

Full Length Research Paper

Flow behaviour of polyvinyl alcohol (PVOH) modified blends of polyvinyl acetate (PVAc)/natural rubber (NR) latexes

Stephen Shaibu Ochigbo

Department of Chemistry, Federal University of Technology, P. M. B. 65, Minna, Niger State, Nigeria.

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During compounding processes, polymer latexes are mixed with various colloidal systems (in particular, PVOH) or surface-active agents to modify the flow behaviour in order to suit the manufacturing process. In this study, the flow behaviour of aqueous dispersed PVAc, NR and different mixed dispersions were investigated both in the absence and presence of PVOH as flow modifier, using an Ostwald glass capillary viscometer. The results show an almost linear decrease in the relative viscosity of the NR/PVAc dispersion mixtures in the absence of a modifier, but the presence of different amounts of PVOH gave rise to significant deviations from this behaviour. It was found that these changes in the relative viscosities are governed by a balance between the following four effects: (i) the higher mobility of the NR chains compared to those of PVAc, which generally caused a decrease in the viscosities of the dispersion mixtures; (ii) the physical adsorption of PVOH on the NR chains that slowed down the movement of these chains and caused an increase in relative viscosity; (iii) the chemical interaction between the functional groups on PVAc and PVOH that gave rise to latex thickening and increased the relative viscosity; (iv) a dilution effect which reduced the viscosity, unless counterbalanced by one or more of the other effects.

Key words: Dispersion flow behaviour, viscosity, rubber latex, polyvinyl alcohol, polyvinyl acetate.

INTRODUCTION

Latexes are polymer particles dispersed in water. Their prominence has arisen because of mounting pressure from Environmental Protection Agencies (EPAs) against industrialists and researchers to replace solvent based systems with water based counterparts. Latex-based systems are all water based, without organic content, using only very small amounts of the latter to modify the final film properties, paint flow or rheological properties (Amalvy and Soria, 1996; Nabuurs et al., 1996; Meng et al., 2008). Because water is inexhaustible, cheap and readily available in comparison to organic solvents, latex based systems have corresponding advantages over their solvent based counterparts. In addition, the use of

latex-based systems controls pollution, reduces risks of fire occurrence, and improves aspects of occupational health and safety (Zhaoying et al., 2001; Tambe et al., 2008; Kosto and Schall, 2007; Chen et al., 2005).

Polyvinyl acetate (PVAc) is an example of a synthetic polymer latex, for which the term "emulsion" is usually used in preference to latex, because it is a product of emulsion polymerization of the vinyl acetate monomer. PVAc emulsions have been used in large quantities in several application fields, especially in adhesives of papers and woods (Okaya et al., 1993; Backman and Lindberg, 2004; Kim and Kim, 2006). Because of its structural configuration, PVAc film is resistant to both oils

and ultra-violet (UV) radiation. However, the pendant acetate groups restrict free rotation along the C-C axis, thus resulting in a dry film which, besides having poor resistance to water, is too brittle and hence unsuitable in packaging applications unless in the presence of added plasticizer. On the other hand, natural rubber (NR) latex is a natural biosynthetic polymer which is derived from the tree *Hevea brasiliensis*. The latex that is obtained fresh from the tree (field latex) contains about 70% water, part of which should be removed to concentrate the latex for a wide variety of applications. The resulting latex concentrate has excellent physical properties and is used for the manufacture of dipped goods, adhesives/binders, thread, carpets/rugs, and moulded foams. Among these, the dipped goods, which include hand gloves, balloons, condoms, bladders, and catheters/tubes account for up to 60% NR latex usage (Haque et al., 1995; Sanguansap et al., 2005; Yip and Cacioli, 2002). However, the film cast from NR latex, unlike PVAc, is soft and tacky and possesses poor resistance to oil (Sirisinha et al., 2003), as well as poor resistance to both ultra violet (UV) radiation and ozone. Blending of polymer emulsions or dispersions is required in order to balance factors such as ease of application, wettability, drying characteristics, bond strength, clarity, environmental resistance, and especially cost (Meng et al., 2008). NR latex has intrinsic water resistance and toughness and therefore can improve water resistance behaviour of PVAc while the former simultaneously can improve in oil and ozone resistance when the latex and emulsion are blended together.

During the compounding processes, latexes are mixed with various colloid systems, in particular, poly (vinyl alcohol) (PVOH) or surface-active agents to modify the flow behaviour in order to suit the manufacturing process (Schoeder and Brown, 1951; Brown and Garrett, 1959; Irving, 1990; Geurink et al., 1996; Hellgren et al., 1999). The flow behaviour of latexes is a critical factor, as it provides a guide for the formulation and ease of processing. A latex compound with a low viscosity and some thixotropic nature is good for dipping operations. The count of a latex thread is influenced by its viscosity (Peethambaran et al., 1990; Blackley, 1966; Calvert, 1982). Studies were carried out to examine the effect of PVOH on a PVAc emulsion (Dibbern-Brunelli and Atvars, 1995; Dibbern-Brunelli et al., 1998) and on NR latex (Peethambaran et al., 1990). An emulsion stabilized with PVOH has many advantages over surfactants, including Newtonian fluidity, superior primary wet tackiness, high strength and creep resistant film properties (Nakamae et al., 1999). This study used an Ostwald glass capillary viscometer to examine the flow behaviour of blends of PVAc/NR latexes in the presence of PVOH as a flow modifier. Owing to its simplicity, viscometry is popularly employed for studying compatibility as well as flow behaviour of polymers in solution (Singh and Singh, 1983; Kuleznev et al., 1978; Hourston and Hughes, 1978).

MATERIALS AND METHODS

A PVAc homopolymer emulsion was obtained from Makeean Polymers, South Africa with the trade name ML50 (solids contents = 52.5%, pH = 6.5). Field NR latex was provided by the Rubber Research Institute of Nigeria (RRIN), Iyanomo. It has a solid content of 45%. The PVOH was a Merck grade quality.

A dilute aqueous dispersion of the PVAc emulsion was prepared with a fixed concentration of 10 wt.%, designated PVAc₁₀. NR latex was prepared in different concentrations of 10 wt.% (NR₁₀), 5 wt.% (NR₅), and 1 wt.% (NR₁). All the dispersions were prepared relative to the respective dry solids contents of the original latexes. The prepared dispersions were in each case immediately passed through a stainless steel sieve with aperture 150 µm in order to remove any foreign suspended particles that may block the capillary of the Ostwald viscometer. An appropriate amount of PVOH was dissolved in water, under magnetic stirring at 90°C, to obtain a 2 wt.% stock solution from which lower concentrations of 1 wt.% and 0.5 wt.% were in turn prepared by successive dilution using de-ionised water. NR₁₀/PVAc₁₀, NR₅/PVAc₁₀, and NR₁/PVAc₁₀ were respectively blended into w/w compositions of 0/100, 25/75, 50/50, 75/25 and 100/0. This mixing method whereby the concentration of one component, PVAc (called the host polymer) is held constant while the concentration of the second, NR (called the guest polymer) is varied is known as the polymer-solvent method (Danait and Deshpande, 1995; Papanagopoulos and Dondos, 1996; Haiyang et al., 2000). In this paper, the method was applied to polymer dispersions rather than to conventional solution based polymer systems.

The flow rate (efflux time) of the different samples were directly observed as the time, t , needed for the liquid to pass through the capillary (Billmeyer, 1984). Measurements were made in the absence and presence of PVOH at a temperature of $22 \pm 0.5^\circ\text{C}$. From the efflux times, the relative viscosities were calculated using Equation 1.

$$\eta_{\text{rel}} = t/t_0 \quad (1)$$

Where, η_{rel} = relative viscosity, t = efflux time of dispersion, t_0 = efflux time of pure water.

RESULTS AND DISCUSSION

The variation of relative viscosity with blend composition is represented by NR₁₀/PVAc₁₀ blend, as shown in Figure 1. With increases in NR content, it is observed that the relative viscosity for the untreated sample (0 wt.% PVOH) decreases more rapidly than those for the samples containing different amounts of PVOH. This is attributed to the fact that NR latex is a pseudoplastic fluid, and even at rest the rubber particles are in random motion (Peethambaran et al., 1990). Therefore, as NR content increases, there results a corresponding increase in random motion and hence, an enhanced flow which leads to the observed marked decrease in viscosity of the untreated sample. On the other hand, the dispersions containing the different amounts (0.5, 1 and 2 wt.%) of PVOH show gradual and parallel decreases in viscosity with increasing NR content. It is suggested that the observed gradual and parallel decrease in viscosity of the PVOH-modified samples with increasing NR content, compared to that of the untreated sample, might be due

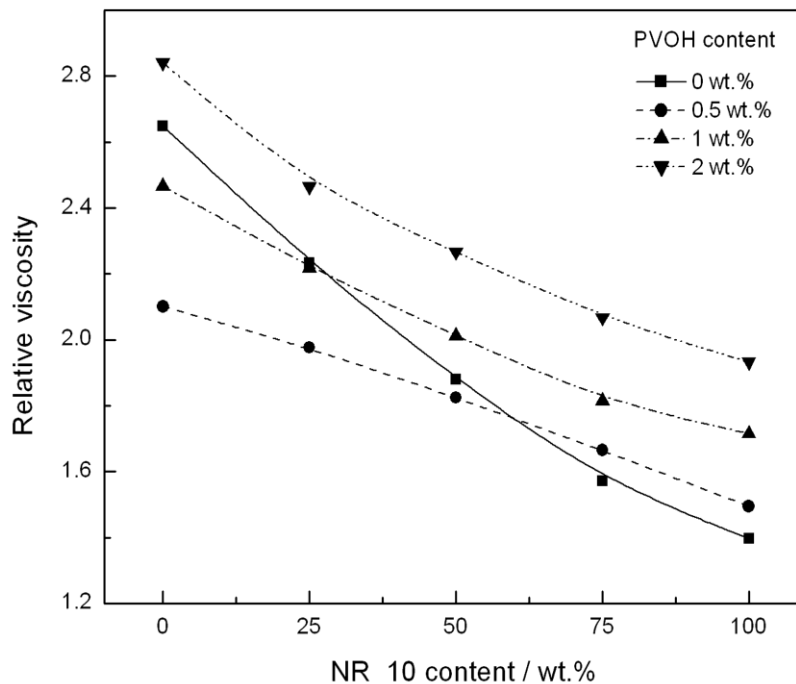


Figure 1. Dependence of relative viscosity on the blends' composition at various contents of PVOH modifier.

to adsorption of PVOH particles onto the NR particles. This adsorption could slow down the speed of the randomly moving NR particles and give rise to the observed trend of decrease in viscosity of the mixtures in the presence of PVOH. This agrees with the results of Peethambaran et al. (1990) in a study carried out to investigate the role of various surfactants on the viscosity of natural rubber latex.

Figure 2 presents the change in relative viscosity of the various unblended dispersions against different PVOH contents. The viscosity of pure PVAc (PVAc₁₀) is at maximum throughout the concentration range of the surfactant. Primarily, the viscosity of PVAc is intrinsically due to restricted mobility of the chains arising from steric hindrance between the acetate groups on one hand and then intermolecular dipole-dipole attraction between adjacent acetate functional groups. In addition, the high concentration of the PVAc₁₀ (that is, 10wt.%) which means that there are much chains condensed within a small volume, permitting intermolecular entanglements contributes to observed high viscosity. The viscosity of NR₁₀ of equivalent concentration (that is, 10 wt.%) by comparison is considerably lower than that of PVAc₁₀ as observed due to the fact that the particles of natural rubber is in constant random motion (pseudoplastic). Of course, NR₅ and NR₁ have lowered viscosity comparatively due to dilution effect and also pseudoplastic nature of the natural rubber latex as stated earlier.

The addition of the 0.5% PVOH immediately results in a significant drop in the relative viscosity curve for PVAc₁₀ observed. This concentration of PVOH is very dilute. So the accompanying relatively high water content imparts a plasticizing effect on the PVAc emulsion and thus causing its viscosity to drop sharply as observed. However, with higher concentration of PVOH, the viscosity values of PVAc₁₀ slightly improve after the depression. This improvement is as a result of the overshadowing of any plasticizing effect of the water content of the modifier by viscosity increase attributed firstly to adsorption of PVOH onto PVAc particles. An additional reason for the increase in viscosity is a consequence of the partial hydrolysis of the acetate functional group into carboxylate ions which in turns allows absorption (dissolution) of PVAc into PVOH (Lloyd, 1989; Hornby and Peach, 1993). These ions are capable of taking part in hydrogen bonded interactions with the hydroxyl groups of the modifier and, therefore, can contribute to the viscosity increase of the mixture. Interactions of this kind between particles of emulsion and aqueous polymeric solutions, leading to viscosity increases, have earlier been reported and the phenomenon is called latex thickening (Brown and Garrett, 1959). Several competitive interactions were postulated to account for the overall rheological behaviour of such mixtures. There were a number of observations providing evidence that the process involved in latex thickening is not merely that of the

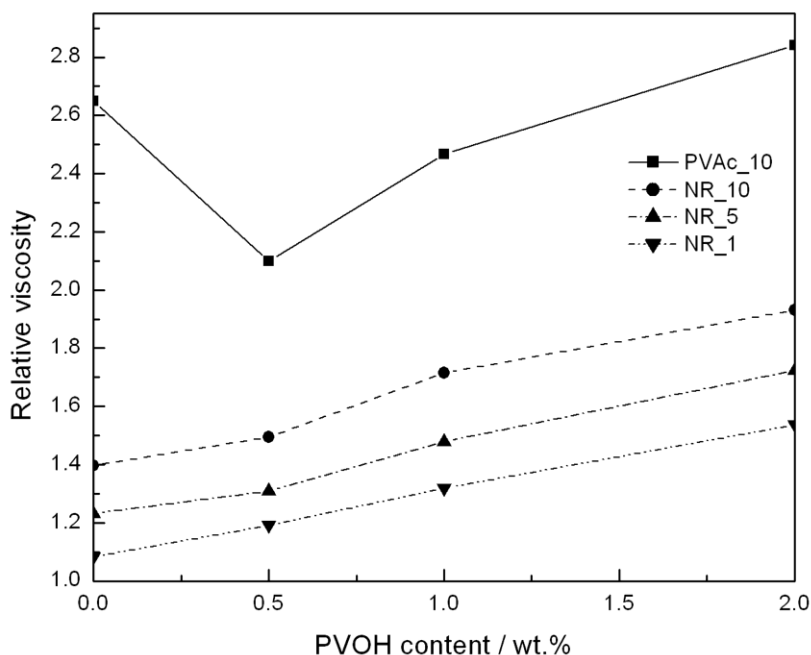


Figure 2. Dependence of relative viscosity on PVOH modifier content for various unblended aqueous dispersions.

enhancement of the viscosity of the continuous (water) phase by the water soluble polymer. There was also very little correlation between the aqueous viscosity of a polymer and its efficiency in thickening latexes. The significant drop in relative viscosity at 0.5% PVOH is attributed to the corresponding drop in concentration of the emulsion (PVAc_10) due to a dilution effect caused by the mixing of the two dispersions, which at this PVOH concentration dominated the latex thickening effect. The viscosity increase observed for the higher concentrated PVOH-modified samples is because of the latex thickening effect becoming more dominant.

The relative viscosities of the NR-based dispersions (with and without PVOH) are generally lower than that of the PVAc dispersion, which is due to the pseudoplasticity of NR, while the differences between the different NR dispersions are attributed to their corresponding differences in concentration. The relative viscosities of all the NR dispersions increase more or less linearly with increasing PVOH content. This behaviour shows that a completely different mechanism decides the interaction between NR and PVOH. As previously reported (Peethambaran et al., 1990), this involves a physical adsorption of PVOH solutes on the surfaces of the NR particles, which reduces the mobility of the NR particles.

The changes in the relative viscosities of the blended dispersions as a function of PVOH content are shown in Figures 3 - 5. These results clearly show the competition between the different influences discussed earlier. For all the blended dispersions, the viscosity generally increases

with increasing PVOH content, but decreases according to the order: NR_10/PVAc_10 > NR_5/PVAc_10 > NR_1/PVAc_10. The increase with increasing PVOH content is the result of a combination of the latex thickening and physical adsorption effects discussed previously, while the decrease with increasing NR_10/5/1:PVAc_10 ratio is the result of the higher mobility of the NR chains. However, a dilution effect comes into play when more dilute NR dispersions are used, and therefore there is a decrease in relative viscosity with decreasing NR content in the NR dispersions that were mixed with the PVAc_10 dispersion at a constant ratio. This dilution effect also manifests itself in the lower than expected viscosities at 0.5% PVOH (as discussed above), but the physical adsorption between PVOH and NR becomes more dominant as the NR_10/5/1:PVAc_10 ratio increases in the dispersion mixtures, and the decrease in viscosity for the 0.5% PVOH containing samples disappears for the 75:25 NR_10/5/1:PVAc_10 dispersion mixture.

Utracki and Kaniel (1982) divided viscosity-composition curves into three types on the basis of their deviation from the log-additivity rule ($\ln \eta_b = \sum \Phi_i \ln \eta_i$, in which η_b represents the blend viscosity, and Φ_i and η_i are the volume fraction and viscosity of component i in the blend). Based on this rule, Figures 6 - 9 were obtained, showing a comparison of the experimental and theoretical relative viscosities as a function of dispersion composition in the presence of different amounts of PVOH. As seen, all the experimental curves show

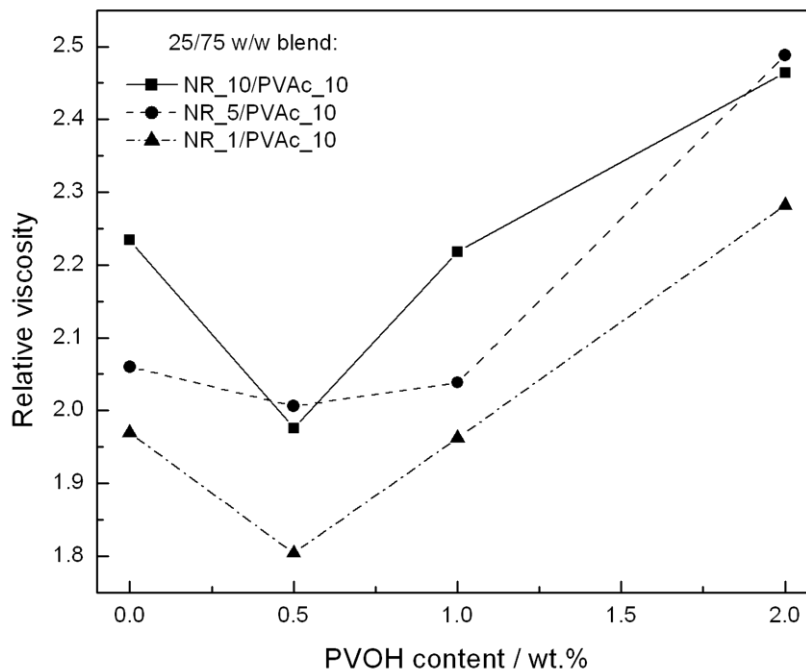


Figure 3. Dependence of relative viscosity on PVOH modifier content for different 25:75 w/w NR/PVAc blends.

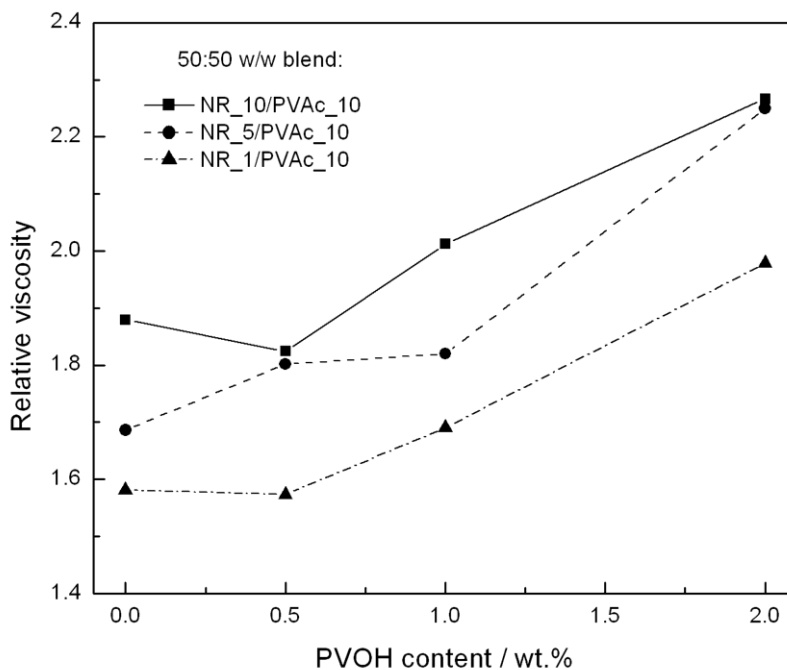


Figure 4. Dependence of relative viscosity on PVOH modifier content for different 50:50 w/w NR/PVAc blends.

deviations from the theoretical values. The linear (theoretical) curves indicate ideal behaviour which is

exemplified by a situation in which particles of the mixed components consist of similar sizes in a given medium.

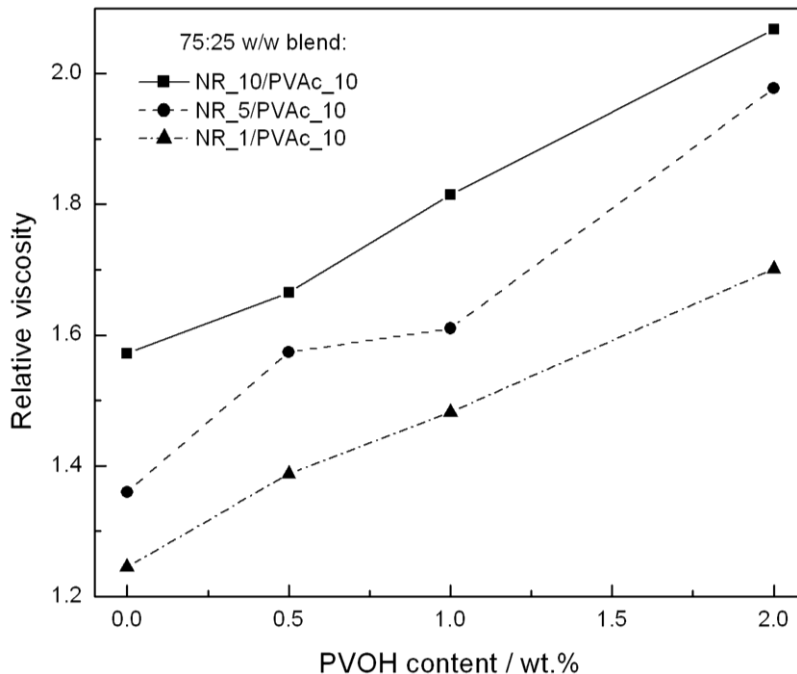


Figure 5. Dependence of relative viscosity on PVOH modifier content for 75:25 w/w NR/PVAc blends.

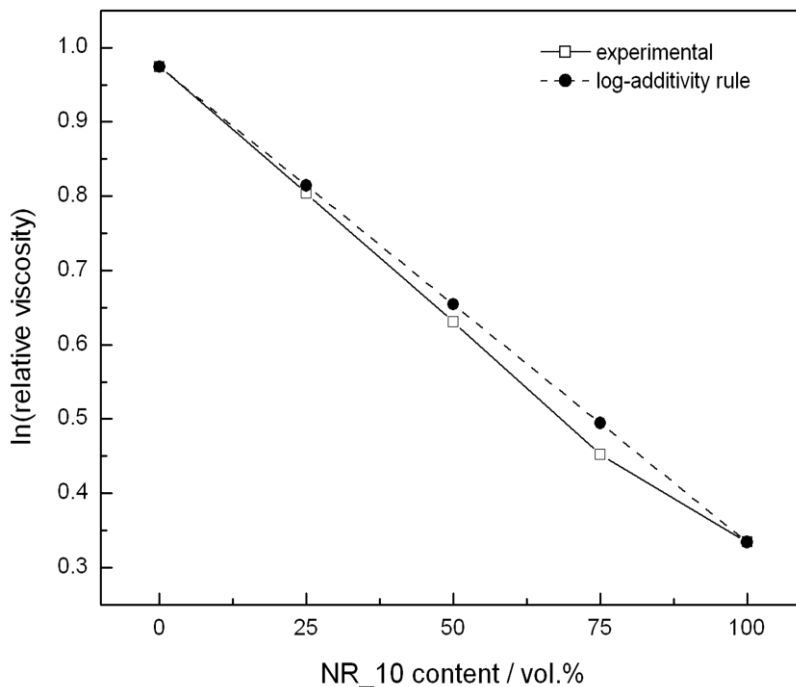


Figure 6. Comparison between experimental and theoretical viscosities for aqueous dispersions of NR_10/PVAc_10 without PVOH.

Such behaviour is in agreement with the additive rule (Wong, 1991). The observed deviations are evidence of

interactions taking place between the mixed components, namely NR, PVAc, PVOH and water. Negative deviations

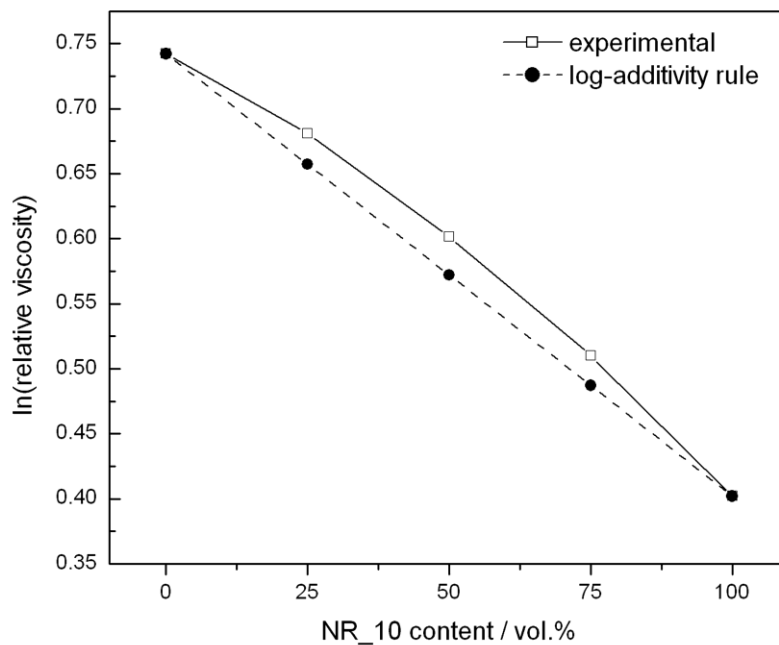


Figure 7. Comparison between experimental and theoretical viscosities for aqueous dispersions of NR_10/PVAc_10 with 0.5 wt.% PVOH.

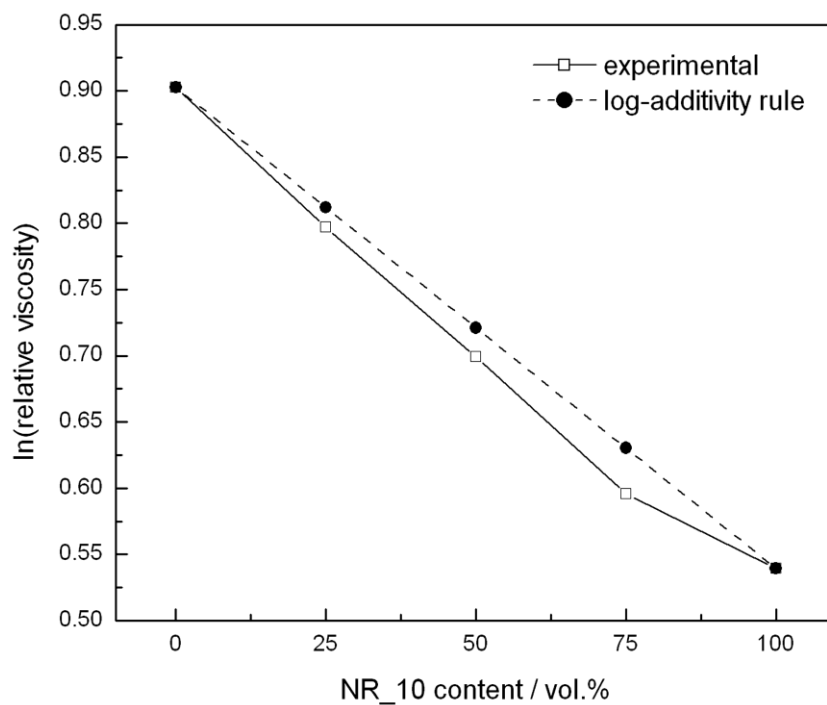


Figure 8. Comparison between experimental and theoretical viscosities for aqueous dispersions of NR_10/PVAc_10 with 1 wt.% PVOH.

are attributed to lowered mobility of particles, and hence reduced interactions between components, whereas

positive deviations indicate that there are enhanced interactions between the components due to high mobility

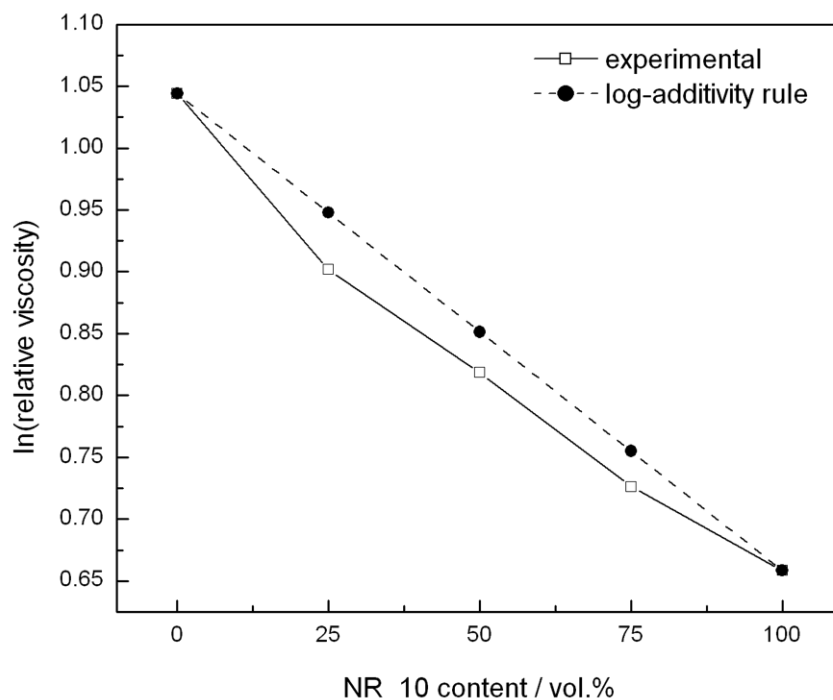


Figure 9. Comparison between experimental and theoretical viscosities for aqueous dispersions of NR_10/PVAc_10 with 2 wt.% PVOH.

of particles. These interactions are not anticipated by theoretical prediction. A number of factors can be adduced for the reduced mobility of the particles. They include repulsive forces between the mixed components because of dissimilarity in their chemical natures, as for example, NR and PVAc, and high viscosity of medium which prevent free mobility, and hence interactions between components. While the first factor might be the reason for the negative deviation observed for the pure blends of NR_10 and PVAc_10 (Figure 6), the case of negative deviations observed with the blends containing 1 and 2% PVOH (Figures 8 and 9, respectively) might be due to high viscosity of the system. In Figure 7, the introduction of 0.5% PVOH enhances freedom of intermolecular interactions between the mixed components. This increased mobility is thus observed as the positive deviation from the theoretical prediction.

Conclusions

The flow behaviours of NR latexes and PVAc dispersions, and mixtures of these dispersions, in aqueous medium, as well as the addition of a PVOH modifier to these dispersions, were investigated. The results clearly showed that changes in the relative viscosities of mixtures of NR, PVAc and PVOH dispersions are governed by a balance between the following four effects:

- (i) The higher mobility of the NR chains compared to those of PVAc, which generally caused a decrease in the viscosities of the dispersion mixtures,
- (ii) The physical adsorption of PVOH on the NR chains that slowed down the movement of these chains and caused an increase in relative viscosity,
- (iii) The chemical interaction between the functional groups on PVAc and PVOH that gave rise to latex thickening and increased the relative viscosity,
- (iv) A dilution effect which reduced the viscosity, unless counterbalanced by one or more of the other effects.

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REFERENCES

- Amalvy JI, Soria DB (1996). Vibrational spectroscopic study of distribution of sodium dodecyl sulphate in latex films. *Progr. Org. Coat.* 28:279-283.
- Backman AC, Lindberg KAH (2004). Interaction between wood and polyvinyl acetate glue studied with Dynamic Mechanical Analysis and Scanning Electron Microscopy. *J. Appl. Polym. Sci.* 91:3009-3015.
- Billmeyer FW Jr. (1984). *Textbook of Polymer Science*, 3rd ed.; Wiley: New York. P. 149.
- Blackley DC (1966). *High Polymer Latices*, Vol. 2. Applied Science, London.

- Brown GL, Garrett BS (1959). Latex thickening: Interactions between aqueous polymeric dispersions and solutions. *J. Appl. Polym. Sci.* 1:283-295.
- Calvert KO (1982). *Polymer Latices*. Applied Science, London.
- Chen J, Spear SK, Huddleston JG, Rogers RD (2005). Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem.* 7:64-82.
- Danait A, Deshpande DD (1995). A novel method for determination of polymer-polymer miscibility by viscometry, *Eur. Polym. J.* 31:1221-1225.
- Dibbern-Brunelli D, Atvars TDZ (1995). Study of miscibility of poly (vinyl acetate) and poly (vinyl alcohol) blends by fluorescence spectroscopy. *J. Appl. Polym. Sci.* 55:889-902.
- Dibbern-Brunelli D, Atvars TDZ, Joekes I, Barbosa VC (1998). Mapping phases of poly (vinyl alcohol) and poly (vinyl acetate) blends by FTIR microspectroscopy and optical fluorescence microscopy. *J. Appl. Polym. Sci.* 69:645-655.
- Geurink PJA, van Dalen L, van der Ven LGJ, Lamping RR (1996). Analytical aspects and film properties of two-pack acetoacetate functional latexes, *Prog. Org. Coat.* 27:73-78.
- Haiyang Y, Pingping Z, Feng R, Yuanyuan W, Tiao Z (2000). Viscometric investigations on the intermolecular interactions between poly (methyl methacrylate) and poly (vinyl acetate) in various solvents, *Eur. Polym. J.* 36:21-26.
- Haque ME, Akhtar F, Dafader NC, Al-Siddique FR, Sen AR, Ahmad MU (1995). Characterization of natural rubber latex concentrate from Bangladesh, *Macromolecular Reports A32 suppl.* 4:435-445.
- Hellgren A, Weissenborn P, Holmberg K (1999). Surfactants in waterborne paints. *Prog. Org. Coat.* 35:79-87.
- Hornby M, Peach J (1993). *Foundations of Organic Chemistry*; Oxford University Press, New York.
- Hourston DJ, Hughes ID (1978). Dynamic mechanical and sonic velocity behaviour of polystyrene-poly (vinyl methyl ether) blends. *Polymer* 19:1181-1185.
- Irving S (Ed.) (1990). *Handbook of Adhesives Third Ed.* Van Nostrand Reinhold, New York.
- Kim S, Kim HJ (2006). Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on the adhesion for engineered flooring in under heating system. *ONDOL Thermochemica Acta* 444:134-140.
- Kosto KB, Schall DC (2007). Low-temperature waterborne pavement marking paints: a road assessment of this LOW-VOC option. Presented at the 2007 FutureCoat! Conference, sponsored by Federation of Societies for Coatings Technology, in Toronto, Ont., Canada, October 3-5, 2007.
- Kuleznev VN, Melnikova OL, Klykova VD (1978). Dependence of modulus and viscosity upon composition for mixtures of polymers. Effects of phase composition and properties of phases. *Eur. Polym. J.* 14:455-461.
- Lloyd DA (1989). *A First Course in Organic Chemistry*. Wiley, Chichester.
- Meng W, Wu L, Chen D, Zhong A (2008). Ambient self-crosslinkable acrylic microemulsion in the presence of reactive surfactants. *Iran. Polym. J.* 17(7):555-564.
- Nabuurs T, Baijards RA, German AL (1996). Alkyd-acrylic hybrid systems for use as binders in waterborne paints. *Prog. Org. Coat.* 27:163-172.
- Nakamae M, Yuki K, Sato T, Maruyama H (1999). Preparation of polymer emulsions using a poly (vinyl alcohol) as a protective colloid, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 153:367-372.
- Okaya T, Tanaka T, Yuki K (1993). Study on physical properties of poly (vinyl acetate) emulsion films obtained in batchwise and in semicontinuous systems. *J. Appl. Polym. Sci.* 50:745-751.
- Papanagopoulos D, Dondos A (1996). Difference between the dynamic and static behaviour of polymers in dilute solutions. 3. Influence of the host polymer on the dimensions of the guest polymer, *Polymer* 37:1053-1055.
- Peethambaran NR, Kuriakose B, Rajan M, Kuriakose AP (1990). Rheological behaviour of natural rubber latex in the presence of surface-active agents. *J. Appl. Polym. Sci.* 41:975-983.
- Sanguansap K, Suteewong T, Saendee P, Buranabunya U, Tangboriboonrat P (2005). Composite natural rubber based latex particles: A novel approach. *Polymer* 46:1373-1378.
- Schoeder WD, Brown GL (1951). *Carboranesiloxane Polymers*. Rubber Age 69:433.
- Singh YP, Singh RP (1983). Compatibility studies on solutions of polymer blends by viscometric and ultrasonic techniques. *Eur. Polym. J.* 19:535-541.
- Sirisinha C, Limcharoen S, Thunyarittikorn J (2003). Oil resistance controlled by phase morphology in natural rubber/nitrile rubber blends. *J. Appl. Polym. Sci.* 87:83-89.
- Tambe SP, Singh SK, Patri M, Kumar D (2008). Ethylene vinyl acetate and ethylene vinyl alcohol copolymer for thermal spray coating application. *Prog. Org. Coat.* 62:382-386.
- Utracki LA, Kanial MR (1982). Melt rheology of polymer blends. *Polym. Eng. Sci.* 22:96-114.
- Wong ACY (1991). The Study of the Relationships Between Melt Index, Density and Blend Ratio of Binary Polyethylene Blends. *Polym. Eng. Sci.* 31(21):549.
- Yip E, Cacioli P (2002). The manufacture of gloves from natural rubber latex. *J. Allergy Clin. Immunol.* 110:S3-S14.
- Zhaoying Z, Yuhui H, Bing L, Guangming C (2001). Studies on particle size of waterborne emulsions derived from epoxy resin. *Eur. Polym. J.* 37:1207-1211.