy input (apart from the energy requirements of the energy source), by introducing a curable composition to the dewatered web and curing the curable composition, wherein the curable polymer is chosen to cure exothermically. Judicious selection of the curable composition and its concentration in the dewatered web can provide a significant evolution of heat upon curing, and thereby drives off any remaining or residual water from the web. For example, a substantially dewatered web of cellulosic material may have between about 80 to 85 weight % of its total weight in residual water. The present invention provides a significant reduction in this residual water, thereby saving significant drying costs. It will be appreciated that any residual water may be removed by standard drying processing, however it will be appreciated that the drying sections may be significantly reduced in length since the a significant amount of water has been removed by the introduction of the exothermically curable compositions of the invention.

Preferably the curable composition is chosen to both increase the mechanical properties of a cellulose-based product and cure exothermically to substantially dry the web. It will also be appreciated that a significant advantage of the present invention is that it can be applied to conventional papermaking machinery. It will also be appreciated that the present invention could significantly reduce the capital cost of
papermaking machinery since it can now be designed to have shorter drying sections. It will be appreciated that, in preferred embodiments, the curable composition is cured in the minimum time possible to release heat as fast as possible, thereby to "flash off" the remaining/residual water from the substrate. In order to effect this embodiment, the cure is initiated by electron beam irradiation.

As highlighted above, since lower quality cellulosic fibres can now be used to manufacture paper products with "maintained" or improved mechanical properties, and/or the energy requirement for drying may be reduced, the methods of the invention significantly reduce the carbon footprint of the papermaking process. Further reductions in the carbon footprint are provided by the methods of the invention since the level of refining required to fibrillate the fibres is now reduced, and as the skilled person will appreciate the refining process is relatively energy intensive. Additional reductions in the carbon footprint are provided since recycled fibre can be used. Also, use of e-beam curing provides even further reductions in the carbon footprint since the e-beam curing process uses relatively less power than other methods of curing, such as thermal. For example EB uses about 20% of the power of other heat energy methods. The carbon footprint of the papermaking industry is a major global concern due the combination of high energy input requirements and the consumption of forests for raw materials for pulp.

In another embodiment of the present invention, the curable composition may be introduced to a preformed substrate defining a supporting web, such as a non-woven needle punched polymeric felt. This web may be impregnated or coated with the compositions of the invention and then cured with electron beam curing. A sufficient amount of the composition may be introduced to create a smooth surface on both sides. It will be appreciated that only sufficient cellulose fibre would need to be introduced to
produce the look and feel of conventional paper. Further, conventional fillers could be also used as is well known in the art. The manufacturing process in this embodiment is a coating process for coating the carrier web rather than manufacturing from a wet slurry form. Of course it will also be appreciated that non-cellulosic fibres could also be used to "fill" the polymeric felt or web.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about". The examples are not intended to limit the scope of the invention. In what follows, or where otherwise indicated, "%" will mean "weight %", "ratio" will mean "weight ratio" and "parts" will mean "weight parts".

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 illustrates the wet end of a typical Fourdrinier paper machine in simplified diagrammatic form, showing, in one embodiment where the composition of the invention could be introduced to the supporting web;

Figure 2 illustrates the key components of the drying section (the "dry end") of the Fourdrinier machine as shown in Figure 1;

Figure 3 shows an embodiment for producing sheet material according to the invention using a synthetic non-woven web support;
Figure 4 shows an alternative embodiment for producing sheet material according to the invention using a synthetic non-woven web support; and

Figure 5 shows a further embodiment for producing sheet material according to the invention, wherein the synthetic non-woven web support is produced in situ.

DEFINITIONS

In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments of the invention only and is not intended to be limiting. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one having ordinary skill in the art to which the invention pertains.

The recitation of a numerical range using endpoints includes all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

The terms "preferred" and "preferably" refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

For the purposes of this invention, the term "introducing", when referring for example to introducing the curable composition to the supporting web of dewatered cellulosic fibres, should be understood to encompass any means for introducing the curable composition to the web. This may be "downstream" and/or "upstream" in the manufacturing process. For example, the curable composition may be coated or sprayed directly onto the web (either before or after dewatering), or introduced by way of a
suitable carrier. Alternatively, the curable composition may be introduced by drawing the web through a reservoir of curable composition. In a further variation, the curable composition may be mixed into the fibre pulp, prior to formation of the web. Yet other variations may also be feasible and should be considered to fall within the scope of the invention as presently contemplated.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will now be described with reference to the following examples which should be considered in all respects as illustrative and non-restrictive.

Turning initially to Figures 1 and 2, the wet and dry ends respectively of a typical Fourdrinier paper-making machine are shown. The positions in the process where the curable composition may be introduced to the substrate are labelled as A to D. Suitable methods for introducing the curable composition are described in the following examples with respect to these Figures.

Example 1

In a first embodiment, the curable composition is introduced at point 'A' in the mixing chest 1, which will also typically include the cellulose slurry and other typical paper-making chemicals. The slurry is transferred to the head box 2 and then continuously deposited onto the forming wire 3 of the paper machine, as is well known in the art. Preferably the concentration of curable composition introduced to the mixing chest 1 is selected to account for the various losses which will occur through dewatering on the forming wire 3. Polymerisation of the curable composition may be achieved by EB radiation after the press section 4 and before the drying section 5. In this example, the curable composition is distributed uniformly throughout the thickness of the paper web, which the Applicant has found provides improved tensile strength by the polymerised cross-linked structure of the curable composition.
Example 2

In this example, the curable composition is introduced at 'B' through fine spray nozzles onto both sides of the partially formed paper web 8. Since the web at this point will generally still have between 80% and 85% water content, the curable composition, which is preferably water-soluble, will penetrate the web 8 to some extent but will have greater concentrations closer the web's surface. Similarly to the previous example, polymerisation of the curable composition may be achieved by EB radiation after the press section 4 and before the drying section 5.

Example 3

The curable composition is introduced to the paper web at 'C', which is after the press section 4 and the before the drying section 5. In this example the paper web is partially formed with a water content which has been reduced to between about 70% and 75% by the pressing action. The curable composition is contacted with the web via fine spray nozzles and is polymerised immediately by EB radiation before the web enters the drying section 5.

Example 4

In this example, the curable composition is contacted with the dewatered paper web 8 at point 'D' as a coating. The composition of the coating may be as follows:

- curable composition up to about 10%
- CaCO₃ 40 to about 60% (including other complementary fillers)
- H₂O up to about 30%
- Acrylic Emulsion up to about 10%

The dewatered web 8 may be coated with any appropriate means, including but not limited to: roller coating, blade coating, air knife, etc. It will be appreciated that the rheology of the curable composition may be adjusted to provide for different coating
methods. Preferably the flow is Newtonian and the viscosity is adjusted between 30 and 40 seconds Zhan 2.

The curable composition is polymerised immediately after being introduced to the substrate by electron beam radiation with the water content of the coating (up to 30% water) being almost instantaneously evaporated by the exotherm generated by the polymerisation process and transition from hydrophilic monomer to hydrophobic polymer.

Turning now to Figures 3 to 5, an alternative method to produce sheet material according to the present invention is shown wherein the substrate is a non woven polymeric web 10. These Figures are discussed in more detail in the following Examples.

**Example 5**

Referring to Figure 4, forming wire 3 passes through a mixture 6 comprising cellulose slurry and the curable composition. A vacuum inside the drum 7 draws the mixture 6 through the forming wire 3 to form a web 8. Any mixture drawn through the drum 7 is recycled to the mixture 6. A mixing chest ("head box") 11 also comprises cellulose slurry and the curable composition which is deposited onto the forming wire 3. A roll 9 of non-woven fabric 10 is drawn through the machine and receives a coating on both sides of the cellulose fibre/curable composition web 8. The coated non-woven fabric 10 is pressed between rollers 12 to dewater the substrate and is then cured via EB radiation 13.

In this example, the polymeric non-woven substrate 10 is coated on both sides with a mixture comprising a combination of calcium carbonate, fillers, a relatively small quantity of cellulosic fibre and the curable composition as described herein to produce a sheet material 20 in the form of a paper product which has a look and feel of traditional
papers but uses a relatively reduced amount of cellulosic fibre, and providing relatively improved strength and tear resistance.

In an alternative example, the lower forming wire 21 includes a charge potential and passes through a fluidized bed of dry fiber particles having an opposite charge and being coated with the curable composition. A quantity of dry fiber particles may be attracted to the lower forming wire 21 and the web thus formed is then covered/coated with the non-woven fabric 10. The top layer of fibres and curable composition is then coated with further fibres/curable composition, and the cured via EB. Since this process would be substantially dry no water needs to be evaporated.

**Example 6**

Turning now to Figure 5, a papermaking process similar to Figure 4 is shown, wherein like features have been given like reference numerals. In this case the non-woven polymeric substrate 10 is produced *in situ*. To explain, an extruder 14 having a rotating/oscillating head continuously produces the non-woven fabric 10 on top of the web 8. A further layer of cellulose fibres is then laid down on top of the non-woven fabric 10 from the mixing chest ("head box") 11, which is drawn through the forming wire 3 by the application of vacuum 15.

The non-woven polymeric substrate 10 formed *in situ* can be for example from a reactive oligomer of very high molecular weight which can remain liquid upon being extruded then later along the processing line become thermoset after being subjected to a form of radiation. In this embodiment the upper and lower coatings of cellulose fibre and curable composition are bonded to this non-woven polymeric substrate 10.

In another embodiment, as best shown in Figure 3, the non-woven polymeric substrate 10 may be unrolled from a take-off reel 16 and drawn through a pair of coating rollers 17 for applying the curable composition and cellulose slurry, and then
immediately cured as discussed previously and wound up in a take-up reel 18. In this embodiment it may be possible to form the sheet material of the invention without any carrier solvents *i.e.* a totally dry system. However, it may be preferably to coat the non-woven polymeric substrate 10 with a slurry, wherein the water added to the web is substantially evaporated by the exothermic curing process.

In another embodiment, the non-woven fabric substrate 10 could be extruded as a high softening point hot-melt. In this case no radiation is required as the web is formed as the composition cools. The polymer could be nylon or any other suitable synthetic polymer.

In related aspects, the non-woven fabric substrate 10 may be a high molecular weight urethane with free NCO end groups. It will be appreciated that the coated substrate may be passed through a chamber of amine gas which triggers the reactive end groups to cross link (polymerize), again without any need for a liquid carrier.

**Example 7**

By way of example, 36 g per square meter (gsm) newsprint was contacted on both sides with the following curable composition and cured with EB:

- Amide ether acrylate: 10%
- Acrylic emulsion: 10%
- Antifoam: 0.4%
- Wetting agent: 0.6%
- Clay: 50%
- Titanium dioxide: 10%
- Darocure 1173: 3%
- Water: q.s.
The cured sheet exhibited a tensile strength increase in the machine direction from 1.47 kNm to 1.98 kNm, and from 0.916 kNm to 1.13 kNm in the cross direction. These results were obtained from an average of 15 individual tests. These results are all the more surprising since, at a dosage rate of 3 MRads used for the trials, the mechanical strength characteristics of most papers are significantly reduced.

Although the invention has been described with reference to specific examples, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms. In particular features of any one of the various described examples may be provided in any combination in any of the other described examples.
CLAIMS:

1. A method for making sheet material, said method comprising the steps of:
   introducing a quantity of a curable composition to a substrate and curing said
   curable composition, wherein a sufficient quantity of said curable composition is
   introduced to said substrate to increase or improve the mechanical properties of
   the resultant said sheet material compared to a sheet material formed from said
   substrate without the cured composition.

2. A method according to claim 1 wherein said sheet material displays improved
   tensile strength in the machine and/or the cross-machine direction when
   compared to standard paper products.

3. A method according to claim 2 wherein said improved tensile strength in the
   machine direction is greater than 1% compared to a sheet material formed from
   said substrate without the cured composition.

4. A method according to claim 2 or claim 3 wherein said improved tensile strength
   in the machine direction is greater than 10% compared to a sheet material formed
   from said substrate without the cured composition.

5. A method according to any one of claims 2 to 4 wherein said improved tensile
   strength in the machine direction is greater than 25% compared to a sheet
   material formed from said substrate without the cured composition.

6. A method according to any one of claims 2 to 5 wherein said improved tensile
   strength in the machine direction is greater than 35% compared to a sheet
   material formed from said substrate without the cured composition.

7. A method according to any one of claims 2 to 6 wherein said improved tensile
   strength in the cross-machine direction is greater than 1% compared to a sheet
   material formed from said substrate without the cured composition.
8. A method according to any one of claims 2 to 7 wherein said improved tensile strength in the cross-machine direction is greater than 5% compared to a sheet material formed from said substrate without the cured composition.

9. A method according to any one of claims 2 to 8 wherein said improved tensile strength in the cross-machine direction is greater than 10% compared to a sheet material formed from said substrate without the cured composition.

10. A method according to any one of claims 2 to 9 wherein said improved tensile strength in the cross-machine direction is greater than 25% compared to a sheet material formed from said substrate without the cured composition.

11. A method according to any one of the preceding claims wherein said substrate comprises a supporting web comprised substantially of a web of dewatered cellulosic fibres.

12. A method according to any one of the preceding claims wherein said substrate comprises a web of nonwoven polymeric fibres.

13. A method according to any one of the preceding claims wherein said sheet material is adapted for use as paper or a paper product.

14. A method according to claim 13 wherein said sheet material is adapted to be printable and displays a similar flexibility to standard paper products.

15. A method according to any one of claims 1 to 12 wherein said sheet material is adapted to be sponge-like to simulate absorbent paper towelling.

16. A method according to any one of claims 1 to 12 wherein said sheet material is adapted to be cloth-like in its look and feel.

17. A method according to any one of claims 1 to 12 wherein said sheet material has the look and feel of wood-free paper, newspaper print or magazine print.
18. A method according to any one of the preceding claims including the step of printing on said sheet material, wherein the printability is at least equivalent to sheet material formed from said substrate without the cured composition.

19. A method according to any one of the preceding claims wherein said sheet material is produced with relatively reduced total energy requirements compared to a sheet material produced from said substrate without the cured composition.

20. A method for making a cellulose-based product, said method comprising the steps of: contacting a quantity of a curable composition with a web of dewatered cellulosic fibres and curing the curable composition, wherein a sufficient quantity of the curable composition is introduced to the web to increase or improve the mechanical properties of a cellulose-based product as compared to a corresponding cellulose-based product without the cured composition.

21. A method according to claim 20 wherein a sufficient quantity of the curable composition is introduced to the web to at least maintain the mechanical properties of the cellulose-based product when using relatively lower quality cellulosic fibres as compared to a cellulose-based product having regular cellulosic fibres.

22. A method for removing water from a substrate, said method comprising the steps of: introducing a quantity of a curable composition to the substrate and curing the curable composition, the curable composition being adapted to reduce the water content of the substrate.

23. A method according to claim 22 wherein the curable composition cures exothermically and provides a sufficient release of heat to reduce the water content of the substrate.
24. A method according to claim 22 or claim 23 wherein the curable composition is water soluble and cures to a substantially water insoluble composition, wherein water is expelled from said sheet material upon curing of said curable composition thereby reducing the water content of the substrate.

25. A method for removing water from a web of substantially dewatered cellulosic fibres, said method comprising the steps of: introducing a quantity of a curable composition to said web and curing said curable composition, said curable composition being chosen to cure exothermically and wherein said quantity of said curable composition is sufficient to reduce the water content of the substrate.

26. A method according to claim 25 wherein said quantity of said curable composition is sufficient to provide a sufficient release of heat to substantially dry said web.

27. A method according to claim 25 or claim 26 wherein the curable composition is water soluble and cures to a substantially water insoluble composition, wherein water is expelled from said sheet material upon curing of said curable composition thereby reducing the water content of the substrate.

28. A method according to any one of the preceding claims wherein said curable composition is one or more monomers, pre-polymers, polymers, or oligomers or combinations thereof.

29. A method according to claim 28 wherein said monomers, pre-polymers, polymers, or oligomers are water soluble, or emulsified, or are in the form of a dispersion, are in solution, or are in the form of a high-solids waterborne system.

30. A method according to claim 28 or claim 29 wherein said monomer is N-methylol amide ether acrylate.
31. A method according to any one of the preceding claims wherein the curable composition is curable by UV radiation, electron beam radiation, X-ray radiation or thermally.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2008/001473

A. CLASSIFICATION OF SUBJECT MATTER
IPC: D21H 17/33, D21H 19/16, D21H 21/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI-D21H 17/6c, D21H 13/6c, D21H 21/6c and keywords (cur+ and sheet or paper and radiation or electron or ultra+ or gamma or EB or UV or Xray and exothermic)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US, 3887510, A (CHAN, et al.) 3 June 1975 This citation teaches the addition of water soluble polymerisable compositions to cellulosic substrates to provide improved strength. See in particular column 4 lines 65-68 and column 5 lines 1-32. Potential products are taught as being absorbent tissues and paper towels as well as wrapping paper.</td>
<td>1,2,11-18, 20, 22, 24, 27-29, 31</td>
</tr>
<tr>
<td>Y</td>
<td>US, 6162842, A (FRECHE, et al.) 19 December 2000 This citation teaches the application of a radiation curable coating composition to a substrate such as paper. Also taught is the use of ultraviolet radiation or electron beams to cure the coating composition. See column 5 last paragraph and column 6 lines 24-43</td>
<td>1-18, 20-22, 24, 27, 28, 29, 31</td>
</tr>
</tbody>
</table>

[X] Further documents are listed in the continuation of Box C  [X] See patent family annex

* Special categories of cited documents:
  'A' document defining the general state of the art which is not considered to be of particular relevance
  'E' earlier application or patent but published on or after the international filing date
  'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  'O' document referring to an oral disclosure, use, exhibition or other means
  'P' document published prior to the international filing date but later than the priority date claimed

  'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  '&amp;' document member of the same patent family

Date of the actual completion of the international search: 23 DEC 2008
Date of mailing of the international search report: 

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer
A Davies

AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No : +61 2 6283 2072

Form PCT/ISA/210 (second sheet) (July 2008)
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</table>
| X        | US, 4333971, A (EENAM, et al) 8 June 1982<br>  
This citation teaches the improvement of the wet and dry strength of a cellulosic substrates by the application of polymerisable compositions to the substrate followed by curing. The composition can be added to the wet end of the paper making process or sprayed on to the web at a downstream location. | 1,2,11-18,20,22,24,27-29,31 |
| Y        | With regard to the Y category citations it is intended to combine Chan with Freche and then Eenam with Freche | 1-18,20-22, 24, 27,28, 29, 31 |
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.