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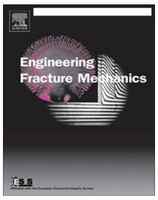

Rate effects on adhesion energy between polyethylene films and different substrates

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Adhesion properties of LLDPE "stretch" films have been investigated. Adhesion fracture energy has been measured by means of the fracture mechanics approach to peel testing. Rate/temperature dependence of the adhesion energy has been examined, and found to be related to the linear viscoelastic behaviour of the LLDPE materials. The presence of an "adhesive phase", closely related to the viscoelastic β-relaxation, is proposed. A semi-quantitative model, first proposed by Gent and Petrich, has been successfully applied to the results and has been shown to account for the observed features of the adhesion energy vs. rate master curves.

1. Introduction

Stretch wrap is a widespread packaging application of Polyethylene (PE) films, used to hold together and protect many possible products of varying number, sizes and weights. A key feature of stretch wrap films is their adhesive property, by virtue of which the wrap can be easily closed onto itself. Such adhesive behaviour is very much similar to that of "pressure-sensitive adhesives" (PSAs).

PE stretch films are usually multi-layer films, and suitable PE grades have to be used into one of the surface layers to achieve the desired adhesive strength. Typically, Linear Low Density grades (LLDPEs) with comparatively low density values are chosen, because of their known good adhesive ("cling") properties, while it is generally known that the "cling" effect is reduced for increasing densities. In the High Density PE grades (HDPE), as a comparison, adhesive properties are totally absent.

As for PSAs, the adhesive properties of PE stretch films can be conveniently measured by "peel testing". Many standard methods exist, (e.g. those published by ASTM or ISO [1–4]), and the results of such tests are strongly dependent on test geometry, on the possible plastic deformation occurring in the peel arm(s), and on peeling rate and temperature.

The fracture mechanics approach to peel testing of flexible laminates, introduced by Kinloch et al. in 1994 [5], defines an adhesive fracture energy G_c which can be determined when energy losses due to plastic or viscoelastic bending and tensile deformation of the peel arm are measured and taken into account. G_c is a parameter, independent of peel testing geometry, which properly characterizes the energy required to fracture the adhesive bond, as opposed to the measured peel force in which the extraneous energy losses mentioned above are included. Further work [6] has been done more recently to address the correct description of the cohesive zone at the crack tip, and a computer code ("IC-Peel" [7]) has been developed and is

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Nomenclature

G	total input fracture energy
G_c	adhesive fracture energy
R	peel front propagation rate
T	temperature
T_R	reference temperature
a_T	shift factor
σ	stress
ε	strain
E	Young modulus
G'	shear storage modulus
$\tan\delta$	dissipation factor
σ_Y	yield stress
f_f	stress at failure of adhesive bond
f_a	maximum tensile stress of bonded interface
f_b	tensile strength of adhesive

available to perform the required numerical calculations, combining the peel test geometry and results and the stress–strain properties of the peel arms to obtain G_c.

The rate/temperature dependence of peel strength in PSAs has been discussed in the literature with reference to the viscoelastic nature of the adhesives. Gent and Petrich [8] and Kaelble [9] have shown that peel strength vs. peeling rate curves measured at different temperatures can be shifted on the rate axis and superimposed into “master curves”, much in the same way as it is conventionally done for the linear-viscoelastic functions of polymers measured versus frequency or time. Furthermore, the shift factors a_T relating equivalent peeling rates at a temperature T and at a reference temperature T_R were shown to be equal to those for the time–temperature superposition of the relaxation modulus [9] or the modulus vs. strain rate [8] measured on the relevant adhesive, provided that a correct estimation of the extensional strain rate imposed to the adhesive itself during peeling is given. These results indicate a fundamental relationship between the adhesion properties and the linear viscoelasticity of the adhesive.

A general feature of the peel strength master curves reported in the above mentioned literature is an increase of peel strength as a function of reduced rate up to a maximum, after which the peel strength sharply decreases showing a steep negative slope. Usually, in the negative slope region stick–slip behaviour is observed. The negative slope region has been shown to be related to the transition of the adhesive to its unrelaxed (glassy) state. In many cases, a second maximum at lower rates is observed, usually associated with the observation of a transition from cohesive to adhesive fracture.

The aim of the present work is to measure the adhesive energy G_c of PE stretch films onto themselves and on different substrates, by taking advantage of the fracture mechanics approach in order to account for the high flexibility and deformability of these films. Then, the measured rate/temperature dependence of G_c will be studied with direct reference to the linear viscoelastic behaviour of the materials used in the stretch films, in order to explore the structure–property relationships which could enlighten the molecular mechanisms involved in the adhesion and detachment processes.

In this respect, we need here to define the term “adhesive phase”, which will be used throughout the present paper to identify the specific part of the material’s structure which makes the adhesion possible.

Usually, in the literature on PSAs, the properties of an adhesive material have been studied by placing the adhesive material itself between suitable substrates (“cellophane” or cellulose acetate sheets in [8,9], Mylar®, polystyrene or polyethylene sheets in [8], “cotton cloth” or metal sheets in [9]), which are therefore joined together by means of the adhesive material. After that, the substrates are peeled apart from each other, thus measuring the force, or the energy, required to detach them.

In the present case, we do not have an “adhesive material”. Our polyethylene stretch films are “self-adhesive”, i.e. they stick together without the need of an interposed adhesive layer. We must therefore assume that something inside the polyethylene materials used to make the stretch films is responsible for the adhesive effect. Polyethylene is known to be a semi-crystalline polymer, in which different phases can be identified [10]: a crystalline phase, where a regular packing of molecular segments exists, which is solid below its melting temperature and comparatively rigid (low molecular mobility below the melting temperature); an amorphous phase, which at room temperature is above its glass transition temperature (higher molecular mobility); often a third, partially ordered “interphase” is considered to exist near the boundary of the crystalline domains (intermediate molecular mobility) [11]. Due to the complex, multi-phase structure of the material, we must consider that the self adhesive properties exhibited by the polyethylene stretch films are not a property of the polyethylene as a whole, but are to be ascribed to some part of the structure, which is present on the film surface and acts like a “pressure sensitive adhesive” (PSA). We do not know “a priori” which part of the multiphase structure is this. However, we assume that inside the material an “adhesive phase” exists: such an “adhesive phase” is not present (or its amount is negligible) in High Density Polyethylenes (HDPE’s), which show no adhesive properties; it is present in linear low density grades (LLDPE’s), which show adhesive properties, particularly when the amorphous-phase content is high; however, its presence and amount

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