Rheology to understand operational parameter, as a predictive method to avoid off specifications and maximizing the packaging process.

S. Carrà[1], F. Chiozza[2], F. Curto[3], and M. Ferraioli[2]

[1]Mapei S.p.A., Tileadhesives Department, via Cafiero, 22 – Milano (MI) Italy
[2]Vinavil S.p.A., R&D Department, via Toce, 7 – Villadossola (VB) Italy
[3]Mapei S.p.A., Rheology Department, via Cafiero, 22 – Milano (MI) Italy

ABSTRACT

Recent market investigation have confirmed that paper and packaging industry is one of the most exciting and challenging operating field. In fact, the increasing of specific needs of the end users acting in the very well- known business like food, luxury and graphic art packaging, obliged the involved operators to develop a huge number of processes by increasing the quality and maximizing the profits. Although paper, ink and coating are commonly considered as the main parameters affecting the complex world of paper industry, the glue plays a very important role because drives the main output of the paper chain that is the packaging design / assembly. This work is introducing a study on a polymeric adhesive able to satisfy the process requests.
 The suitability of polyvinyl-acetate based glues is well known in the paper industry.
The tuning of the formula composition of the glue have been investigated in order to optimize the process parameters.
Preliminary applicative tests have been carried out like wet tack development and delamination tests in order to investigate the ideal glue properties for paper industry application. In this paper the possibility to help the formulator through alternative and simplified methods like rheological characterization is considered.

The use of rheology allowed to predict the best performances of the adhesive employed for packaging, by combining the results from a stress controlled and capillary rheometer. The flow curves in a wide range of shear rates give a prediction of the glue behaviour both at initial flow state and at regime state (10^5 s^{-1}). The shear thinning behaviour was investigated in order to avoid instability.
Furthermore dynamic measurements has been carried out highlighting that under oscillatory shear, the elastic modulus of some glue formulations showed a weak dependence on frequency over the range 1-100Hz.
The apparent viscosities, pseudoplasticity, yield stress of different adhesives are all dependent on their formula composition.
A correct comprehension of rheological approach applied to the specific industry guarantees the maximum efficiency of the entire packaging process.

INTRODUCTION
The paper packaging industry is one of the growing industry as a consequence of the increasing demand for wrapped products in the market. In addition, economic competition forces companies, especially the ones involved in the consumer products market, to enhance the packaging appearance in order to improve the aesthetic

of their products and, as a consequence, the profits.

Paper coating is a clear example showing how to pursue this purpose; it consists into a process where coating film is applied onto paper to impart certain qualities including weight, surface gloss, smoothness and protection. Paper coating formulation generally consists of inorganic pigments (as calcium carbonate, kaolin) water and polymeric binder.

Furthermore paperboards are usually coated in order to improve their optical properties, especially printability. The use of mineral pigment in dispersion coating, to provide improved barrier properties, has determined a big problem for glues. In fact this barrier, even if is important to protect / preserve the goods or food, depresses the adhesive performance, because it has to build up a bond on a coated surface.

In addition to all these considerations, the adhesive producer has to consider the specific type of applicative system employed in the plant which the product is destined to.

As it is known, the world of packaging includes a wide range of different operating systems according to the kind of final manufacture; this means different applicative machines and technologies and, from the point of view of the adhesive, different kind of stresses to be subjected to. For example, an adhesive has to exhibit different flow and deformation properties when applied by nozzles or by rolls (see Figures 3, 4 and 5) and this implies that the glue should show a proper rheological behaviour in order to make it suitable for the specific application system.

Furthermore, environmental regulatory legislation as well as reduction or elimination of Volatile Organic Compound in adhesives, has quickened the growth and development of solvent free adhesives. Water based (w/b) adhesives are the largest and oldest category of solvent free systems; they are considered the most conventional

solvent free adhesive technology and the main alternative to solvent based (s/b) one.

W/b products are generally more difficult to dry compared to solvent based, since water generally evaporates much slower than the solvents typically used. The use of increased air flow and of porous substrates (such as paper) can limit the cited disadvantage.

Water based adhesives usually have higher surface tension than solvent based ones and can have difficulties in wetting out substrates, particularly plastic foils (having low surface energy.)

Unlike for s/b systems, the viscosity of w/b system does not depend on molecular weight since the polymer is contained in discrete particles. Viscosity in this case is a function of particle size, solid content and percentage of water soluble part of the polymer. Typical latexes are 35-65% solids with relatively low viscosity. All the changes imposed by the use of w/b systems obliged to an adhesives customization related to the end–use needs. W/b polymer emulsions can be compounded and formulated with a wide variety of materials (such as plasticizers, tackifiers, surfactants, wetting agents, thickeners, fillers, adhesion promoters, crosslinker agents) to give specific properties to the final adhesive [1]. They are suitable for a wide range of applications including packaging, lamination, labelling, woodworking, bookbinding, flooring and construction. W/b adhesives have demonstrated many benefits including improved end use performances and low environmental impact in areas like packaging and lamination.

In this paper we will consider polyvinyl acetate (PVAc) based adhesives and polyvinyl acetate – ethylene copolymer (VAcE) based adhesives, Fig. 1. PVAc based adhesives are useful in a very wide range of application as by the proper formulation is possible to improve several properties like tensile strength, toughness, flexibility, adhesion and mechanical stability. For all these reasons and for the
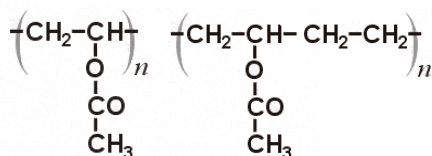
Figure 1. PVAc and VAcE structure

relative low costs, PVAc based adhesives are very wide spread.

VAcE dispersions are interesting for different reasons. First of all they can be defined as "environmentally-friendly", since they allow to obtain higher polymer flexibility without plasticizer addition [2].

Plasticizers are organic solvents commonly added to homopolymeric vinyl acetate dispersions to improve film formation at room temperature. Organic solvents reduce air quality and produce toxic oxidants that are damaging to the atmosphere. National and international environmental agencies are imposing strict constraints on the maximum allowable contents of Volatile Organic Compounds of dispersions for adhesive applications, drastically reducing the employment of conventional plasticizers. Moreover, plasticizers tend to migrate and might pollute the substrate and that problem is particularly significant in paper applications.

Copolymerization with ethylene lowers the Tg of the polymer producing what is called a "permanent and internal" plasticization, avoiding the need of adding organic solvents, thus improving the environmental properties of the product. The use of VAE dispersions is also beneficial in terms of applicative properties [3].

With respect to the correspondent polyvinyl acetate homopolymer, ethylene copolymers display a better adhesion to difficult supports, such as polyolefin substrates. When compared to other polyvinyl acetate copolymers commonly used, such as vinyl versatate, or acrylates, VAcE copolymers show better cohesion, workability and resistance to temperature variations [4].

SAMPLES PREPARATION
The evaluation of a suitable adhesive for cardboard/packaging is not always an immediate issue, because of the all factors contributing to the final manufacture performances. As it is known, adhesion is a multidisciplinary science embracing the fields of chemistry, physics of surfaces, up to the mechanisms of deformation and failure of the adhesive joint.

The optimization of this characteristics usually concerns adhesive and cohesive behaviours. Adhesion deals with to the interaction between the glue and the involved substrates; cohesion has to do with to the interactions within the adhesive layer.

In this work the evaluation of different paper – cardboard adhesives is considered.

The formulations described in present work are studied as modification of the w/b polymer dispersion by means of additives like: softening agent, water retainer, rheological modifier, as shown in Table 1.

The polymers' Vistex is an expression of the length of the polymer' chains and depends on the relative viscosity. (Vistex is obtained by measuring the flowing time of a polymer solution in acetone with the Ubbelholde viscosimeter). The viscosity is related to the molecular weight by Mark-Houwink equation:
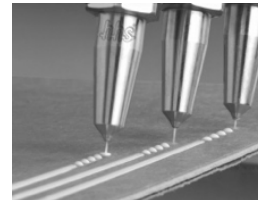

Figure 3. Roller application Figure 3. Segment/wheel application Figure 5. Nozzle application

Table 1.

Formulation	Polymer type	Polymer Vistex (dl/g)	Softening agent (% w/w)	Water retainer (% w/w)	Rheological additive
F1	PVAc	1.6	6	4	PU
F2	PVAc	2.2	6	4	-
F3	PVAc	2.8	6	4	-
F4	VAcE	1.8	6	4	PU
F5	PVAc	1.6	6	4	-
F6	PVAc	1.8	6	4	-

$$[\eta] = K'M^a$$

Where "M" is called "viscosimetric mean molecular weight" and "K'" and "a" are constant values which are specific for each polymer – solvent combination.

Each sample is prepared in the laboratory by using standard raw materials, according to the following procedure:

- weigh the polymer dispersion in a jar and keep it under stirring;
- add the softening agent and stir until homogenization;
- add the water retainer solution
- add the amount of distilled water
- add the rheological additive
- keep under stirring until complete homogenization.

In Table 2 chemical and physical characteristics of the formulations are reported.

Table 2. (*) Brookfield RVT, 23°C, 20rpm

Formulation	Viscosity mPa.s (*)	Solid Content %
F1	7.000	44.5
F2	8.000	45.0
F3	5.800	45.0
F4	6.500	47.7
F5	5.900	42.0
F6	6.500	47.5

EXPERIMENTAL SETUP

Samples characterization was performed through different measurement protocols, conducted in order to evaluate overall mechanical performances of the final product according to the specific application requirements.

A Brookfield RVT viscometer has used for the apparent viscosity measurement. Once the correct range of viscosity according to the experience was verified, the next step was to measure the wet tack development in paper -paper application; for this purpose FIPAGO test, in accordance to UNI 10115:1993, was performed.

These characteristics / properties are not sufficient to guarantee a proper industrial suitability of the adhesive because flow properties represent a critical limit and a deeper investigation through rheology is important.

FIPAGO test

The evaluation is made in accordance to UNI 10115: 1993. 55 ± 5 g/m² wet of adhesive are spread on a standard paper substrate that is assembled with another sample of the same paper. The test measures the work of adhesion that is the work necessary to separate the paper samples by increasing the closed time, when the open time is fixed at 2".

The results are expressed as work of adhesion vs. closed time, in order to have the trend of the wet tack development.
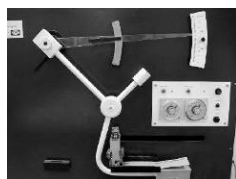
Figure 6.
FIPAGO tester

Figure 7
FIPAGO test paper

Rheological tools and methods.
High shear rate viscosity data were determined by using a capillary rheometer mod. SR20 (by CEAST / INSTRON).
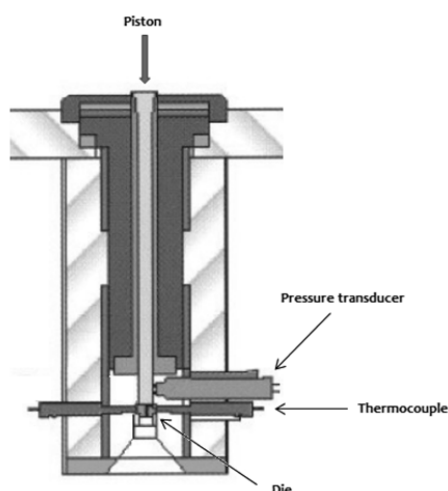A schematic drawing of the instrument is showed in Figure 8.

Figure 8. Capillary rheometer scheme

The volumetric flow rate Q through the capillary (L= 25 mm; = 0.25 mm) is controlled by the piston speed (cross section= 15 mm; L= 300 mm; speed range $24*10^{-3}$ - 47 mm/min) while the software converts the pressure difference and speed in terms of viscosity [5]. The pressure inside the chamber is obtained by a pressure transducer assembled close to the capillary entrance. Thus, the total pressure drop measured, includes the pressure loss along the capillary entrance.
The flow curves at medium-low shear rate were measured trough a stress controlled rheometer mod. ARG2 (by TAInstruments)

equipped by parallel cone / plate geometry (2°, 0', 32") having a diameter of 40 mm, with a 45 μm gap (see Figure 9)
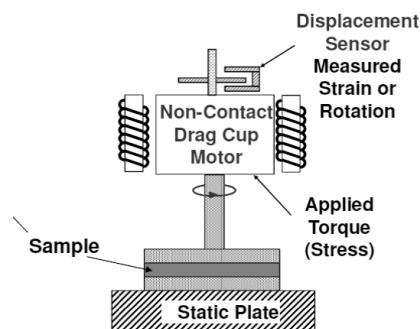

Figure 9. Rotational rheometer scheme

The stress controlled rheometer was used to perform two kinds of measurement protocols: stationary and oscillatory modes.
By the stationary test, the viscosity profile of the four adhesive were measured in a range between $10^{-3} \div 10^{3}$ s^{-1}. These values were linked to the high shear rate viscosity profile got by the capillary rheometer. This test allows to measure viscosity, eventually rheological instability (as shear rate increases) yield value, giving finally all the information to identify the behaviour of the specific formulation from a rheological point of view.
Oscillatory measurements allow to dynamic viscosity and possibly to correlate it to structural rearrangements of polymer chains. The structure/texture or mechanical spectrum was investigated by increasing the stress value from 0 to 1000 Pa at a frequency of 1 Hz. The viscosity evolution in a frequency range from 0.01 to 100 Hz was plotted at a force below the critical stress detected by the spectrum (inner LVR). These tests allow to determine the elastic (G') and loss (G") moduli with different meanings.
The stress sweep indicates the G', G", mechanical imprint; the frequency sweep gives the relaxation time of the system when

a stress occurs: and it is an indication of the behaviour of the product in the plant.

RESULTS

Adhesive performances

Once defined the general dispersion properties (solid content, apparent viscosity), FIPAGO test is necessary to define if the formulations exhibit the sufficient adhesion to suite paper gluing processes. The results are shown in Graph 1.
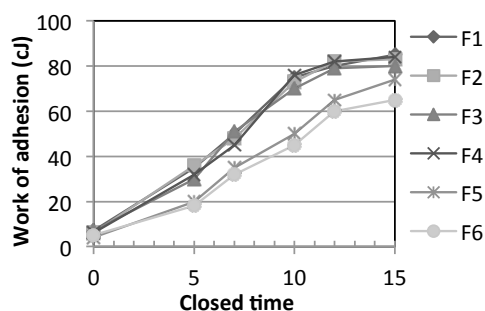

Graph 1. Paper performances

They put in evidence that, in agreement to our experience, the formulations from 1 to 4 have a wet tack development, setting and open time, suitable for the application they are destined to. We decided to avoid further evaluation for formulations 5 and 6 because their performances, even if acceptable, are worse performing than similar formulations containing the rheology modifier.

Rheological characterization

Rheological investigation was carried out through several measurement protocols. They were conducted in order to evaluate flow performances of the final product for the specific application requirements. Normalized standard test alone are not able to guarantee a good industrial suitability because flow properties represent a very crucial aspect which only could be deal with a rheological approach. The knowledge of flow properties is a very important process-stream-design part, for a trouble-free cardboard bonding operations.

For this specific industrial application, a flow description in a wide range of shear rate is important[6]. For that reason it was necessary to collect results by a stress controlled and a capillary rheometer. The experience put in evidence that high speed machinability depends upon a complex interrelation between glue rheology and other adhesive properties. The flow curves profile (Graph 2) shows a viscosity trend according to the polymer molecular weight values reported in Table 1, even though F4 exhibits a yield greater than the one shown by F2, differently from the Vistex values.
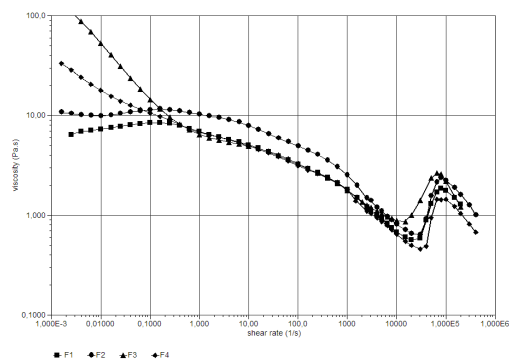
Graph 2. Flow curve

As a matter of fact zero shear viscosity gradually increases as the polymer Mw increases, while the medium shear values are approximately equivalent (as described in literature) [7].

It is evident that the curve is showing a threshold, beyond which the viscous behaviour depends upon the deformation speed. The adhesive viscosity issues are summarized in Table 3. The viscosity read at 3 s^{-1} is correlated to the Brookfield value (see Table 2).

The effect of different polymer content has been investigated: F4, based on EVA copolymer, shows a viscosity profile characterized by a relatively high yield value at zero shear and, by the lowest value at a shear up to 10^4 s^{-1}. F2 seems, at medium shear, to have a thickening behaviour and a

Id.	$\eta_{Zero-shear}$	η_{3s-1}	$\eta_{10^3 s-1}$	$\eta_{10^4 s-1}$	$\eta_{10^5 s-1}$
F1	6.4	6.1	1.8	0.68	1.8
F2	11	9.6	2.5	0.81	2.2
F3	110	5.7	1.8	0.88	2.2
F4	33	6.0	1.8	0.64	1.4

Table 3. Viscosity Pa.s

low yield value and this profile does not make it suitable for an high shear application[8].

That behaviour can block the flow in the pipeline and could cause leakage in the "stop and go" steps used in several application processes. An interesting results was exhibited by F3: this formulation has a good zero shear viscosity and, at shear around 10^4 s^{-1} starts to build up. The mechanical moduli were measured by stress and frequency sweep tests; they are not destructive and allow to measure the elastic and viscous properties. For a viscoelastic liquid G">G', while for a viscoelastic solid G'>G". Graph 3 shows G' and G" as function of shear stress investigated by means of oscillatory test performed at variable stress, at constant frequency.
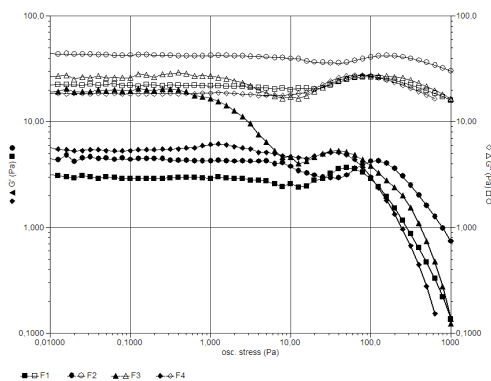

Graph 3. Stress sweep

At low stress, in the linear viscoelastic range (LVR), both G' and G" curves display constant plateau values, even if different (from 10^0 to 10^2 Pa) depending on sample texture. All formulas present G">G' profile evidencing a liquid like character. In this

case, the viscous behaviour dominates the elastic one, especially in the LVR range.

On the other side, F3, even if is characterized by G">G', is showing moduli with very similar absolute values. This means that the interactions of the polymer chains are not based on stable chemical bonding; in particular we can just refer to physical temporary bonding.

As given above, F3 is not stable at low flow velocity and this is even more evident at high shear.

Frequency sweep test was performed on the same samples and the results are shown in Graph 4.
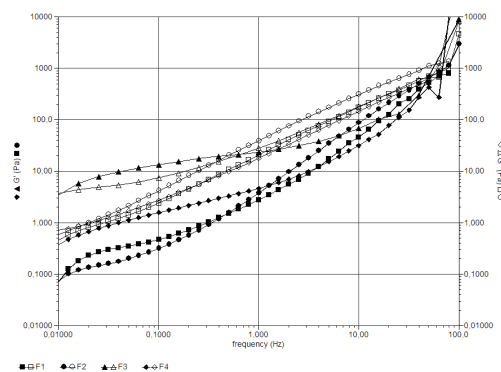
Graph 4. Frequency sweep

The test performed at variable frequencies and constant stress shows a time dependant deformation behaviour for F4, F1 and F2. F3 shows a light plateau at frequencies less than 1 Hz, with an overlap of G' on G" below this value: that trend - the so called rubber elastic plateau - evidences that the longer molecules cannot slide along each other anymore, and therefore, that their entanglements are beginning more and more to form a temporary network.

For frequencies lower than 1 Hz, the G">G' attitude is highlighted, in different way for all considered formulations. That trend is desirable for high speed applications because it allows the system to deform without causing phenomena of die swell at the exit of the nozzles or flow turbulence at the entrance. This frequency dependence,

also called relaxation time, can easily be observed by calculating tan(δ) ratio (see Graph 5).
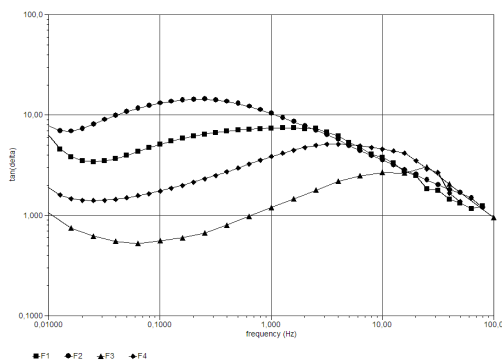
Graph 5. Frequency sweep: tan(d)

This graph shows the behaviour over the time: that can be explained by time-temperature superposition principle [TTS]. At high frequencies i.e. short relaxation time the sample shows the typical low-temperatures behaviour, whereas at low frequencies high temperature i.e. long relaxation time behaviour is displayed [9]. By examining the curves for all the considered systems, a sharp F1 and F2 curve decrease can be noticed for frequencies higher than 1 Hz. In the range between 30 and 100 Hz, all samples apparently show a very comparable behaviour. At long time F3 and F4 formulas have a flat slope indicating different composition. By studying the mechanical properties as a function of frequency, the formulator has a very powerful tool to fine tune the formulation receipt[10].

CONCLUSIONS

The use of FIPAGO equipment can be considered as a general test driving the selection of the best adhesives in terms of setting time, open time and wet tack development. Any further choice should be optimized by experimental industrial test on the specific application process or by means of a rheological study. In fact the flow curve profile was useful to predict eventual flowing problems in the pipeline or leakage formation during the application of the best selected adhesives. Furthermore the investigation by means of Stress sweep curves proved that is possible to distinguish among the different studied recipes by showing the effect of the flow velocity on the type of interaction among the polymer chains. Finally the frequency sweep mode highlighted the relative values of moduli (G' and G'') in the specific frequency range, giving to the formulator the key to project which chemical modification of the formula is able to get the best performance in the specific condition required by the application.

REFERENCES
1. Warson, H. and Finch, C. A. (2001) "Application of synthetic resin latices, Latices in diverse applications". Wiley & Sons Ltd, Chichester **8**, 484-512.

2. Arietti, R., Chiozza, F. and Carrà, S. (2000) "A new solvent free adhesive dispersion for general application". FEICA congress.

3. Skeist I. (1990) "Handbook of Adhesives 3rdEd.", Chapman & Hall, New York, **21**, 384-387.

4. Chiozza F. (2001) "Dispersioni vinil-etileniche per il settore adesivi per cartotecnica e imballaggio". AVISA congress.

5. Macosko C. (1994) "Rheology principles measurements and applications", Wiley-VCH, New York.

6. Norbert W., Wagner, H. G. et al. (1997) "High Shear Rheology of Paper Coating Colors - More Than Just Viscosity" Chem. Eng. Technol. **20**, 557-563.

7. Mezger T.G. (2002) "The rheology Handbook", Vincentz Verlag, Hannover.

8. Rolando T.E. "Rapra Review Reports" n°101, ISSN:0889-3144

9. Menard, K. "Dynamic mechanical analysis"

10. Bousfield, D. W. (2008), Rheology reviews 47-70 "Rheological Issue In The Paper Industry"